6 Carbon Nanotubes

6.1 Enrichment of Single-Walled Carbon Nanotubes by Diameter in Density Gradients

Arnold, M.S., Stupp, S.I. and Hersam, M.C.
Nano Lett., ***5(4)***, *713-718 (2005)*

The bulk enrichment and separation of single-walled carbon nanotubes (SWNTs) by diameter has been achieved through ultracentrifugation of DNA-wrapped SWNTs in aqueous density gradients. The separation is identified by the visual formation of colored bands of SWNTs in the density range of 1.11−1.17 g cm^{-3}. The optical absorbance spectra of the separated SWNTs indicate that SWNTs of decreasing diameter are increasingly more buoyant. This nondestructive and scalable separation strategy is expected to impact the fields of molecular electronics, optoelectronics, and sensing where SWNTs of a monodisperse band gap are essential.

6.2 Sorting carbon nanotubes by electronic structure using density differentiation

Arnold, M.S., Green, A.A., Hulvat, J.F., Stupp, S.I. and Hersam, M.C.
Nature Nanotech., ***1***, *60-65 (2006)*

The heterogeneity of as-synthesized single-walled carbon nanotubes (SWNTs) precludes their widespread application in electronics, optics and sensing. We report on the sorting of carbon nanotubes by diameter, bandgap and electronic type using structure-discriminating surfactants to engineer subtle differences in their buoyant densities. Using the scalable technique of density-gradient ultracentrifugation, we have isolated narrow distributions of SWNTs in which >97% are within a 0.02-nm-diameter range. Furthermore, using competing mixtures of surfactants, we have produced bulk quantities of SWNTs of predominantly a single electronic type. These materials were used to fabricate thin-film electrical devices of networked SWNTs characterized by either metallic or semiconducting behaviour.

6.3 Ultracentrifugation of single-walled nanotubes

Green, A.A. and Hersam, M.C.
Materials Today, ***10(12)***, *59-60 (2007)*

Single-walled carbon nanotubes (SWNTs) are high aspect ratio cylinders of carbon (~1 nm in diameter) whose walls are one atomic layer thick and have an atomic arrangement analogous to graphite. The SWNT atomic structure is defined by a twodimensional chiral vector whose components are specified by a pair of positive integers: (n,m). This chirality of the SWNT dictates its properties. Unfortunately, current methods for producing SWNTs lack control over chirality, leading to significant polydispersity in the properties of as-synthesized SWNTs. Consequently, the widespread use of SWNTs in electronics, photonics, and sensors has been limited by their inhomogeneity.

6.4 Quantum Yield Heterogeneities of Aqueous Single-Wall Carbon Nanotube Suspensions

Crochet, J., Clemens, M. and Hertel, T.
J. Am. Chem. Soc., ***129***, *8058-8059 (2007)*

Aqueous suspensions of single-wall carbon nanotubes (SWNTs) prepared by traditional methods from the supernatant of ultracentrifuged micellar SWNT mixtures are shown to be strongly heterogeneous with respect to the quantum yield of their constituents. The heterogeneities are isolated using preparative ultracentrifugation in iodixanol density gradients and are optically characterized by photoluminescence and linear absorption spectroscopy. We find that the most buoyant fractions with a density of 1.055 ± 0.005 $g{\cdot}cm^{-3}$ have the highest photoluminescence quantum yield η of 1.1%, a factor of 5 higher than that of the supernatant. Denser fractions with lower η make up for about $^{2}/_{3}$ of these samples and contain mostly small ropes in which the quantum yield is reduced by nonradiative decay through coupling to metallic tubes.

6.5 Diameter sorting of carbon nanotubes by gradient centrifugation: role of endohedral water

Hennrich, F., Arnold, K., Lebedkin, S., Quintilla, A., Wenzel, W. and Kappes, M.M.
Phys. Stat. Sol. (b), ***244(11)*** , *3896-3900 (2007)*

We demonstrate that water filling has a significant, tube-diameter dependent effect on the effective mass density of individual single-walled carbon nanotubes suspended in aqueous suspension. On the basis of extensive molecular dynamics simulations of water-filled carbon nanotubes we have estimated the number density and properties of water molecules inside different types of nanotubes. As the tube diameter becomes comparable with the size of a water molecule, the number density of water molecules jumps discontinously. For tube diameters just above this threshold the water molecules organize into a single file. Shell-like arrangements are found for even larger radii. Buoyant densities are predicted to change accordingly

6.6 Optical properties of structurally sorted single-wall carbon nanotube ensembles

Crochet, J., Clemens, M. and Hertel, T.
Phys. Stat. Sol. (b), ***244(11)****, 3964-3968 (2007)*

Using density gradient ultracentrifugation and isopycnic fractionation we structurally sort traditionally prepared single-wall carbon nanotube suspensions, and show that fractions with photoluminescence (PL) quantum yields of over 1% can be isolated. Moreover, we find that traditionally prepared suspensions appear to be composed of a significant fraction of small nanotube aggregates which reduce the quantum yield of the ensembles by a factor of 5 with respect to the most photoluminescent fractions. In order to better understand the nature of the nonradiative decay processes that lead to lower ensemble PL quantum yields, nanotube ropes of diameter enriched tubes are made and compared with the aforementioned ensemble measurements. Changes in the optical properties are discussed in terms of energy transfer to metallic tubes, carbonaceous particles, and smaller band gap tubes.

6.7 Combination of atomic force microscopy and photoluminescence microscopy for the investigation of individual carbon nanotubes on sapphire surfaces

Jester, S-S., Kiowski, O., Lebedkin, S., Henrich, F., Fischer, R., Stürzl, N., Hawecker, J. and Kappes, M.M.
Phys. Stat. Sol. (b), ***244(11)****, 3973-3977 (2007)*

Atomic force microscopy (AFM) and photoluminescence (PL) spectroscopy were applied to characterize single walled carbon nanotubes (SWNTs) deposited on sapphire. The electronic properties and structure of luminescent semiconducting SWNTs can be probed by PL spectroscopy. The diameter, length, spatial position, and angular orientation of deposited SWNTs can be accurately determined by intermittent contact AFM. We describe an approach to combine and compare the spectroscopic (PL) and topographical (AFM) information for the same individual nanotubes as well as nanotube aggregates.

6.8 Dynamics of Surfactant-Suspended Single-Walled Carbon Nanotubes in a Centrifugal Field

Nair, N., Kim, W-J., Braatz, R.D. and Strano, M.S.
Langmuir, ***24****, 1790-1795 (2008)*

A hydrodynamic model is used to describe the motion of surfactant-suspended single-walled carbon nanotubes in a density gradient, while being subjected to a centrifugal field. The number of surfactant molecules adsorbed on each nanotube determines its effective density and, hence, its position in the gradient after centrifugation has been completed. Analysis of the spatial concentration distributions of CoMoCAT nanotubes suspended with 2 w/v% sodium cholate yielded 2.09, 2.14, and 2.08 surfactant molecules adsorbed per nanometer along the length of the (6,5), (7,5), and (8,7) nanotubes, respectively. The estimates are commensurate with experimental values reported in the literature and can be used to predict the fate of sodium cholate-suspended nanotubes in the separation process. Since the density of the surfactant-nanotube assembly is highly sensitive to the number of adsorbed molecules, a perturbation would cause it to be enriched at a different location in the gradient. The level of sensitivity is also reflected in the 95% confidence levels that are reported in this work.

6.9 Highly Stabilized Conductivity of Metallic Single Wall Carbon Nanotube Thin Films

Miyata, Y., Yanaga, K., Maniwa, Y. And Kataura, H.
J. Phys. Chem. C, ***112****, 3591-3596 (2008)*

The extremely stable conductivity against molecular physisorptions was revealed in thin films of high-purity metallic single wall carbon nanotubes (SWCNTs). The stability of the metallic SWCNTs results from their constant electronic density of state near the Fermi level. In the case of a mixture of metallic and semiconducting SWCNTs, the existence of semiconducting SWCNTs in the films makes the sheet resistance more sensitive to the adsorption of molecules mainly due to carrier doping. In the practical use for the transparent electrode, stability of the resistance is important and pure metallic SWCNTs have great advantages for such kind of applications.

6.10 Covalent Functionalization of Single-Walled Carbon Nanotubes Alters Their Densities Allowing

Electronic and Other Types of Separation

Kim, W-J., Nair, N., Lee, C.Y. and Strano, M.S.
J. Phys. Chem. C, ***112****, 7326-7331 (2008)*

We show that covalently attached functional groups can alter the densities of individual single-walled carbon nanotubes (SWNTs) in a predictable and highly controllable manner. A volume-additivity model based on molecular group contributions can be used to estimate the density difference between 4-hydroxyphenyl-functionalized and nonfunctionalized HiPco SWNTs as approximately 98.3 kg/m^3, compared with 97.9 kg/m^3 measured by density-gradient centrifugation. Conversely, the estimated density difference between the (6,5) (0.75 nm diameter) and (9,8) (1.17 nm diameter) SWNTs is smaller at 23.4 kg/m^3. We conclude that covalent functionalization can provide an effective handle to separate particular SWNTs from a typical diameter distribution. We show that SWNT mixtures in which metallic SWNTs have been selectively reacted produce two distinct density fractions corresponding to functionalized metallic and pure semiconducting SWNTs. The results were confirmed by Raman spectroscopy, where the high-density fractions exhibit an increased disorder mode with a corresponding decrease in intensity for the low-density fraction. This method also allows for the first independent measure of (n,m) SWNTs having different chemical conversions with functional groups, which will allow for a more rigorous analysis of SWNT chemistry than is possible with uncalibrated spectroscopies such as Raman or photoluminescence.

6.11 Optical Evaluation of the Metal-to-Semiconductor Ratio of Single-Wall Carbon Nanotubes

Miyata, Y., Yanagi, K., Maniwa, Y. And Kataura, H.
J. Phys. Chem. C., ***112****, 13187-13191 (2008)*

The metal-to-semiconductor ratio for single-wall carbon nanotubes (SWCNTs) produced by laser ablation was investigated using optical absorption spectroscopy. The SWCNTs were separated into metals and semiconductors using the density gradient centrifugation method. The optical absorption spectra of both SWCNTs were measured from the near-infrared to ultraviolet. A simple superposition analysis revealed that the pristine SWCNTs consist of 27 ±3% metallic SWCNTs and 73 ±3% semiconducting SWCNTs without using a theoretical correction. From the detailed oscillator fitting, it was found the absorption coefficient of the first excitonic transition of metallic SWCNTs M_{11} was almost the same as that of semiconducting SWCNTs S_{11} for a diameter distribution of 1.1~1.3 nm. This result provides a simple optical evaluation method to estimate the metal-to-semiconductor ratio of various SWCNT samples produced by different methods.

6.12 Optical Properties of Ultrashort Semiconducting Single-Walled Carbon Nanotube Capsules Down to Sub-10 nm

Sun, X. et al
J.Am. Chem. Soc., ***130****, 6551-6555 (2008)*

Single-walled carbon nanotubes (SWNTs) are typically long ($\gtrsim$100 nm) and have been well established as novel quasi one-dimensional systems with interesting electrical, mechanical, and optical properties. Here, quasi zero-dimensional SWNTs with finite lengths down to the molecular scale (7.5 nm in average) were obtained by length separation using a density gradient ultracentrifugation method. Different sedimentation rates of nanotubes with different lengths in a density gradient were taken advantage of to sort SWNTs according to length. Optical experiments on the SWNT fractions revealed that the UV−vis−NIR absorption and photoluminescence peaks of the ultrashort SWNTs blue-shift up to ~30 meV compared to long nanotubes, owing to quantum confinement effects along the length of ultrashort SWNTs. These nanotube capsules essentially correspond to SWNT quantum dots.

6.13 Transparent Conductive Single-Walled Carbon Nanotube Networks with Precisely Tunable Ratios of Semiconducting and Metallic Nanotubes

Blackburn,. J.L. et al
ASCNano, ***2(6)****, 1266-1274 (2008)*

We present a comprehensive study of the optical and electrical properties of transparent conductive films made from precisely tuned ratios of metallic and semiconducting single-wall carbon nanotubes. The conductivity and transparency of the SWNT films are controlled by an interplay between localized and delocalized carriers, as determined by the SWNT electronic structure, tube−tube junctions, and intentional and unintentional redox dopants. The results suggest that the main resistance in the SWNT thin films is the resistance associated with tube–tube junctions. Redox dopants are found to increase the delocalized carrier density and transmission probability through intertube junctions more effectively for semiconductor-enriched films than for metal-enriched films. As a result, redox-doped semiconductor-enriched films are more conductive than either intrinsic or redox-doped metal-enriched films.

6.14 Selective Enrichment of (6,5) and (8,3) Single-Walled Carbon Nanotubes via Cosurfactant Extraction from Narrow (*n,m*) Distribution Samples

Wei, L. et al
J. Phys. Chem. B, ***112****, 2771-2774 (2008)*

Highly selective enrichment of (6,5) and (8,3) SWCNTs (above 85% of the semiconducting tubes) was achieved through multistep extraction by sodium dodecyl sulfate (SDS) and sodium cholate (SC) cosurfactant solution from narrowly (*n*,*m*) distributed SWCNTs produced by the catalyst Co-MCM-41. A systematic change in the chirality selectivity was observed when the weight ratio between SDS and SC varied in cosurfactant solutions, with maximum enrichment selectivity for (6,5) tubes yielded at 1:4. Furthermore, surfactants were washed away easily to produce "clean" SWCNTs. This observation sheds light on the possibility of obtaining SWCNTs with the desired (*n*,*m*) structure via an easily scalable approach. No selectivity was detected when using sodium dodecyl benzene sulfonate (SDBS)/SC cosurfactants, hence suggesting the need for further exploration of various cosurfactant combinations for more effective extraction of different (*n*,*m*) species.

6.15 Nano-graphene oxide for cellular imaging and drug delivery

Sun, X.S. et al
Nano Res., ***1****, 203-212 (2008)*

Two-dimensional graphene offers interesting electronic, thermal, and mechanical properties that are currently being explored for advanced electronics, membranes, and composites. Here we synthesize and explore the biological applications of nano-graphene oxide (NGO), i.e., single-layer graphene oxide sheets down to a few nanometers in lateral width. We develop functionalization chemistry in order to impart solubility and compatibility of NGO in biological environments. We obtain size separated pegylated NGO sheets that are soluble in buffers and serum without agglomeration. The NGO sheets are found to be photoluminescent in the visible and infrared regions. The intrinsic photoluminescence (PL) of NGO is used for live cell imaging in the near-infrared (NIR) with little background. We found that simple physisorption via π-stacking can be used for loading doxorubicin, a widely used cancer drug onto NGO functionalized with antibody for selective killing of cancer cells in vitro. Owing to its small size, intrinsic optical properties, large specific surface area, low cost, and useful non-covalent interactions with aromatic drug molecules, NGO is a promising new material for biological and medical applications.

6.16 In Situ Raman Spectroelectrochemistry of Single-Walled Carbon Nanotubes: Investigation of Materials Enriched with (6,5) Tubes

Kavan, L. et al
J. Phys. Chem., ***112****, 14179-14187 (2008)*

Single-walled carbon nanotubes (CoMoCat) have been enriched with (6,5) tubes via density-gradient ultracentrifugation. Thin solid films of quasi-isolated nanotubes were fabricated from a solution of sorted nanotubes by vacuum filtration and extraction with water. Optical spectroscopy in the vis–NIR region and Raman spectroscopy were used to characterize these materials. The experimental studies were supported by a theoretical analysis of the electronic and vibrational structure of selected (*n*,*m*) tubes by using density functional theory. Besides the most abundant tubes (6,5), the experimental and theoretical data for tubes (6,4), (7,3), (7,5), (8,3), and (9,1) are also discussed. A detailed investigation by in situ Raman spectroelectrochemistry was focused on the effects of electrochemical p-/n-doping. The experimental analysis of the intensities and frequencies of the radial breathing mode and the tangential displacement modes were correlated with the theoretically calculated optical transition energies and Raman frequencies. It was demonstrated that electrochemical charging is a useful tool for the study of doping effects on the electronic structure of carbon nanotubes.

6.17 Influence of Nanotube Length on the Optical and Conductivity Properties of Thin Single-Wall Carbon Nanotube Networks

Simien, D. et al
ACS Nano, ***2(9)****, 1879-1884 (2008)*

We study the optical and electrical properties of transparent conducting films made from length-sorted single-wall carbon nanotubes (SWCNT). Thin films of length-sorted SWCNTs, formed through filtration from a dispersing solvent onto a filter substrate ("buckypaper"), exhibit sharp changes in their optical properties and conductivity (σ) with increasing SWCNT surface concentration. At a given surface concentration, tubes longer than 200 nm are found to form networks that are more transparent and conducting. We show that changes of σ with SWCNT concentration can be *quantitatively* described by the generalized effective medium (GEM) theory. The scaling universal exponents describing the "percolation" transition from an insulating to a conducting state with increasing concentration are consistent with the two-dimensional (2D) percolation model. Shorter tubes and mixed length tubes form 3D networks. Furthermore, we demonstrate that the conductivity percolation threshold (x_c) varies with the aspect ratio L as, $x_c \sim 1/L$, a result that is also in accordance with the percolation theory. These findings provide a framework for engineering the optical and electrical properties of SWCNT networks for technological applications where flexibility, transparency, and conductivity are required.

6.18 Colored Semitransparent Conductive Coatings Consisting of Monodisperse Metallic Single-Walled Carbon Nanotubes

Green, A.A. and Hersam, M.C.
Nano Lett., ***8(5)****, 1417-1422 (2008)*

Single-walled carbon nanotubes (SWNTs) are promising materials for transparent conduction as a result of their exceptional electrical, optical, mechanical, and chemical properties. However, since current synthetic methods yield polydisperse mixtures of SWNTs, the performance of SWNT transparent conductive films has previously been hindered by semiconducting species. Here, we describe the performance of transparent conductors produced using predominantly metallic SWNTs. Compared with unsorted material, films enriched in metallic SWNTs can enhance conductivity by factors of over 5.6 in the visible and 10 in the infrared. Moreover, by using monodisperse metallic SWNTs sorted with angstrom-level resolution in diameter, semitransparent conductive coatings with tunable optical transmittance can be produced.

6.19 Chiral-Angle Distribution for Separated Single-Walled Carbon Nanotubes

Sato, Y. et al
Nano Lett., ***8(10)****, 3151-3154 (2008)*

Chiral indices (n,m) of metallic and semiconducting single-walled carbon nanotubes (SWNTs) selectively separated via the density-gradient ultracentrifugation process were individually assigned by using an aberration-corrected transmission electron microscope (TEM) operated at 80 kV. Our statistical analysis revealed that armchair (n,n) and chiral (n,n-3) SWNTs with large chiral angles (>20°) are dominant metallic nanotubes in the separated samples, whereas such a noticeable preference of particular indices was not observed for semiconducting nanotubes. Some significant discrepancies were found between the TEM and spectroscopic results on the major chiral indices and the metal/semiconductor ratios in these SWNTs.

6.20 Centrifugal Length Separation of Carbon Nanotubes

Fagan, J.A., Becker, M.L., Chun, J., Nie, P., Bauer, B.J., Simpson, J.R., Hight-Walker, A. and Hobbie, E.K.
Langmuir, ***24(24)****, 13880-13889 (2008)*

Separation of single-wall carbon nanotubes (SWCNTs) by length via centrifugation in a high density medium, and the characterization of both the separated fractions and the centrifugation process are presented. Significant quantities of the separated SWCNTs ranging in average length from <50 nm to ~2 μm were produced, with the distribution width being coupled to the rate of the separation. Less rapid separation is shown to produce narrower distributions; these length fractions, produced using sodium deoxycholate dispersed SWCNTs, were characterized by UV−visible−near-infrared absorption and fluorescence spectroscopy, dynamic light scattering, Raman scattering, and atomic force microscopy. Several parameters of the separation were additionally explored: SWCNT concentration, added salt concentration, liquid density, rotor speed, surfactant concentration, and the processing temperature. The centrifugation technique is shown to support 10 mg per day scale processing and is applicable to all of the major SWCNT production methods. The cost per unit of the centrifugation-based separation is also demonstrated to be significantly less than size exclusion chromatography-based separations.

6.21 Assessment of (n,m) Selectively Enriched Small Diameter Single-Walled Carbon Nanotubes by Density Differentiation from Cobalt-Incorporated MCM-41 for Macroelectronics

Wei, L., Lee, C.W., Li, L-J., Sudibya, G., Wang, B., Chen, L.Q., Chen, P., Yang, Y., Chan-Park, M.B. and Chen, Y.
Chem. Mater., ***20**, 7417-7424 (2008)*

Uniformly semiconducting or metallic single-walled carbon nanotube (SWNT) networks are ideal materials for flexible and large-area electronics (macroelectronics). With the goal of developing optimal enrichment and evaluation solutions toward economical production of monodisperse SWNTs for macroelectronics, we selectively enriched SWNTs, which have small diameters (<0.9 nm) and a narrow (*n*,*m*) distribution, synthesized on cobalt-incorporated MCM-41 catalysts. The (7,5) enriched SWNTs were obtained from sodium cholate (SC) dispersion, whereas (6,5) were from cosurfactant mixtures of sodium dodecyl sulfate (SDS):SC at 1: 4. Density gradient ultracentrifugation was applied to further refine the separation. Subsequently, SWNT thin-film field effect transistors (FETs) were fabricated using enriched SWNTs. We characterized the chiralities by photoluminescence excitation spectroscopy, optical absorption spectroscopy, Raman spectroscopy, and electrical transport measurements. Among these techniques, results demonstrate that the electrical transport measurement (through I_{on}/I_{off} ratio) of thin-film FETs is the most sensitive technique to evaluate the purity of semiconducting SWNTs. Enriched SWNTs via only SC produced more devices with higher on-/off-current ratios (up to 1×10^6) compared to SWNTs obtained from SDS/SC cosurfactants. These results are different from previous studies using laser-ablation-grown SWNTs (1.1−1.4 nm), encouraging more comprehensive models to explain diameter dependent chirality selection using surfactants.

6.22 Thin Film Nanotube Transistors Based on Self-Assembled, Aligned, Semiconducting Carbon Nanotube Arrays

Engel, M., Small, J.P., Steiner, M., Freitag, M., Green, A.A., Hersam, M.C. and Avouris, P.
ACS Nano, ***2(12)**, 2445-2452 (2008)*
Thin film transistors (TFTs) are now poised to revolutionize the display, sensor, and flexible electronics markets. However, there is a limited choice of channel materials compatible with low-temperature processing. This has inhibited the fabrication of high electrical performance TFTs. Single-walled carbon nanotubes (CNTs) have very high mobilities and can be solution-processed, making thin film CNT-based TFTs a natural direction for exploration. The two main challenges facing CNT-TFTs are the difficulty of placing and aligning CNTs over large areas and low on/off current ratios due to admixture of metallic nanotubes. Here, we report the self-assembly and self-alignment of CNTs from solution into micron-wide strips that form regular arrays of dense and highly aligned CNT films covering the entire chip, which is ideally suitable for device fabrication. The films are formed from pre-separated, 99% purely semiconducting CNTs and, as a result, the CNT-TFTs exhibit simultaneously high drive currents and large on/off current ratios. Moreover, they deliver strong photocurrents and are also both photo- and electroluminescent.

6.23 Exciton Energy Transfer in Pairs of Single-Walled Carbon Nanotubes

Qian, H., Georgi, C., Anderson, N., Green, A.A., Hersam, M.C., Novotny, L. and Hartschuh, A.
Nano Lett., ***8(5)**, 1363-1367 (2008)*

We studied the exciton energy transfer in pairs of semiconducting nanotubes using high-resolution optical microscopy and spectroscopy on the nanoscale. Photoluminescence from large band gap nanotubes within bundles is observed with spatially varying intensities due to distance-dependent internanotube transfer. The range of efficient energy transfer is found to be limited to a few nanometers because of competing fast nonradiative relaxation responsible for low photoluminescence quantum yield.

6.24 Visualizing the Local Optical Response of Semiconducting Carbon Nanotubes to DNA-Wrapping

Qian, H., Araujo, P.T., Georgi, C., Gokus, T., Hartmann, N., Green, A.A., Jorio, A., Hersam, M.C., Novotny, L. and Hartschuh, A.
Nano Lett., ***8(9)**, 2706-2711 (2008)*

We studied the local optical response of semiconducting single-walled carbon nanotubes to wrapping by DNA segments using high resolution tip-enhanced near-field microscopy. Photoluminescence (PL) near-field images of single nanotubes reveal large DNA-wrapping-induced red shifts of the exciton energy that are two times higher than indicated by spatially averaging confocal microscopy. Near-field PL spectra taken along nanotubes feature two distinct PL bands resulting from DNA-wrapped and unwrapped nanotube segments. The transition between the two energy levels occurs on a length scale smaller than our spatial resolution of about 15 nm.

6.25 Reversibility, Dopant Desorption, and Tunneling in the Temperature-Dependent Conductivity of Type-Separated, Conductive Carbon Nanotube Networks

Barnes, T.M., Blackburn, J.L., va de Lagemaat, J., Coutts, T.J. and Heben, M.J.
*ACS Nano, **2(9)**, 1968-1976 (2008)*

We present a comprehensive study of the effects of doping and temperature on the conductivity of single-walled carbon nanotube (SWNT) networks. We investigated nearly type-pure networks as well as networks comprising precisely tuned mixtures of metallic and semiconducting tubes. Networks were studied in their as-produced state and after treatments with nitric acid, thionyl chloride, and hydrazine to explore the effects of both intentional and adventitious doping. For intentionally and adventitiously doped networks, the sheet resistance (R_s) exhibits an irreversible increase with temperature above ~350 K. Dopant desorption is shown to be the main cause of this increase and the observed hysteresis in the temperature-dependent resistivity. Both thermal and chemical dedoping produced networks free of hysteresis. Temperature-programmed desorption data showed that dopants are most strongly bound to the metallic tubes and that networks consisting of metallic tubes exhibit the best thermal stability. At temperatures below the dopant desorption threshold, conductivity in the networks is primarily controlled by thermally assisted tunneling through barriers at the intertube or interbundle junctions.

6.26 Hydrodynamic Characterization of Surfactant Encapsulated Carbon Nanotubes Using an Analytical Ultracentrifuge

Arnold, M.S., Suntivich, J., Stupp, S.I. and Hersam, M.C:
*ACS Nano, **2(11)**, 2291-2300 (2008)*

The hydrodynamic properties of surfactant encapsulated single-walled carbon nanotubes (SWNTs) have been characterized by optically measuring their spatial and temporal redistribution *in situ* in an analytical ultracentrifuge. The measured redistribution profiles are fit to the Lamm equation, thus determining the sedimentation, diffusion, and hydrodynamic frictional coefficients of the surfactant encapsulated SWNTs. For sodium cholate encapsulated SWNTs, we demonstrate that the technique of analytical ultracentrifugation can be utilized to determine the linear packing density of surfactant molecules along the length of the SWNTs, $3.6 \pm 0.8\ \mathrm{nm}^{-1}$, and the anhydrous molar volume of the surfactant molecules on the SWNT surfaces, $270 \pm 20\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$. Additionally, analytical ultracentrifugation is used to measure and compare the sedimentation rates of bundled and isolated carbon nanotubes. This study should serve as a guide for designing centrifuge-based processing procedures for preparing samples of SWNTs for a wide variety of applications and studies. Additionally, the results obtained here should aid in understanding the hydrodynamic properties of SWNTs and the interactions between SWNTs and surfactants in aqueous solution.

6.27 Ultrafast Exciton Dephasing in Semiconducting Single-Walled Carbon Nanotubes

Ma, Y-Z., Graham, M.W. and Fleming, G.R.
*Phys. Rev.Lett., **101**, 217402-1-217402-4 (2008)*

Femtosecond two-pulse degenerate four-wave mixing spectroscopy was applied to study the exciton dephasing in a broad range of excitation intensities and lattice temperatures. We find that both exciton-exciton and exciton-phonon scattering have profound effects on the dephasing process. The dominant phonon mode involved in the dephasing is identified as the out-of-plane, transverse optical mode with a frequency of 847 cm^{-1}. The extracted homogeneous linewidths at all measured temperatures are in excellent agreement with the results of a single-tube photoluminescence experiment.

6.28 Length Fractionation of Carbon Nanotubes Using Centrifugation

Fagan, J.A., Becker, M.L., Chun, J. and Hobbie, E.K.
*Advanced Materials, **20**, 1609-1613 (2008)*

Scalable separation of single-walled carbon nanotubes (SWCNTs) by length and chirality is critical to the adaptation of these materials for applications. Ultracentrifugation of SWCNTs within a density gradient produces chiral separation of the NTs, and it is shown here that ultracentrifugation can also be used to produce length fractionated SWCNTs by exploiting their transient motion in response to applied centripetal acceleration.

6.29 **Optical properties of metallic and semiconducting single-wall carbon nanotubes**
Miyata, Y., Yanagi, K., Maniwa, Y., and Kataura, H.
Phys. Stat. Sol. (b), ***245(10)****, 2233-2238 (2008)*

Optical properties of high purity metallic and semiconducting single-wall carbon nanotubes (SWCNTs) were investigated from far infrared to ultraviolet by optical absorption spectroscopy. It was found that the metallic SWCNT thin film has larger infrared absorption intensity than the semiconducting one. Furthermore, little changes in the optical absorption spectrum and the DC sheet resistance against molecular physisorptions were revealed in the metallic SWCNTs thin film. The stability of the metallic SWCNTs results from their constant electronic density of state near the Fermi level. On the other hand, the existence of semiconducting SWCNTs in the films makes their infrared absorption intensity and the sheet resistance more sensitive to the adsorption of molecules mainly due to carrier doping.

6.30 **In-situ Vis/NIR spectroelectrochemistry of single-walled carbon nanotubes enriched with (6,5) tubes**
Frank, O., Kavan, L., Green, A.A., Hersam, M.C. and Dunsch, L.
Phys. Stat. Sol. (b), ***245(10)****, 2239-2242 (2008)*

An in-situ optical Vis/NIR spectroelectrochemistry study was performed on single-walled carbon nanotubes (CoMoCat) enriched with (6,5) tubes via density-gradient ultracentrifugation. Thin semitransparent solid films were prepared from the solution of sorted nanotubes by vacuum filtration and purification with water. Despite the appearance of some bundling of the nanotubes during this procedure, peaks corresponding to optical transitions of tubes with distinct chiralities may be observed in the spectra. The effects of electrochemical redox doping on the electronic state of the nanotubes were investigated in an electrode potential window between –2 and +1.7 V vs. Ag-pseudoreference electrode. The bleaching of ΔE11S and ΔE22S optical transitions is traced for particular tubes, which allows a partial quantification of changes in the electronic density of states (DOS) caused by their filling with electrons or holes.

6.31 **Photoinduced Luminescence Blinking and Bleaching in Individual Single-Walled Carbon Nanotubes**
Georgi, C., Hartmann, N., Gokus, T., Green, A.A., Hersam, M.C. and Hartschuh, A.
Chemphyschem., ***9****, 1460-1464 (2008)*

The temporal evolution of photoluminescence in individual single-walled carbon nanotubes (SWNT) under strong laser irradiation is studied and pronounced blinking and bleaching is observed, caused by photoinduced oxidation that subsequently quenches mobile excitons. The nanotubes are isolated with sodium cholate and spun onto either a glass or mica surface. Their bleaching behavior is investigated for variable laser intensities in air and argon atmosphere. The decay rate for luminescence bleaching generally increases with higher laser intensity, however saturating on mica substrates, which is attributed to limited availability of oxygen in the vicinity of the nanotubes. Step-like events in the luminescence time traces corresponding

6.32 **Processing and properties of highly enriched double-wall carbon nanotubes**
Green, A.A. and Hersam, M.C.
Nature Nanotech., ***4****, 64-70 (2009)*

Carbon nanotubes consist of one or more concentric graphene cylinders and are under investigation for a variety of applications that make use of their excellent thermal, mechanical, electronic and optical properties. Double-wall nanotubes are ideal systems for studying the interwall interactions influencing the properties of nanotubes with two or more walls. However, current techniques to synthesize double-wall nanotubes produce unwanted single- and multiwall nanotubes. Here, we show how density gradient ultracentrifugation can be used to separate double-wall nanotubes from mixtures of single- and multiwall nanotubes through differences in their buoyant density. This technique results in samples that are highly enriched in either single- or double-wall nanotubes of similar outer wall diameter, with the double-wall nanotubes being, on average, ~44% longer than the single-wall nanotubes. The longer average length of the double-wall nanotubes provides distinct advantages when they are used in transparent conductors.

6.33 **Self-Assembly of Ordered Nanowires in Biological Suspensions of Single-Wall Carbon Nanotubes**
Hobbie, E.K., Fagan, J.A., Becker, M.L., Hudson, S.D., Fakhri, N. and Pasquali, M.
Nano, ***3(1)****, 189-196 (2009)*

We investigate the self-assembly of ordered nanowires from length-purified single-wall carbon nanotubes

(SWCNTs) in aqueous suspensions of the biological surfactant sodium deoxycholate. Macroscopically straight and nearly periodic linear arrangements of aligned individual SWCNTs are found to self-assemble in two-dimensional geometries from nanotube suspensions that are otherwise stable in the bulk, which we attribute to a dominance of surface effects under strong confinement. Directed self-assembly is explored through surface patterning, opening up new potential routes to nanotube manipulation for optical diagnostics and applications that require ordered arrangements of mutually aligned SWCNTs. The stability of these structures to thermal fluctuations and changes in solution chemistry are surveyed with near-infrared fluorescence microscopy.

6.34 Electrolyte Tuning of Surfactant Interfacial Behavior for Enhanced Density-Based Separations of Single-Walled Carbon Nanotubes

Niyogi, S., Densmore, C.G. and Doorn, S.K.
J. Am. Chem. Soc., ***131****, 1144-1153 (2009)*

We study the interfacial behavior between the straight-chain alkyl surfactant sodium dodecyl sulfate (SDS) and single-walled carbon nanotubes (SWNTs) as a function of added electrolytes, including NaCl. We observe an increase in photoluminescence intensity and narrowing of spectral line widths with electrolyte addition, indicating a change in SDS aggregation number that leads to a pronounced volume change in the nanotube/SDS composite structure. By tuning the interfacial dynamics through NaCl addition and temperature change, we demonstrate that this volume change can be used to yield diameter-dependent separation of metallic and semiconducting SWNTs, without the use of any additional cosurfactant, through density gradient ultracentrifugation. The diameter-dependent fractionation follows the intrinsic relation expected for the density of unfunctionalized nanotubes, indicating a simple amplification of these inherent density differences as the mechanism for salt enhanced separations. Isolation of enriched metallic and semiconducting fractions further illustrates that the surface aggregation characteristics of SDS on metallic SWNTs are different from that on the semiconducting chiralities. These experiments illustrate the governing behavior of surface phenomena and interfacial forces on the diameter-dependent fractionation of SWNTs and point to new routes for enhancing existing separations strategies.

6.35 Size-Dependent Cellular Uptake and Expulsion of Single-Walled Carbon Nanotubes: Single Particle Tracking and a Generic Uptake Model for Nanoparticles

Jin, H., Heller, D.A., Sharma, R. and Strano, M.S.
Nano, ***3(1),*** *149-158 (2009)*

The cellular uptake and expulsion rates of length-fractionated single-walled carbon nanotubes (SWNT) from 130 to 660 nm in NIH-3T3 cells were measured *via* single particle tracking of their intrinsic photoluminescence. We develop a quantitative model to correlate endocytosis rate with nanoparticle geometry that accurately describes this data set and also literature results for Au nanoparticles. The model asserts that nanoparticles cluster on the cell membrane to form a size sufficient to generate a large enough enthalpic contribution *via* receptor ligand interactions to overcome the elastic energy and entropic barriers associated with vesicle formation. Interestingly, the endocytosis rate constant of SWNT (10^{-3} min^{-1}) is found to be nearly 1000 times that of Au nanoparticles (10^{-6} min^{-1}) but the recycling (exocytosis) rate constants are similar in magnitude (10^{-4} to 10^{-3} min^{-1}) for poly(D,L-lactide-co-glycolide), SWNT, and Au nanoparticles across distinct cell lines. The total uptake of both SWNT and Au nanoparticles is maximal at a common radius of 25 nm when scaled using an effective capture dimension for membrane diffusion. The ability to understand and predict the cellular uptake of nanoparticles quantitatively should find utility in designing nanosystems with controlled toxicity, efficacy, and functionality.

6.36 Colors of carbon nanotubes

Yanagi, K., Miyata, Y., Tanaka, T., Fujii, S., Nishide, D. and Kataura, H.
Diamond & Related Materials, ***18****, 935-939 (2009)*

Single-wall carbon nanotubes (SWCNTs) are graphitic materials whose colors are usually considered to be black. Actually, graphite-like black color is observed for as-synthesized SWCNT samples which are in the mixture state of the metallic and the semiconducting SWCNTs. However, after the separation of the metallic and the semiconducting types from the mixture, SWCNTs can exhibit various colors depending on their electronic types and diameters. These colorful colors are caused by the boundary conditions for the circumferential directions of the cylindrical structures. Here we discuss the underlying physical backgrounds of the colors of SWCNTs and the techniques to obtain such colorful SWCNTs.

6.37 Microscale Polymer−Nanotube Composites
Hobbie, E.K., Fagan, J.A., Obrzut, J. and Hudson, S.D.
Appl. Materials & Interfaces, ***1(7)***, *1561-1566 (2009)*

Polymer colloids with an interfacial coating of purified single-wall carbon nanotubes (SWCNTs) are synthesized from length- and type-sorted SWCNTs. Aqueous nanotube suspensions sorted through density-gradient ultracentrifugation are used to emulsify spherical polymer colloids of microscale dimensions that are characterized through a combination of optical microscopy, transmission electron microscopy, and impedance spectroscopy. The SWCNT−polymer composite particles exhibit electrical conductivities comparable to or better than those of bulk SWCNT−polymer composites at nanotube loadings of more than 1 order of magnitude lower. The composite particles retain the unique electronic and optical characteristics of the parent SWCNT solution with potential applications as microelectronic and microoptical components.

6.38 Quantifying the Semiconducting Fraction in Single-Walled Carbon Nanotube Samples through Comparative Atomic Force and Photoluminescence Microscopies
Naumov, A.V., Kuznetsov, O.A., Harutyunyan, A.R., Green, A.A., Hersam, M.C., Resasco, D.E., Nikolaev, P.N. and Weisman, R.B.
Nano Lett., ***9(9)***, *3203-3208 (2009)*

A new method was used to measure the fraction of semiconducting nanotubes in various as-grown or processed single-walled carbon nanotube (SWCNT) samples. SWCNT number densities were compared in images from near-IR photoluminescence (semiconducting species) and AFM (all species) to compute the semiconducting fraction. The results show large variations among growth methods and effective sorting by density gradient ultracentrifugation. This counting-based method provides important information about SWCNT sample compositions that can guide controlled growth methods and help calibrate bulk characterization techniques.

6.39 Do Inner Shells of Double-Walled Carbon Nanotubes Fluoresce?
Tsyboulski, D.A., Hou, Y., Fakhri, N., Ghosh, S., Zhang, R., Bachilo, S.M., PAsquali, M., Chen, L., Liu, J. and Weisman, R.B.
Nano Lett., ***9(9)***, *3282-3289 (2009)*

The reported fluorescence from inner shells of double-walled carbon nanotubes (DWCNTs) is an intriguing and potentially useful property. A combination of bulk and single-molecule methods was used to study the spectroscopy, chemical quenching, mechanical rigidity, abundance, density, and TEM images of the near-IR emitters in DWCNT samples. DWCNT inner shell fluorescence is found to be weaker than SWCNT fluorescence by a factor of at least 10 000. Observable near-IR emission from DWCNT samples is attributed to SWCNT impurities.

6.40 Isolation of single-walled carbon nanotube enantiomers by density differentiation
Green, A.A., Duch, M.C. and hersam, M.C.
Nano Res., ***2***, *69-77 (2009)*

Current methods of synthesizing single-walled carbon nanotubes (SWNTs) result in racemic mixtures that have impeded the study of left- and right-handed SWNTs. Here we present a method of isolating different SWNT enantiomers using density gradient ultracentrifugation. Enantiomer separation is enabled by the chiral surfactant sodium cholate, which discriminates between left- and right-handed SWNTs and thus induces subtle differences in their buoyant densities. This sorting strategy can be employed for simultaneous enrichment by handedness and roll-up vector of SWNTs having diameters ranging from 0.7 to 1.5 nm. In addition, circular dichroism of enantiomer refined samples enables identification of high-energy optical transitions in SWNTs.

6.41 Carbon nanotubes in biology and medicine: In vitro and in vivo detection, imaging and drug delivery
Liu, Z., Tabakman, S., Welsher, K. and Dai, H.
Nano Res., ***2***, *85-120 (2009)*

Carbon nanotubes exhibit many unique intrinsic physical and chemical properties and have been intensively explored for biological and biomedical applications in the past few years. In this comprehensive review, we summarize the main results from our and other groups in this field and clarify that surface functionalization is critical to the behavior of carbon nanotubes in biological systems. Ultrasensitive detection of biological species with carbon nanotubes can be realized after surface passivation to inhibit the non-specific binding of biomolecules on the hydrophobic nanotube surface. Electrical nanosensors based on nanotubes provide a label-free approach to biological detection. Surface-enhanced Raman spectroscopy of carbon nanotubes opens up a method of protein microarray with detection sensitivity down to 1 fmol/L. In vitro and in vivo toxicity studies reveal that highly water soluble and serum stable nanotubes are biocompatible, nontoxic, and potentially useful for biomedical applications. In vivo biodistributions vary with the functionalization and possibly also size of nanotubes, with a tendency to accumulate in the reticuloendothelial system (RES), including the liver and spleen, after intravenous administration. If well functionalized, nanotubes may be excreted mainly through the biliary pathway in feces. Carbon nanotube-based drug delivery has shown promise in various In vitro and in vivo experiments including delivery of small interfering RNA (siRNA), paclitaxel and doxorubicin. Moreover, single-walled carbon nanotubes with various interesting intrinsic optical properties have been used as novel photoluminescence, Raman, and photoacoustic contrast agents for imaging of cells and animals. Further multidisciplinary explorations in this field may bring new opportunities in the realm of biomedicine.

6.42 **Selective suspension in aqueous sodium dodecyl sulfate according to electronic structure type allows simple separation of metallic from semiconducting single-walled carbon nanotubes**
Moshammer, K., Hennrich, F. and Kappes, M.M.
Nano Res., ***2***, *599-606 (2009)*

Both density gradient centrifugation and gel electrophoresis have been reported to allow high throughput separation of metallic from semiconducting single-walled carbon nanotubes (SWNTs) when using aqueous sodium dodecyl sulphate (SDS) suspensions. We show here that both methods rely on an initial dispersion-by-sonication step, which is already selective with respect to electronic structure type. The corresponding aqueous SDS “starting” suspensions obtained after sonication and purification by simple centrifugation (70,000 g, 1 h) contain semiconducting SWNTs primarily in the form of small bundles whereas metallic SWNTs are predominantly suspended as individual tubes. Density gradient centrifugation then separates the bundles from the individual tubes on the basis of differences in their overall buoyant densities. Gel electrophoresis separates the longer bundles from the shorter individual tubes on the basis of their different mobilities. We also demonstrate that such starting suspensions can be fractionated according to electronic structure type by even simpler techniques such as size exclusion chromatography or gel filtration, thus opening the way for simple scale-up.

6.43 **Anchoring of Rare-Earth-Based Single-Molecule Magnets on Single-Walled Carbon Nanotubes**
Kyatskaya, S., Mascaros, J.R.G., Bogani, L., Hennrich, F., Kappes, M., Wernsdorfer, W. and Ruben, M.
J. Am. Chem. Soc., ***131***, *15143-15151 (2009)*

A new heteroleptic bis(phthalocyaninato) terbium(III) complex **1**, bearing a pyrenyl group, exhibits temperature and frequency dependence of ac magnetic susceptibility, typical of single-molecule magnets. The complex was successfully attached to single-walled carbon nanotubes (SWNTs) using π−π interactions, yielding a **1**−SWNT conjugate. The supramolecular grafting of **1** to SWNTs was proven qualitatively and quantitatively by high-resolution transmission electron microscopy, emission spectroscopy, and atomic force spectroscopy. Giving a clear magnetic fingerprint, the anisotropy energy barrier and the magnetic relaxation time of the **1**−SWNT conjugate are both increased in comparison with the pure crystalline compound **1**, likely due to the suppression of intermolecular interactions. The obtained results propose the **1**−SWNT conjugate as a promising constituent unit in magnetic single-molecule measurements using molecular spintronics devices.

6.44 **Modulation of Single-Walled Carbon Nanotube Photoluminescence by Hydrogel Swelling**
Barone, P.W., Yoon, H., Ortiz-Garcia, R., Zhang, J., Ahn, J-H., Kim, J-H. and Strano, M.S.
ACS Nano, ***3(12)***, *3869-3877 (2009)*

We demonstrate the use of hydrogel swelling as a mechanism to reversibly induce solvatochromic shifting in single-walled carbon nanotube (SWNT) near-infrared emission within a biocompatible hydrogel. The optical sensor reports the degree of the swelled state and glucose concentration when apo-glucose oxidase is used to cross-link the hydrogel. Photoluminescence emission maxima from dispersed nanotubes in a poly(vinyl alcohol) hydrogel shift as cross-linking is increased, with a maximum of −48 meV for the (6,5) nanotube. The Raman tangential mode also red shifts up to 17 cm^{-1}, indicative of nanotube lattice strain equivalent to an effective hydrostatic pressure of 3 GPa. While the electronic band gaps of SWNTs are known to either increase or decrease with uniaxial strain or lattice deformation depending on chiral vector, we show that the mechanism of detection is counterintuitively non-strain-dependent. Instead, the data are well-described by a model that accounts for changes in dielectric screening of the 1-D exciton, as the osmotic pressure forces conformational distortions in the PVA by rotating more polar groups to the nanotube surface. The model describes observed changes with hydration state and cross-linking density variation from 0 to 14%. Cross-linking with apo-glucose oxidase renders the hydrogel glucose responsive, and we demonstrate rapid and reversible detection of glucose from these systems after repeated cycling of 10 mM glucose. We also demonstrate detection and imaging in the near-infrared of implanted hydrogel sensors in a mouse tissue model, showing excellent signal-to-noise of 8.6 and contrast with integration times of 60 s.

6.45 Near Monochiral Single-Walled Carbon Nanotube Dispersions in Organic Solvents
Stürzl, N., Hennrich, F., Lebedkin, S. and Kappes, M.M.
J. Phys. Chem. C., ***113****, 14628-14632 (2009)*

We describe simple procedures to obtain near monochiral samples of several single-walled carbon nanotube (SWNT) species starting from SWNT raw material. (7,5), (7,6), (10,5), and (9,7) nanotubes were obtained with respective enrichments of up to ~90% (as estimated from photoluminescence and absorption spectra) by their selective dispersion in toluene with various fluorene-based polymers and subsequent centrifugation. Further highly enriched samples, for instance of (6,5) nanotubes, were prepared by implementing density gradient centrifugation of dispersions of SWNTs in organic solvents with 2,4,6-tribromotoluene as the density gradient additive.

6.46 Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation
Green, A.A. and Hersam, M.C.
Nano Lett., ***9(12)****, 4031-4036 (2009)*

Graphene flakes with controlled thicknesses are isolated in solution using density gradient ultracentrifugation. These stable graphene dispersions are produced using the bile salt sodium cholate, which promotes graphite exfoliation and results in graphene−surfactant complexes having buoyant densities that vary with graphene thickness. The sorted graphene flakes are characterized using atomic force microscopy and Raman spectroscopy. Graphene dispersions produced using density differentiation offer superior performance in transparent conductors than those produced using conventional sedimentation-based centrifugation techniques.

6.47 Transmission Electron Microscopy and UV-vis-IR Spectroscopy Analysis of the Diameter Sorting of Carbon Nanotubes by Gradient Density Ultracentrifugation
Fleurier, R., Lauret, J-S., Lopez, U. and Loiseau, A.
Adv. Funct. Mater., ***19(4)****, 2219-2223 (2009)*

Diameter separation of single-walled carbon nanotubes is achieved via the density gradient ultracentrifugation process. Statistical analysis of the separated samples is performed using high-resolution transmission electron microscopy (HRTEM). The evolution of the diameter distribution with respect to the gradient density is extracted by analyzing hundreds of HRTEM images, and the results are found to be consistent with those estimated by UV-vis-IR spectroscopy. The efficiency of the separation process can be quantitatively characterized by the standard deviation of the diameter distribution, which is determined from the TEM analyses. This particular study indicated that for electric arc nanotubes dispersed in sodium cholate, diameter sorting is more efficient in the upper part of the gradient.

6.48 80 GHz field-effect transistors produced using high purity semiconducting single-walled carbon nanotubes
Nougaret, L., Happy, H., Dambrine, g., Derycke, V., Bourgoin, J.P., Green, A.A. and Hersam, M.C.
Appl. Phys. Lett., ***94****, 243505-1-243505-3 (2009)*

This paper presents the high frequency performance of single-walled carbon nanotube (SWNT) field-effect transistors, with channel consisting of dense networks of high purity semiconducting SWNTs. Using SWNT samples containing 99% pure semiconducting SWNTs, we achieved operating frequencies above ,80 GHz. This record frequency does not require aligned SWNTs, thus demonstrating the remarkable potential of random networks of sorted SWNTs for high frequency electronics.

6.49 Fractioning HiPco and CoMoCAT SWCNTs via density gradient ultracentrifugation by the aid of a novel perylene bisimide derivative surfactant
Backes, C., Hauke, F., Schmidt, C.D. and Hirsch, A.
Chem. Commun., ***19****, 2643-2645 (2009)*

6.50 Separation of Nanoparticles in a Density Gradient: FeCo@C and Gold Nanocrystals
Sun, X., Tabakman, S.M., Seo, W-S., Zhang, L., Shang, G., Sherlock, S., Bai, L and Dai, H.
Angewandte Chemie Int. Ed., ***48****, 939-942 (2009)*

HiPco and CoMoCAT single-walled carbon nanotubes (SWCNT) were fractionated with the aid of a novel perylene bisimide surfactant by combined co-surfactant and replacement density gradient ultracentrifugation (DGU).

6.51 Efficient Separation of (6,5) Single-Walled Carbon Nanotubes Using a "Nanometal Sinker"
Kato, Y., Niidome, Y. and Nakashima, N.
Angewandte Chemie Int. Ed., ***48****, 5435-5438 (2009)*

Sort it out! Density-gradient ultracentrifugation is used to separate single-walled carbon nanotubes (SWNTs) of a single chirality. A "nanometal sinker" ($AuCl_4^-$ ions) adsorbs onto specific SWNTs and allows the separation of adsorbed SWNTs and nonfunctionlized SWNTs (see picture). (6,5) SWNTs have been successfully separated from as-prepared SWNTs in a process termed "SWNT chirality fishing".

6.52 Metallic single-wall carbon nanotubes separated by density gradient ultracentrifugation
Chernov, A.I. and Obraztsova, E.O.
Phys. Status Solidi B, ***246(11-12)****, 2477-2481 (2009)*

A density gradient ultracentrifugation (DGU) technique recently applied for separation of single-wall carbon nanotubes (SWNTs) over diameter also appeared to be efficient for the nanotube separation according to their electronic structure. In this work we used DGU for extraction of a highly metallic (>97 wt%) nanotube fraction from a raw soot of arc-discharge SWNTs. The process parameters (the surfactant type and concentration, the treatment time, the approach to the gradient formation) have been optimized. A variation of surfactant concentration allowed obtaining the highly metallic nanotube fractions with different dominant diameter distribution resulting in the "blue" or "green" top fractions. Sodium taurodeoxycholate (TDOC) was efficiently used for DGU separation of raw, non-purified SWNTs. The fractions have been studied with the UV–Vis–NIR absorption and Raman spectroscopy.

6.53 Sorting and transmission electron microscopy analysis of single or double wall carbon nanotubes
Fleurier, R., Lauret, J-S., Flahaut, E. and Loiseau, A.
Phys. Status Solidi B, ***246(11-12)****, 2675-2678 (2009)*

On the basis of the recent progress on the sorting of carbon nanotubes' structure with respect to their diameter or number of walls, we investigate by transmission electron microscopy the sorting efficiency, with a comparison with optical absorption spectroscopy measurements. We study density gradient ultracentrifugation sorted single walled or double walled carbon nanotubes, showing obviously the ability to separate carbon nanotubes of different diameters or/and number of walls. This microscopic approach affords accurate information about the sorted samples such as the real mean diameter, the relative concentration of double walled carbon nanotubes over single walled carbon nanotubes, standard deviation, and the real diameter distribution of carbon nanotubes, even beyond any possible accurate analysis from optical absorption spectroscopy. Therefore, we demonstrate that the diameter analysis of the sorted samples by TEM can indeed afford some information about the relevant optical properties of carbon nanotubes.

6.54 Tuning of Sorted Double-Walled Carbon Nanotubes by Electrochemical Charging
Kalbac, M., Green, A.A., hersam, M.C. and Kavan, L.
ACS Nano, ***4(1)****, 459-469 (2010)*

Double-walled carbon nanotubes sorted by density gradient ultracentrifugation were examined by Raman spectroscopy and by *in situ* Raman spectroelectrochemistry. The sorted samples had a narrow distribution of diameters of both inner and outer tubes, which enabled a comparison of the behavior of inner metallic tubes and inner semiconducting nanotubes as a function of the applied electrochemical potential. The metallic inner tubes were efficiently doped even though they were protected from electrolyte ions by the outer wall, whereas the doping of semiconducting inner tubes was observed only at high magnitudes of the electrode potential. These results indicate that the doping response of inner tubes is predominantly controlled by inner tube electronic properties. On the other hand, the effect of electronic structure of the outer tube on the behavior of inner tube is weak. Furthermore, the efficiency of the charge transfer from outer to inner wall depends on the doping level. A low doping level corresponds to a high efficiency of the charge-transfer, while a high doping level shows low charge-transfer efficiency.

6.55 Sequence-Specifically Addressable Hairpin DNA−Single-Walled Carbon Nanotube Complexes for Nanoconstruction

Müller, K., Malik, S. and Richert, C.
ACS Nano, ***4(2)****, 649-656 (2010)*

Single-walled carbon nanotubes (SWCNTs) are attractive building blocks for molecular electronics and novel materials. Generating functional architectures with SWCNTs requires methodologies for dispersing, purifying, and binding these highly insoluble quasi one-dimensional molecules. We have previously shown that unstructured DNA strands bind to carbon nanotubes so tightly that it is difficult to address them with complementary strands. Here we show that hairpin oligonucleotides give SWCNT suspensions more concentrated than those obtainable with previously optimized DNA sequences. Further, hairpin-forming oligonucleotides and (6,5)-SWCNTs form complexes that are addressable with complementary, triplex-forming oligonucleotides. As proof of principle, we show that DNA−SWCNT complexes can be bound sequence-specifically with oligonucleotides featuring fluorophores or quantum dots. The new method brings SWCNTs of exquisite purity into the realm of DNA-based nanostructuring.

6.56 Controllable Expansion of Single-Walled Carbon Nanotube Dispersions Using Density Gradient Ultracentrifugation

Zhao, P., Einarsson, E., Xiang, R., Murakami, Y., and Maruyama, S.
J. Phys. Chem. C, ***114****, 4831-4834 (2010)*

We present a protocol to selectively isolate single-walled carbon nanotubes (SWNTs) with different chiralities in a full-colored “rainbow” expansion using density gradient ultracentrifugation (DGU). Starting with SWNTs synthesized by the alcohol catalytic chemical vapor deposition (ACCVD) method, we used sodium deoxycholate (DOC) and sodium dodecyl sulfate (SDS) as cosurfactant encapsulating agents to form a DOC-restricted SDS wrapping morphology around the SWNTs. This enhances the density differences between nanotubes of different diameters, which leads to efficient chirality redistribution when combined with an appropriate density gradient profile. UV−vis-NIR absorbance spectra and photoluminescence excitation (PLE) maps show the optical properties of each fraction, and 97% pure isolation of (6,5) SWNTs achieved from the rainbow is also reported.

6.57 Enrichment of Armchair Carbon Nanotubes *via* Density Gradient Ultracentrifugation: Raman Spectroscopy Evidence

Haroz, E.H., Rice, W., Lu, B.Y., Ghosh, S., hauge, R.H., Weisman, R.B., Doorn, S.K. and Kono, J.
ACS Nano, ***4(4)****, 1955-1962 (2010)*

We have used resonant Raman scattering spectroscopy to fully analyze the relative abundances of different (n,m) species in single-walled carbon nanotube samples that are metallically enriched by density gradient ultracentrifugation. Strikingly, the data clearly show that our density gradient ultracentrifugation process enriches the metallic fractions in armchair and near-armchair species. We observe that armchair carbon nanotubes constitute more than 50% of each $(2n + m)$ family.

6.58 Influence of Aromatic Environments on the Physical Properties of β-Carotene

Yanagi, K., Miyata, Y., Liu, Z., Suenaga, K., Okada, S. and Kataura, H.
J: Phys. Chem. C, ***114(6)****, 2524-2530 (2010)*

The influence of the surrounding aromatic environment on the properties of β-carotene (Car) was investigated for a simple system comprising single-walled carbon nanotubes (SWCNTs) encapsulating Car molecules. Both metallic- and semiconducting-type SWCNTs encapsulating Car were prepared, and their physical properties were investigated using optical measurements and first-principles calculations. The optical absorption peaks of encapsulated Car in metallic and semiconducting SWCNTs were slightly different, which is thought to be caused by the difference in polarizability of the two types of SWCNTs. The Raman frequency of the C═C stretching mode of Car in the metallic SWCNTs was 3 cm^{-1} down-shifted from that in the semiconducting SWCNTs. This down-shift could not be explained by the difference of dielectric environments of the metallic and the semiconducting SWCNTs. One possible origin for the shift is a difference in the amount of charge on the encapsulated Car, which was supported by theoretical calculations. From the results of this study, it can be concluded that the electronic structure of the nanotube walls influences the properties of encapsulated molecules.

6.59 Engineering Therapeutic Nanocarriers with Optimal Adhesion for Targeting

Haun, J.B., Robbins, G.P. and Hammer, D.A.
J. Adhesion, ***86****, 131-159 (2010)*

There is considerable interest in developing therapeutic delivery carriers that can be targeted *via* receptor-ligand interactions to sites within the blood stream. The adhesion of carriers is determined by the combined effects of transport phenomena, hydrodynamic force, and the dynamics of multivalent receptor/ligand bonding. Optimizing the adhesion of carriers requires developing relationships between these factors and carrier properties such as size and receptor coating density. Recently, we developed canonical relationships for the binding of antibody-conjugated 200 nm particles to surfaces coated with a vascular adhesion molecule, intercellular adhesion molecule-1. Here we extend our previous studies of adhesion to particles of different size, including 40 nm and 1 μm particles. Particle binding is assessed under fluid flow in a parallel plate flow chamber while varying particle receptor density, substrate ligand density, and flow rate. Using a stochastic simulation and transport-reaction model we then extract multivalent kinetic rate constants for particle attachment and detachment from the binding data. We demonstrate that particles go though a maximum in binding with particle size. For small particles, increasing size increases receptor-ligand encounter rates; for larger particles, fluid shear force begins to dominate, leading to higher forces and decreased adhesion. Our methods provide a means for optimizing particle size and receptor density for the selective binding of particles to vascular endothelium under flow.

6.60 Advanced sorting of single-walled carbon nanotubes by nonlinear density-gradient ultracentrifugation

Ghosh, S., Bachilo, S.M. and Weisman, R.B.
Nature Nanotech., ***5****, 443-450 (2010)*

Existing methods for growing single-walled carbon nanotubes produce samples with a range of structures and electronic properties, but many potential applications require pure nanotube samples. Density-gradient ultracentrifugation has recently emerged as a technique for sorting as-grown mixtures of single-walled nanotubes into their distinct (*n,m*) structural forms, but to date this approach has been limited to samples containing only a small number of nanotube structures, and has often required repeated density-gradient ultracentrifugation processing. Here, we report that the use of tailored nonlinear density gradients can significantly improve density-gradient ultracentrifugation separations. We show that highly polydisperse samples of single-walled nanotubes grown by the HiPco method are readily sorted in a single step to give fractions enriched in any of ten different (*n,m*) species. Furthermore, minor variants of the method allow separation of the mirror-image isomers (enantiomers) of seven (*n,m*) species. Optimization of this approach was aided by the development of instrumentation that spectroscopically maps nanotube contents inside undisturbed centrifuge tubes.

6.61 Separation and Characterization of Double-Wall Carbon Nanotube Subpopulations

Huh, J.Y., Walker, A.R.H., Ro, H.W., Obrzut, J., Mansfield, E., Geiss, R. andf Fagan, J.A
J. Phys. Chem. C., ***114****, 11343-11351 (2010)*

Surfactant-encapsulated double-wall carbon nanotubes (DWCNTs) synthesized by the high-pressure carbon monoxide decomposition (HiPco) process were separated by length and electronic characteristics using density gradient ultracentrifugation (DGU). To ensure our study focuses only on the behavior of DWCNTs, dispersed DWCNTs were first isolated following the method of Green et al. [Green, A. A.; Hersam, M. C. *Nat. Nanotechnol.* **2008**, *264*, 1], utilizing the differences in buoyant density of DWCNTs from that of impurity single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes contained in the parent soot. By increasing the density difference between the nanotubes and the density gradient medium, we exploited the length-dependent translation of the nanotubes in response to applied centrifugation to isolate narrow length distribution DWCNT fractions. The length-dependent intrinsic optical response of DWCNTs is consistent compared with the previously reported values for SWCNTs. The controlled addition of cosurfactants is shown to allow resolution of DWCNTs by electronic structure, as demonstrated through optical absorbance, Raman spectra, and electrical conductivity measurements. Measurements of conducting films prepared from separated fractions exhibit significant property differences in the enriched materials.

6.62 Sorting Single-Walled Carbon Nanotubes by Electronic Type Using Nonionic, Biocompatible Block Copolymers
Antaris, A.L., Seo, J-W., T., Green, A.A. and Hersam, M.C.
*ACSNano, **4(8)**, 4725-4732 (2010)*

As-synthesized single-walled carbon nanotubes (SWNTs) typically possess a range of diameters and electronic properties. This polydispersity has hindered the development of many SWNT-based technologies and encouraged the development of postsynthetic methods for sorting SWNTs by their physical and electronic structure. Herein, we demonstrate that nonionic, biocompatible block copolymers can be used to isolate semiconducting and metallic SWNTs using density gradient ultracentrifugation. Separations conducted with different Pluronic block copolymers reveal that Pluronics with shorter hydrophobic chain lengths lead to higher purity semiconducting SWNTs, resulting in semiconducting purity levels in excess of 99% obtained for Pluronic F68. In contrast, X-shaped Tetronic block copolymers display an affinity for metallic SWNTs, yielding metallic purity levels of 74% for Tetronic 1107. These results suggest that high fidelity and high yield density gradient separations can be achieved using nonionic block copolymers with rationally designed homopolymer segments, thus generating biocompatible monodisperse SWNTs for a range of applications.

6.63 Printed, Sub-3V Digital Circuits on Plastic from Aqueous Carbon Nanotube Inks
Ha, M., Xia, Y., Green, A.A., Zhang, W., Renn, M.J., Kim, C.H., Hersam, M.C. and Frisbie, C.D.
*ACSNano, **4(8)**, 4388-4395 (2010)*

Printing electronic components on plastic foils with functional liquid inks is an attractive approach for achieving flexible and low-cost circuitry for applications such as bendable displays and large-area sensors. The challenges for printed electronics, however, include characteristically slow switching frequencies and associated high supply voltages, which together impede widespread application. Combining printable high-capacitance dielectrics with printable high-mobility semiconductors could potentially solve these problems. Here we demonstrate fast, flexible digital circuits based on semiconducting carbon nanotube (CNT) networks and high-capacitance ion gel gate dielectrics, which were patterned by jet printing of liquid inks. Ion gel-gated CNT thin-film transistors (TFTs) with 50 μm channel lengths display ambipolar transport with electron and hole mobilities >20 cm^2/V·s; these devices form the basis of printed inverters, NAND gates, and ring oscillators on both polyimide and SiO_2 substrates. Five-stage ring oscillators achieve frequencies >2 kHz at supply voltages of 2.5 V, corresponding to stage delay times of 50 μs. This performance represents a substantial improvement for printed circuitry fabricated from functional liquid inks.

6.64 Solution-Processable Carbon Nanotubes for Semiconducting Thin-Film Transistor Devices
Lee, C.W., Han, X., Chen, F., Wei, J., Chen, Y., Chan-Park, M.B. and Li, L-J.
*Adv. Mater., **22**, 1278-1282 (2010)*

CoMoCat single-walled carbon nanotubes (SWNTs) treated with diazonium salts can be used to fabricate solution-processable field-effect transistors (FETs) with a full semiconductor device yield. By increasing the network thickness, the effective mobility of the devices can be raised to ~ 10 cm2 V−1 s−1 while keeping the on–off ratio higher than 5000. The removal of impurities is essential to achieve high-on–off-ratio devices. This approach is promising for preparation of SWNT inks for printing high-performance devices in flexible electronics.

6.65 Tailored Distribution of Single-Wall Carbon Nanotubes from Arc Plasma Synthesis Using Magnetic Fields
Volotskova, O., Fagan, J.A., Huh, J.Y., Phelan, F.R., Shashurin, A. and Keidar, M.
*ACS Nano, **4(9)**, 5187-51192 (2010)*

We report a method for tuning the distribution of single-wall carbon nanotubes (SWCNTs) produced by the anodic arc production method *via* the application of nonuniform magnetic fields to the gap region during synthesis. Raman, ultraviolet−visible−near-infrared absorbance and near-infrared fluorescence spectroscopies were used to characterize samples together with scanning electron microscopy. Application of the nonuniform magnetic field 0.2−2 kG results in a broadening of the diameter range of SWCNTs produced toward decreased diameters, with substantial fractions of produced SWCNTs being of small diameter, less than ~1.3 nm, at the highest field. The ability to tune production of the arc production method may allow for improvement in achievable SWCNT properties.

6.66 **Photoelectrochemical complexes for solar energy conversion that chemically and autonomously regenerate**
Ham, M-H., Choi, J.H., Boghossian, A.A., Jeng, E.S., Graff, R.A., Heller, D.A., Chang, A.C., Mattis, A., Bayburt, T.H., Grinkova, Y.V., Zeiger, A.S., Van Nliet, K.J., Hobbie, E.K., Sligar, S.G., Wraight, C.A. and Strano, M.S.
Nature Chem., ***2****, 929-936 (2010)*

Naturally occurring photosynthetic systems use elaborate pathways of self-repair to limit the impact of photo-damage. Here, we demonstrate a complex consisting of two recombinant proteins, phospholipids and a carbon nanotube that mimics this process. The components self-assemble into a configuration in which an array of lipid bilayers aggregate on the surface of the carbon nanotube, creating a platform for the attachment of light-converting proteins. The system can disassemble upon the addition of a surfactant and reassemble upon its removal over an indefinite number of cycles. The assembly is thermodynamically metastable and can only transition reversibly if the rate of surfactant removal exceeds a threshold value. Only in the assembled state do the complexes exhibit photoelectrochemical activity. We demonstrate a regeneration cycle that uses surfactant to switch between assembled and disassembled states, resulting in an increased photoconversion efficiency of more than 300% over 168 hours and an indefinite extension of the system lifetime.

6.67 **Density Gradient Ultracentrifugation of Nanotubes: Interplay of Bundling and Surfactants Encapsulation**
Bonaccorso, F., Hasan, T., Tan, P.H., Sciascia, C., Privitera, G., Di Marco, G., Gucciardi, P.G. and Ferrari, A.C.
J. Phys. Chem C, ***114(41)****, 17267-17285 (2010)*

Density gradient ultracentrifugation (DGU) has emerged as a promising tool to prepare chirality enriched nanotube samples. Here, we assess the performance of different surfactants for DGU. Bile salts (e.g., sodium cholate (SC), sodium deoxycholate (SDC), and sodium taurodeoxycholate (TDC)) are more effective in individualizing Single Wall Carbon Nanotubes (SWNTs) compared to linear chain surfactants (e.g., sodium dodecylbenzene sulfonate (SDBS) and sodium dodecylsulfate (SDS)) and better suited for DGU. Using SC, a narrower diameter distribution (0.69−0.81 nm) is achieved through a single DGU step on CoMoCAT tubes, when compared to SDC and TDC (0.69−0.89 nm). No selectivity is obtained using SDBS, due to its ineffectiveness in debundling. We assign the reduced selectivity of dihydroxy bile salts (SDC and TDC) in comparison with trihydroxy SC to the formation of secondary micelles. This is determined by the number and position of hydroxyl (−OH) groups on the α-side of the steroid backbone. We also enrich CoMoCAT SWNTs in the 0.84−0.92 nm range using the Pluronic F98 triblock copolymer. Mixtures of bile salts (SC) and linear chain surfactants (SDS) are used to enrich metallic and semiconducting laser-ablation grown SWNTs. We demonstrate enrichment of a single chirality, (6,5), combining diameter and metallic versus semiconducting separation on CoMoCAT samples.

6.68 **Optical Properties of Single-Walled Carbon Nanotubes Separated in a Density Gradient: Length, Bundling, and Aromatic Stacking Effects**
Tabakman, S.M., Welscher, K., Hong, G. and Dai, H.
J. Phys. Chem. C, ***114(46)****, 19569-19575 (2010)*

Single-walled carbon nanotubes (SWNTs) are promising materials for in vitro and in vivo biological applications due to their high surface area and inherent near-infrared photoluminescence and Raman scattering properties. Here, we use density gradient centrifugation to separate SWNTs by length and degree of bundling. Following separation, we observe a peak in photoluminescence quantum yield (PL QY) and Raman scattering intensity where the SWNT length is maximized and bundling is minimized. Individualized SWNTs are found to exhibit a high PL QY and high resonance-enhanced Raman scattering intensity. Fractions containing long, individual SWNTs exhibit the highest PL QY and Raman scattering intensities compared with fractions containing single, short SWNTs or SWNT bundles. Intensity gains of approximately ~1.7- and 4-fold, respectively, are obtained compared with the starting material. Spectroscopic analysis reveals that SWNT fractions at higher displacement contain increasing proportions of SWNT bundles, which causes reduced optical transition energies and broadening of absorption features in the UV−vis-NIR spectra and reduced PL QYs and Raman scattering intensities. Finally, we adsorb small aromatic species on "bright," individualized SWNT sidewalls and compare the resulting absorption, PL, and Raman scattering effects to that of SWNT bundles. We observe similar effects in both cases, suggesting that aromatic stacking affects the optical properties of SWNTs in an analogous way to SWNT bundles, likely due to electronic structure perturbations, charge transfer, and dielectric screening effects, resulting in reduction of the excitonic optical transition energies and exciton lifetimes.

6.69 Solution-Phase Extraction of Ultrathin Inner Shells from Double-Wall Carbon Nanotubes
Miyata, Y., Suzuki, M., Fujihara, M., Asada, Y., Kitaura, R. and Shinohara, H.
*ACS Nano, **4(10)**, 5807-5812 (2010)*

We present an efficient method to extract inner shells of double-wall carbon nanotubes (DWCNTs) in liquid phase. The extraction of inner from outer shells is achieved by cutting the DWCNTs with vigorous sonication in water containing surfactants. The extracted shells are perfectly isolated single-wall carbon nanotubes (SWCNTs) and can be separated using density gradient ultracentrifugation. Statistical analysis using high-resolution transmission electron microscopy reveals that the enrichment of SWCNTs with narrow diameter (0.62−1.0 nm) up to 100% is achieved from highly pure DWCNTs. Furthermore, the (5,4) SWCNTs, which have the diameter of 0.62 nm, are concentrated. Our findings provide a novel way to obtain very narrow, highly isolated SWCNTs with ultraclean surface that have not been obtained in conventional synthesis methods.

6.70 Prolonging Charge Separation in P3HT−SWNT Composites Using Highly Enriched Semiconducting Nanotubes
Holt, J.M., Ferguson, A.J., Kopidakis, N., Larsen, B.A., Bult, J., Rumbles, G. and Blackburn, J.L.
*Nano Lett., **10(11)**, 4627-4633 (2010)*

Single-walled carbon nanotubes (SWNTs) have potential as electron acceptors in organic photovoltaics (OPVs), but the currently low-power conversion efficiencies of devices remain largely unexplained. We demonstrate effective redispersion of isolated, highly enriched semiconducting and metallic SWNTs into poly(3-hexylthiophene) (P3HT). We use these enriched blends to provide the first experimental evidence of the negative impact of metallic nanotubes. Time-resolved microwave conductivity reveals that the long-lived carrier population can be significantly increased by incorporating highly enriched semiconducting SWNTs into semiconducting polymer composites.

6.71 Saturation of Surfactant Structure at the Single-Walled Carbon Nanotube Surface
Duque, J.G., Densmore, C.G. and Doorn, S.K.
*J. Am. Chem. Soc., **132(45)**, 16165-16175 (2010)*

Density gradient ultracentrifugation (DGU) and fluorescence spectroscopy are used to probe the limiting behaviors of the dynamic response of surfactant structure at the single-walled carbon nanotube (SWNT) surface to reorganizing forces, including changes in surfactant concentration and electrolyte screening. DGU results indicate that, as surfactant (sodium dodecyl sulfate, SDS) concentration is increased, SDS adsorbed on metallic SWNTs becomes limited in its ability to reorganize before SDS adsorbed on semiconducting species. A diameter-dependent enhancement is observed in photoluminescence intensities from semiconducting SWNTS upon initial titration with NaCl. This response to electrostatic screening diminishes as SDS concentration is increased. The results are understood as a saturation of the surfactant structural response, defined as both a loss in ability to increase SDS loading at the SWNT surface and a loss in ability to reorient surface structure in response to a reorganizing force. Saturation of response is found to be reversible and also occurs as a result of restricting SDS mobility. These results confirm several aspects of recent molecular dynamics simulations of SDS behavior on SWNTs and have important implications for tunability of density-based separation approaches using cosurfactant systems that include SDS.

6.72 Evaluation of sorted semi-conducting carbon nanotube films for gas sensing applications
Battie, Y., Ducloux, O., Thobois, P., Coffinier, Y. and Loiseau, A.
Comptes Rendus Physique, ***11(5-6)***, *397-404 (2010)*

This work focuses on the elaboration of sorted semi-conducting single walled carbon nanotube films (SC-SWCNT films), and the evaluation of a gas microsensor based on these films. First, we show that semi-conducting carbon nanotubes could be sorted from solutions containing both metallic and semi-conducting nanotubes by ultracentrifugation in a density gradient. SC-SWCNT films were then obtained by filtration through a nitrocellulose membrane, then transferred on TLM (transmission line method) electrodes to separately measure the resistivity and the contact resistance. We finally show characterization results obtained using NO_2 and NH_3 as a target gas.

6.73 Photoluminescence of single-wall carbon nanotube films
Chernov, A.I. and Obraztsova, E.D.
Phys. Status Solidi B., ***247(11-12)***, *2805-2809 (2010)*

In this work, we report the photoluminescence (PL) studies of the films produced by different methods from pristine single-wall carbon nanotubes (SWNTs). The suspensions of CoMoCAT and HiPCO SWNTs were used to make two different types of films: the polymer films with embedded SWNTs and the SWNT films deposited onto quartz substrates through filtration. A density gradient ultracentrifugation (DGU) has been used for enrichment of the initial carbon nanotube suspensions with semiconducting SWNTs and extraction of various diameter nanotubes to reveal a role of the nanotube interaction in the films. Optical diagnostic techniques including Raman spectroscopy, UV–VIS–NIR absorption spectroscopy, and PL have been used for characterization and comparison of the initial suspensions and films formed from them. A PL mapping has revealed an arrangement of carbon nanotubes inside the films. A cross-linkage between the individual SWNTs appeared to be higher inside the films deposited via filtration than in the polymer films with dispersed SWNTs.

6.74 Determination of the Surfactant Density on SWCNTs by Analytical Ultracentrifugation
Backes, C., Karabudak, E., Schmidt, C.D., Hauke, F., Hirsch, A. and Wohlleben, W.
Chem. Eur. J., ***16***, *13176-13184 (2010)*

We report on the extensive characterization of single-walled carbon nanotubes (SWCNTs) dispersed in a variety of surfactants, such as sodium dodecyl benzene sulfonate (SDBS), sodium cholate (SC), and three synthesized perylene-based surfactants, by using differential sedimentation in H_2O and D_2O. Multidimensional evaluation of the absorption profiles over radius, wavelength, and time allows the determination of the anhydrous specific volumes of the SWCNT–surfactant complexes as well as the concentration of the surfactant reservoir in free micelles with very slow sedimentation coefficients (<1 Svedberg). Among the perylene bisimide surfactants, the smallest derivative is densely adsorbed on the nanotube backbone with an anhydrous specific volume significantly above that of SC or SDBS. Bulky Newkome dendritic groups on one or both ends of the perylene moiety gradually reduce the adsorption density, in accord with the absolute adsorption between 0.66 and 1.7 mmol surfactant per gram SWCNTs. Furthermore, hydrodynamic analysis reveals that SDBS favors the “tails-on” configuration. The distribution of sedimentation coefficients of SWCNTs prepared by high-pressure carbon monoxide decomposition (HiPco) is broader and shifted to faster sedimentation than those prepared by using cobalt–molybdenum catalysis (CoMoCAT), which reflects the polydispersity in diameter and length.

6.75 Diffusion Limited Photoluminescence Quantum Yields in 1-D Semiconductors: Single-Wall Carbon Nanotubes
Hertel, T., Himmelein, S., Ackermann, T., Stich, D. and Crochet, J.
ACSNano, ***4(12)***, *7161-7168 (2010)*

Photoluminescence quantum yields and nonradiative decay of the excitonic S_1 state in length fractionated (6,5) single-wall carbon nanotubes (SWNTs) are studied by continuous wave and time-resolved fluorescence spectroscopy. The experimental data are modeled by diffusion limited contact quenching of excitons at stationary quenching sites including tube ends. A combined analysis of the time-resolved photoluminescence decay and the length dependence of photoluminescence quantum yields (PL QYs) from SWNTs in sodium cholate suspensions allows to determine the exciton diffusion coefficient $D = 10.7 \pm 0.4\ \mathrm{cm^2 s^{-1}}$ and lifetime τ_{PL} for long tubes of 20 ± 1 ps. PL quantum yields Φ_{PL} are found to scale with the inverse diffusion coefficient and the square of the mean quenching site distance, here $l_d = 120 \pm 25$ nm.

The results suggest that low PL QYs of SWNTs are due to the combination of high-diffusive exciton mobility with the presence of only a few quenching sites.

6.76 Electron Paramagnetic Resonance Investigation of Purified Catalyst-free Single-Walled Carbon Nanotubes
Zaka, M., Ito, Y., Wang, H., Yan, W., Robertson, A., Wu, Y.A., Rümmeli, M.H., Staunton, D., Hashimoto, T., Morton, J.J.L., Ardavan, A., Briggs, G.A.D. and Warner, J.H.
ACSNano, ***4(12)****, 7708-7716 (2010)*

Electron paramagnetic resonance of single-walled carbon nanotubes (SWCNTs) has been bedevilled by the presence of paramagnetic impurities. To address this, SWCNTs produced by laser ablation with a nonmagnetic PtRhRe catalyst were purified through a multiple step centrifugation process in order to remove amorphous carbon and catalyst impurities. Centrifugation of a SWCNT solution resulted in sedimentation of carbon nanotube bundles containing clusters of catalyst particles, while isolated nanotubes with reduced catalyst particle content remained in the supernatant. Further ultracentrifugation resulted in highly purified SWCNT samples with a narrow diameter distribution and almost no detectable catalyst particles. Electron paramagnetic resonance (EPR) signals were detected only for samples which contained catalyst particles, with the ultracentrifuged SWCNTs showing no EPR signal at X-band (9.4 GHz) and fields < 0.4 T.

6.77 Dispersion of single walled carbon nanotubes using poly(3-dodecylthiophene-2,5-diyl)
Stuparu, A., Stroh, C., Hennrich, F. and Kappes, M.M.
Phys. Status Sollidi B, ***247(11-12)****, 2653-2655 (2010)*

We describe a procedure to suspend single walled carbon nanotubes with poly(3-dodecylthiophene-2,5-diyl) and to purify them using density gradient centrifugation with 2,4,6-tribromotoluene or dodecyloxy-2,4,6-triiodobenzene as density gradient medium. In contrast to fluorene-based polymers, (*n*,*m*) selective solubilization is not observed.

6.78 Improved sorting of carbon nanotubes according to electronic type by density gradient ultracentrifugation
Posseckardt, J., Battie, Y., Fleurier, R., Lauret, J-S., Loiseau, A., Jost, O. and Mertig, M.
Phys. Status Sollidi B, ***247(11-12),*** *2687-2690 (2010)*

A variety of fabrication methods for single-walled carbon nanotubes (SWCNTs) has been developed, but none of them has been proven to generate tubes of only one chirality. Hence, a sample of as-produced SWCNTs always consists of a mixture of metallic and semiconducting tubes. By this, the application of SWCNTs in electronics, optics and sensing is limited today. Recently, the sorting of carbon nanotubes using density gradient ultracentrifugation (DGU) has been demonstrated. We report on an improved sorting according to electronic type by applying a two-step procedure: In the first step, we enriched semiconducting SWCNTs via DGU. In the second step, the sorted fractions have been reinserted and a second DGU was performed, winnowing metallic SWCNTs. Employing this procedure, we were able to reduce the content of metallic SWCNTs from 38 to 11%. Furthermore, we assembled carbon nanotube field-effect transistors with a high ON/OFF ratio from the sorted fraction in a single step by dielectrophoresis.

6.79 Sorting single-wall carbon nanotubes combining gel chromatography and density-gradient ultracentrifugation
Nishide, D., Liu, H., Tanaka, T. and Kataura, H.
Phys. Status Sollidi B, ***247(11-12)****, 2746-2749 (2010)*

High level structure sorting and metal/semiconductor separation of single-wall carbon nanotubes (SWCNTs) was demonstrated by combining two separation techniques, gel chromatography and density gradient ultra-centrifugation (DGU). Pristine SWCNTs were firstly separated into metallic and semiconducting parts by a gel column chromatography. Then a structure sorting of semiconducting SWCNTs was done by DGU method. Finally, highly (6,5) enriched semiconducting SWCNTs were obtained. Structure sorted SWCNTs obtained by this method were free from metallic SWCNT impurities, which cannot be achieved by simple DGU method.

6.80 Revealing new electronic behaviours in the Raman spectra of chirality-enriched carbon nanotube ensembles

Duque, J.G., Chen, H., Swan, A.K., Haroz, E.H., Kono, J., Tu, X., Zheng, M. and Doorn, S.K.
Phys. Status Sollidi B, ***247(11-12)****, 2768-2773 (2010)*

We present Raman spectroscopy of single-walled carbon nanotubes (SWNTs) that are enriched in metallic species by density gradient ultracentrifugation (DGU) and enriched in single semiconducting chiralities through DNA-based separations. Radial breathing mode (RBM) spectra demonstrate that DGU samples are highly enriched in armchair chiralities. The enrichment allows acquisition of pure G-band spectra of the armchair SWNTs and reveals that the LO mode is absent in these structures. Raman excitation profiles for the G-band in nearly pure (10,2) samples reveals a strong asymmetry in the intensities of the resonance coupling to incident and scattered photons. The experimental data may be fit using a four-level molecular model for Raman scattering and the strong asymmetry can be understood as a consequence of the presence of non-Condon effects. The result requires a reassessment of the assumption that the incident and scattered resonances are equivalent. The consequences of such non-Condon effects on other SWNT electronic and optical processes will be an important topic for future study.

6.81 High-Efficiency Separation of Single-Wall Carbon Nanotubes by Self-Generated Density Gradient Ultracentrifugation

Feng, Y., Miyata, Y., Matsuishi, K. and Kataura, H.
J. Phys. Chem. C, ***115(5)****, 1752-1756 (2011)*

We report an efficient density gradient ultracentrifugation (DGU) method for separation of metallic and semiconducting single-walled carbon nanotubes (SWCNTs) using a self-generated density gradient. A uniform-density SWCNT dispersion (33% v/v in iodixanol) was used to completely fill a centrifuge tube. After ultracentrifugation, separation of the metallic and semiconducting SWCNTs was achieved with a purity comparable to that achieved by DGU using a steplike density gradient. Because the SWCNTs were dispersed within the entire tube during this procedure, a large amount of SWCNTs can be separated at one time.

6.82 Improved Monodispersity of Plasmonic Nanoantennas via Centrifugal Processing

Tyler, T.P., Henry, A-I., Van Duyne, R.P and Hersam, M.C.
J. Phys. Chem. Lett., ***2(3)****, 218-222 (2011)*

Noble metal nanoparticle clusters underlie a variety of plasmonic devices and measurements including surface-enhanced Raman spectroscopy (SERS). Because of the strong dependence of plasmonic properties on nanoparticle cluster aggregation state, the elimination of non-SERS-active structures and the refinement of the nanoparticle cluster population are critical to realizing uniform and reproducible structures for plasmonic nanoantenna applications such as SERS-based sensors. In this Letter, we report a centrifugal sorting technique for gold core/silica shell nanoparticles that host SERS reporter molecules at the gold/silica interface. The relatively massive nanoparticle clusters are sorted by sedimentation coefficient via centrifugation in a high-viscosity density gradient medium, iodixanol, which yields solutions that contain a preponderance of one aggregation state and a diminished monomer population, as determined by transmission electron microscopy, extinction spectroscopy, and SERS. A quantitative analysis of the nanoparticle sedimentation coefficients is presented, thus allowing this approach to be predictably generalized to other nanoparticle systems.

6.83 Nanoseparations: Strategies for size and/or shape-selective purification of nanoparticles

Kowalczyk, B., Lagzi, I. and Grzybowski, B.A.
Current Opinion in Colloid & Interface Science, ***16(2)****, 135-148 (2011)*

This paper reviews techniques currently available for size- and shape-selective purification of nanoscopic objects. The methods discussed range from variants of familiar chromatographic, centrifugation, or filtration techniques, to purification schemes deriving from nanoscale-specific phenomena, including shape-selective reactivity, or propensity to form organized superstructures.

6.84 Properties and Application of Double-Walled Carbon Nanotubes Sorted by Outer-Wall Electronic Type

Green, A.A. and Hersam, M.C.
ACSNano, ***5(2)****, 1459-1467 (2011)*

Double-walled carbon nanotubes (DWNTs) can adopt four distinct permutations arising from the electronic type (metallic or semiconducting) of their inner and outer walls. This polydispersity limits the utility of DWNTs in applications such as thin film electronics. We demonstrate that density gradient ultracentrifugation can be employed to address this source of heterogeneity by producing DWNTs with well-defined outer-wall electronic types. Optical absorption measurements of sorted DWNTs reveal outer-wall purities of 96% and 98% for sorted semiconducting and metallic samples, respectively. Electrical characterization of semiconducting and metallic outer-wall DWNTs in thin film transistors directly confirms the efficacy of these separations, with semiconducting DWNT devices yielding on/off ratios 2 orders of magnitude higher than comparable metallic DWNT devices.

6.85 Structural Stability of Transparent Conducting Films Assembled from Length Purified Single-Wall Carbon Nanotubes
Harris, J.M., Iyer, G.R.S., Simien, D.O., Fagan, J.A., Huh, J.Y., Chung, J.Y., Hudson, S.D., Obrzut, J., Douglas, J.F., Stafford, C.M. and Hobbie, E.K.
J. Phys. Chem. C., ***115(10)****, 3973-3981 (2011)*

Single-wall carbon nanotube (SWCNT) films show significant promise for transparent electronics applications that demand mechanical flexibility, but durability remains an outstanding issue. In this work, thin membranes of length purified single-wall carbon nanotubes (SWCNTs) are uniaxially and isotropically compressed by depositing them on prestrained polymer substrates. Upon release of the strain, the topography, microstructure, and conductivity of the films are characterized using a combination of optical/fluorescence microscopy, light scattering, force microscopy, electron microscopy, and impedance spectroscopy. Above a critical surface mass density, films assembled from nanotubes of well-defined length exhibit a strongly nonlinear mechanical response. The measured strain dependence reveals a dramatic softening that occurs through an alignment of the SWCNTs normal to the direction of prestrain, which at small strains is also apparent as an anisotropic increase in sheet resistance along the same direction. At higher strains, the membrane conductivities increase due to a compression-induced restoration of conductive pathways. Our measurements reveal the fundamental mode of elasto-plastic deformation in these films and suggest how it might be suppressed.

6.86 Analyzing Absorption Backgrounds in Single-Walled Carbon Nanotube Spectra
Naumov, A.V., Ghosh, S., Tsyboulski, D.A., Bachilo, S.M. and Weisman, R.B.
ACSNano, ***5(3)****, 1639-1648 (2011)*

The sources of broad backgrounds in visible–near-IR absorption spectra of single-walled carbon nanotube (SWCNT) dispersions are studied through a series of controlled experiments. Chemical functionalization of nanotube sidewalls generates background absorption while broadening and red-shifting the resonant transitions. Extensive ultrasonic agitation induces a similar background component that may reflect unintended chemical changes to the SWCNTs. No major differences are found between spectral backgrounds in sample fractions with average lengths between 120 and 650 nm. Broad background absorption from amorphous carbon is observed and quantified. Overlapping resonant absorption bands lead to elevated backgrounds from spectral congestion in samples containing many SWCNT structural species. A spectral modeling method is described for separating the background contributions from spectral congestion and other sources. Nanotube aggregation increases congestion backgrounds by broadening the resonant peaks. Essentially no background is seen in sorted pristine samples enriched in a single semiconducting (*n,m*) species. By contrast, samples enriched in mixed metallic SWCNTs show broad intrinsic absorption backgrounds far from the resonant transitions. The shape of this metallic background component and its absorptivity coefficient are quantitatively assessed. The results obtained here suggest procedures for preparing SWCNT dispersions with minimal extrinsic background absorptions and for quantifying the remaining intrinsic components. These findings should allow improved characterization of SWCNT samples by absorption spectroscopy.

6.87 A Scalable, CMOS-Compatible Assembly of Ambipolar Semiconducting Single-Walled Carbon Nanotube Devices
Ganzhorn, M., Vijayaraghavan, A., Green, A.A., Dehm, S., Voigt, A., Rapp, M., hersam, M.C. and Krupke, R.
Adv. Mater., ***23****, 1734-1738 (2011)*

Semiconducting single-walled carbon nanotubes are integrated into high-density arrays using dielectrophoresis, which is a CMOS-compatible, bottom-up assembly technique. The devices are statistically analyzed by voltage-contrast scanning electron microscopy and electron transport measurements. Annealing and the choice of parylene substrate are shown to improve device performance.

6.88 High-Performance Hydrogen Production and Oxidation Electrodes with Hydrogenase Supported on Metallic Single-Wall CarbonNanotube Networks
Svedruzic, D., Blackburn, J:L., Trenent, R.C., Rocha, J-D.R., Vinzant, T.B., heben, M.J. and King, P.W.
J. Am.Chem. Soc., ***133***, *4299-4306 (2011)*

We studied the electrocatalytic activity of an [FeFe]-hydrogenase from *Clostridium acetobutylicum* (CaH2ase) immobilized on single-wall carbon nanotube (SWNT) networks. SWNT networks were prepared on carbon cloth by ultrasonic spraying of suspensions with predetermined ratios of metallic and semiconducting nanotubes. Current densities for both proton reduction and hydrogen oxidation electrocatalytic activities were at least 1 order of magnitude higher when hydrogenase was immobilized onto SWNT networks with high metallic tube (m-SWNT) content in comparison to hydrogenase supported on networks with low metallic tube content or when SWNTs were absent. We conclude that the increase in electrocatalytic activities in the presence of SWNTs was mainly due to the m-SWNT fraction and can be attributed to (i) substantial increases in the active electrode surface area, and (ii) improved electronic coupling between CaH2ase redox-active sites and the electrode surface.

6.89 Gas sensors based on thick films of semi-conducting single walled carbon nanotubes
Battie, Y., Ducloux, O., Thobois, P., Dorval, N., Lauret, J.S., Attal-Tretout, B. and Loiseau, A.
Carbon, ***49****, 3544-3552 (2011)*

A comparative study was made of sorted semi-conducting single walled carbon nanotube (SWCNT) films and unsorted SWCNT films for gas sensing applications. The transmission line method is used to monitor separately the SWCNTs film resistance and the contact resistance between electrodes and the SWCNTs, thus revealing that the sensing mechanism mainly relies on a modification of the tube conductivity during gas exposure. The fabricated sensors demonstrate a detection limit of 20 ppb NO_2 and 600 ppb NH_3 mainly attributed to experimental setup limitations. Moreover, semi-conducting nanotubes happened to be 2.5 times more sensitive to NH_3 than unsorted ones, thus proving that selectivity can be improved by sorting the SWCNTs. The temperature dependence of the sensor sensitivity was studied, and a good agreement was found between experimental results and the Langmuir adsorption model.

6.90 Chirality-Dependent Changes in the Density of Single-Walled Carbon Nanotubes Oxidized by Tetrachloroaurate
Kato, Y., Niidome, Y. and Nakashima, N.
Mol. Cryst. Liq. Cryst., ***539***, *184-189 (2011)*

Density change of single-walled carbon nanotubes (SWCNTs) with tetrachloroaurate enables chirality sorting of the SWCNTs. In this study, we examined in detail about the density change behavior of individually solubilized (n,m)-SWCNTs caused by tetrachloroaurate using density gradients centrifugation and vis-near IR absorption spectroscopy. The (7,5)-, (8,4)- and (8,3)- SWCNTs showed a linear relationship between the density and the degree of the oxidation of the corresponding SWCNTs. Although the (6,5)-SWCNTs was hardly oxidized by tetrachloroaurate, their density increased by the addition of tetrachloroaurate.

6.91 Electrodynamic and Excitonic Intertube Interactions in Semiconducting Carbon Nanotube Aggregates
Crochet, J.J., Sau, J.D., Duque, J.G., Doorn, S.K. and Cohen, M.
ACS Nano, ***5(4)***, *2611-2618 (2011)*

The optical properties of selectively aggregated, nearly single chirality single-wall carbon nanotubes were investigated by both continuous-wave and time-resolved spectroscopies. With reduced sample heterogeneities, we have resolved aggregation-dependent reductions of the excitation energy of the S_1 exciton and enhanced electron−hole pair absorption. Photoluminescence spectra revealed a spectral splitting of S_1 and simultaneous reductions of the emission efficiencies and nonradiative decay rates. The observed strong deviations from isolated tube behavior are accounted for by enhanced screening of the intratube Coulomb interactions, intertube exciton tunneling, and diffusion-driven exciton quenching. We also provide evidence that density gradient ultracentrifugation can be used to structurally sort single-wall carbon nanotubes by aggregate size as evident by a monotonic dependence of the aforementioned optical properties on buoyant density.

6.92 Separation of Empty and Water-Filled Single-Wall Carbon Nanotubes
Fagan, J.A., Huh, J.Y., Simpson, J.R., Blackburn, J.L., Holt, J.M., Larsen, B.A. and Hight Walker, A.R.
ACS Nano, ***5(5)****, 3943-3953 (2011)*

The separation of empty and water-filled laser ablation and electric arc synthesized nanotubes is reported. Centrifugation of these large-diameter nanotubes dispersed with sodium deoxycholate using specific conditions produces isolated bands of empty and water-filled nanotubes without significant diameter selection. This separation is shown to be consistent across multiple nanotube populations dispersed from different source soots. Detailed spectroscopic characterization of the resulting empty and filled fractions reveals that water filling leads to systematic changes to the optical and vibrational properties. Furthermore, sequential separation of the resolved fractions using cosurfactants and density gradient ultracentrifugation reveals that water filling strongly influences the optimal conditions for metallic and semiconducting separation.

6.93 Electron Correlation Effects on the Femtosecond Dephasing Dynamics of E_{22} Excitons in (6,5) Carbon Nanotubes
Schneck, J.R., Walsh, A.G., Green, A.A., Hersam, M.C., Ziegler, L.D. and Swan, A.K.
J. Phys. Chem. A, ***15(16)****, 3917-3923 (2011)*

Highly nonlinear pump fluence dependence was observed in the ultrafast one-color pump−probe responses excited by 38 fs pulses resonant with the E_{22} transition in a room-temperature solution of (6,5) carbon nanotubes. The differential probe transmission ($\Delta T/T$) at the peak of the pump−probe response ($\tau = 20$ fs) was measured for pump fluences from $\sim 10^{13}$ to 10^{17} photons/pulse cm^2. The onset of saturation is observed at $\sim 2 \times 10^{15}$ photons/pulse cm^2 ($\sim 8 \times 10^5$ excitons/cm). At pump fluences $>4 \times 10^{16}$ photons/pulse cm^2 ($\sim 1.6 \times 10^6$ excitons/cm), $\Delta T/T$ decreases as the pump fluence increases. Analogous signal saturation behavior was observed for all measured probe delays. Despite the high exciton density at saturation, no change in the E_{22} population decay rate was observed at short times (<300 fs). The pump probe signal was modeled by a third-order perturbation theory treatment that includes the effects of inhomogeneous broadening. The observed $\Delta T/T$ signal is well-fit by a pump-fluence-dependent dephasing rate linearly dependent on the number of excitons created by the pump pulse. Therefore, the observed nonlinear pump intensity dependence is attributed to the effects of quasi-elastic exciton−exciton interactions on the dephasing rates of single carbon nanotubes. The low fluence total dephasing time is 36 fs, corresponding to a homogeneous width of 36 meV (290 cm^{-1}), and the derived E_{22} inhomogeneous width is 68 meV (545 cm^{-1}). These results are contrasted with photon-echo-derived parameters for the E_{11} transition.

6.94 Hydrogen Spillover in Pt-Single-Walled Carbon Nanotube Composites: Formation of Stable C−H Bonds
Bhowmick, R., Rajasekaran, S., Friebel, D., Beasley, C., Jiao, L., Ogaswara, H., Dai, H., Clemens, b. and Nilsson, A.
J. Am. Chem. Soc., ***133(14)****, 5580-5586 (2011)*

Using in situ electrical conductivity and ex situ X-ray photoelectron spectroscopy (XPS) measurements, we have examined how the hydrogen uptake of single-walled carbon nanotubes (SWNTs) is influenced by the addition of Pt nanoparticles. The conductivity of platinum-sputtered single-walled carbon nanotubes (Pt-SWNTs) during molecular hydrogen exposure decreased more rapidly than that of the corresponding pure SWNTs, which supports a hydrogenation mechanism facilitated by “spillover” of dissociated hydrogen from the Pt nanoparticles. C 1s XPS spectra indicate that the Pt-SWNTs store hydrogen by means of chemisorption, that is, covalent C−H bond formation: molecular hydrogen charging at elevated pressure (8.27 bar) and room temperature yielded Pt-SWNTs with up to 16 ± 1.5 at. % sp^3-hybridized carbon atoms, which corresponds to a hydrogen-storage capacity of 1.2 wt % (excluding the weight of Pt nanoparticles). Pt-SWNTs prepared by the Langmuir−Blodgett (LB) technique exhibited the highest Pt/SWNT ratio and also the best hydrogen uptake.

6.95 The Potential of Perylene Bisimide Derivatives for the Solubilization of Carbon Nanotubes and Graphene
Backes, C., Hauke, F. and Hirsch, A.

Adv. Mater., ***23***, *2588-2601 (2011)*

Carbon nanotubes and graphene are outstanding materials of the 21st century with a broad spectrum of applications. However, major challenges are faced such as the intrinsically low solubility of both sp^2 carbon allotropes. To overcome this hurdle the potential of noncovalent functionalization is summarized with a special focus on the establishment of the perylene bisimide unit as aromatic anchor to the graphitic surface. Rational surfactant design is unmasked as the key to solubilization of the carbon allotropes, while at the same time tailoring their surface properties, or even electronic properties in a fully reversible fashion.

6.96 Tunable separation of single-walled carbon nanotubes by dual-surfactant density gradient ultracentrifugation

Zhao, P., Einarsson, E., Lagoudas, G., Shiomi, J., Chiashi, S. and Maruyama, S.
Nano Res., ***4(7)***, *623-634 (2011)*

We present a systematic study of the effects of surfactants in the separation of single-walled carbon nanotubes (SWNTs) by density gradient ultracentrifugation (DGU). Through analysis of the buoyant densities, layer positions, and optical absorbance spectra of SWNT separation using the bile salt sodium deoxycholate (DOC) and the anionic salt sodium dodecyl sulfate (SDS), we clarify the roles and interactions of these two surfactants in yielding different DGU outcomes. The separation mechanism described here can also help in designing new DGU experiments by qualitatively predicting outcomes of different starting recipes, improving the efficacy of DGU and simplifying post-DGU fractionation.

6.97 Preparation of Surface-Enhanced Raman Scattering-Active Au/Al2O3 Colloids by Sonoelectrochemical Methods

Mai, F-D., Yu, C-C., Liu, Y-C., Yang, K-H., and Junag, M-Y.
J. Phys. Chem. C, ***115(28)***, *13660-13666 (2011)*

As shown in the literature, surface-enhanced Raman scattering (SERS)-active Au or Ag nanoparticle films in agglomerated states on substrates were generally prepared by salting-out the colloidal solutions with $NaClO_4$ or NaCl. In this work, we report a new pathway to prepare SERS-active Au/Al_2O_3 colloids by sonoelectrochemical methods. The prepared colloids demonstrate strong SERS effects on substrates without an additional salting-out procedure. The particle size of prepared Au nanoparticles (NPs) coated on Al_2O_3 NPs is ca. 20 nm in diameter. Experimental results indicate that the synthesized SERS-active Au/Al_2O_3 colloids demonstrate a large Raman scattering enhancement for Rhodamine 6G with a detection limit of 2×10^{-10} M, which is lower than most of those shown in the literature based on Au NPs.

6.98 Molar Extinction Coefficient of Single-Wall Carbon Nanotubes

Schöppler, F., Mann, C., Hain, T.C., Neubauer, F.M., Privitera, G., Bonaccorso, F., Chu, D., Ferrari, A.C. and hertel, T.
J. Phys. Chem. C, ***115(30)***, *14682-14686 (2011)*

The molar extinction coefficient of single-wall carbon nanotubes (SWNTs) is determined using fluorescence tagging, as well as atomic force microscopy (AFM) imaging, which facilitate the correlation of nanotube concentrations with absorption spectra. Tagging of SWNTs is achieved using fluorescence-labeled single-strand DNA oligomers as the dispersion additive, while AFM imaging is used to determine the mass of SWNTs in the retentate of vacuum-filtered colloidal SWNT suspensions. The resulting absorption cross section for the first exciton transition of (6,5) nanotubes of 1.7×10^{-17} cm^2 per C-atom corresponds to an extinction coefficient of (4400 ± 1000) $M^{-1} \cdot cm^{-1}$, which is equivalent to an oscillator strength of 0.010 per carbon atom.

6.99 Synthesis of single-walled carbon nanotubes by an arc-discharge method using selenium as a promoter

Huang, L., Wu, B., Chen, J., Xue, Y., Liu, Y, Kajiura, H. and Li, Y.
Carbon, ***49***, *4792-4800 (2011)*

Single-walled carbon nanotubes (SWCNTs) with high purity and very narrow diameter distribution have been synthesized using the dc arc-discharge method with Y–Ni alloy as catalyst and selenium (Se) as promoter. The SWCNTs show a very narrow diameter distribution mainly at about 1.5 nm, and can further be readily purified up to >99% purity with traditional purification including HNO_3 reflux and air oxidation. The key factor of the wetting effect of Se in the SWCNTs growth improvement process is proposed and discussed. Moreover, a new less-destructive purification method including electrolysis, air-oxidation and centrifugation has been introduced, and SWCNTs with semiconducting content up to 94% have been produced through density gradient ultracentrifugation method.

6.100 **Selective Bundling of Zigzag Single-Walled Carbon Nanotubes**
Blum, C., Stürzl, N., Hennrich, F., Lebedkin, S., Heeg, S., Dumlich, H., Reich, S. and Kappes, M.M.
*ACS Nano, **5(4)**, 2847-2854 (2011)*

A simple, high throughput fractionation procedure for aqueous/SDS (sodium dodecyl sulfate) suspensions of single-walled carbon nanotubes (SWNTs) is presented, which yields thin bundles of semiconducting-SWNTs with small chiral angles. To demonstrate this we show the photoluminescence signatures of nanotube suspensions that contain almost exclusively zigzag and near-zigzag tubes. Starting suspensions and resulting fractions were characterized using optical absorption, resonance Raman and photoluminescence spectroscopies as well as scanning force microscopy. Taken together with literature observations, our findings suggest that near zigzag edge tubes of similar diameters in a bundle are harder to separate from each other than for other chiral index combinations. We discuss the implications of these observations for SWNT growth and dispersion.

6.101 **Density Gradient Ultracentrifugation on Carbon Nanotubes According to Structural Integrity as a Foundation for an Absolute Purity Evaluation**
Backes, C., Bosch, S., Mundloch, U., Hauke, F. and Hirsch, A.
*ChemPhysChem., **12(14)**, 2576-2580 (2011)*

Ultrapure: The absolute purity of defect-free and structurally perfect single-walled carbon nanotubes in a bulk sample can be determined with density gradient ultracentrifugation (see picture). The experimental protocol offers a quick and reliable tool and is applicable to a broad variety of nanotube materials to evaluation production and purification procedures.

6.102 **Dynamics and Transient Absorption Spectral Signatures of the Single-Wall Carbon Nanotube Electronically Excited Triplet State**
Park, J., Deria, P. and Therien, M.J.
*J. Am. Chem. Soc., **133(43)**, 17156-17159 (2011)*

We utilize femtosecond-to-microsecond time domain pump–probe transient absorption spectroscopy to interrogate for the first time the electronically excited triplet state of individualized single-wall carbon nanotubes (SWNTs). These studies exploit (6,5) chirality-enriched SWNT samples and poly[2,6-{1,5-bis(3-propoxysulfonic acid sodium salt)}naphthylene]ethynylene (PNES), which helically wraps the nanotube surface with periodic and constant morphology (pitch length = 10 ± 2 nm), providing a self-assembled superstructure that maintains structural homogeneity in multiple solvents. Spectroscopic interrogation of such PNES-SWNT samples in aqueous and DMSO solvents using E_{22} excitation and a white-light continuum probe enables E_{11} and E_{22} spectral evolution to be monitored concomitantly. Such experiments not only reveal classic SWNT singlet exciton relaxation dynamics and transient absorption signatures but also demonstrate spectral evolution consistent with formation of a triplet exciton state. Transient dynamical studies evince that (6,5) SWNTs exhibit rapid $S_1 \rightarrow T_1$ intersystem crossing (ISC) ($\tau_{ISC} \sim 20$ ps), a sharp $T_1 \rightarrow T_n$ transient absorption signal ($\lambda_{max}(T_1 \rightarrow T_n) = 1150$ nm; full width at half-maximum ≈ 350 cm^{-1}), and a substantial T_1 excited-state lifetime ($\tau_{es} \approx 15$ μs). Consistent with expectations for a triplet exciton state, T_1-state spectral signatures and T_1-state formation and decay dynamics for PNES-SWNTs in aqueous and DMSO solvents, as well as those determined for benchmark sodium cholate suspensions of (6,5) SWNTs, are similar; likewise, studies that probe the ^{3}[(6,5) SWNT]* state in air-saturated solutions demonstrate $^3O_2$ quenching dynamics reminiscent of those determined for conjugated aromatic hydrocarbon excited triplet states.

6.103 **Photoluminescence from Inner Walls in Double-Walled Carbon Nanotubes: Some Do, Some Do Not**
Yang, S.Y., parks, A.N., Saba, S.A., Ferguson, P.L. and Liu, J.
*Nano Lett., **11(10)**, 4405-4410 (2011)*

Double-walled carbon nanotubes (DWNTs) have recently been recognized as important members in the carbon nanotube family because they are expected to have certain unique properties. For example, DWNTs are expected to replace single-walled carbon nanotubes (SWNTs) in biomarker applications and optoelectronics if the observed luminescence from DWNTs can be verified. However, due to unavoidable byproducts, such as SWNTs, optical properties of DWNTs still remain controversial. There is an ongoing debate concerning the ability of DWNTs to exhibit photoluminescence (PL). In this report, we aim to clearly resolve this debate through the study of carefully separated DWNTs. DWNTs were successfully separated from SWNTs using density gradient ultracentrifugation. Here we clearly show that light is emitted from the inner wall of DWNTs; however, the intensity of the emission is significantly quenched. Interestingly, it was found that a very narrow range of diameters of the inner walls of DWNTs is required for PL to be observable. All other diameters led to complete PL quenching in DWNTs. In short, we have shown that both sides of the debate are correct under certain situations. The real answer to the question is that some DWNTs do emit light but most DWNTs do not.

6.104 Electronically Monodisperse Single-Walled Carbon Nanotube Thin Films as Transparent Conducting Anodes in Organic Photovoltaic Devices
Tyler, T.P., Brock, R.E., karmel, H.J., marks, T.J. and hersam, M.C.
*Adv. Energy Mater., **1(5)**, 785-791 (2011)*

Single-walled carbon nanotubes (SWNTs) sorted by electronic type are employed as organic photovoltaic device anodes. Metal-enriched SWNT films yield device efficiencies that are fifty times greater than their semiconducting counterparts. Through sheet resistance, UV-vis-NIR optical absorbance, and X-ray photoelectron spectroscopy measurements, the OPV charge blocking layer PEDOT:PSS is found to reverse the original chemical doping of the SWNT films. The relative insensitivity of metallic SWNTs to chemical doping thus explains the improved performance of metal-enriched SWNT films as OPV anodes.

6.105 Chemometric determination of the length distribution of single walled carbon nanotubes through optical spectroscopy
Si, R., Wang, K., Chen, T. and Chen, Y.
*Analytica Chimica Acta, **708**, 28-36 (2011)*

Current synthesis methods for producing single walled carbon nanotubes (SWCNTs) do not ensure uniformity of the structure and properties, in particular the length, which is an important quality indicator of SWCNTs. As a result, sorting SWCNTs by length is an important post-synthesis processing step. For this purpose, convenient analysis methods are needed to characterize the length distribution rapidly and accurately. In this study, density gradient ultracentrifugation was applied to prepare length-sorted SWCNT suspensions containing individualized surfactant-wrapped SWCNTs. The length of sorted SWCNTs was first determined by atomic force microscope (AFM), and their absorbance was measured in ultraviolet–visible near-infrared (UV–vis-NIR) spectroscopy. Chemometric methods are used to calibrate the spectra against the AFM-measured length distribution. The calibration model enables convenient analysis of the length distribution of SWCNTs through UV–vis-NIR spectroscopy. Various chemometric techniques are investigated, including pre-processing methods and non-linear calibration models. Extended inverted signal correction, extended multiplicative signal correction and Gaussian process regression are found to provide good prediction of the length distribution of SWCNTs with satisfactory agreement with the AFM measurements. In summary, spectroscopy in conjunction with advanced chemometric techniques is a powerful analytical tool for carbon nanotube research.

6.106 Discovery of Surfactants for Metal/Semiconductor Separation of Single-Wall Carbon Nanotubes via High-Throughput Screening
Tanaka, T., Urabe, Y., Nishide, D. and Kataura, H.
*J. Am. Chem. Soc., **133(44)**, 17610-17613 (2011)*

We report novel surfactants that can be used for the separation of metallic (M) and semiconducting (S) single-wall carbon nanotubes (SWCNTs). Among the M/S separation methods using surfactants in an aqueous solution, sodium dodecyl sulfate plays a key role in density gradient ultracentrifugation (DGU) and agarose gel separations. In this study, we screened 100 surfactants for M/S separation using a high-throughput screening system. We identified five surfactants, which could be used for both DGU and agarose gel separations, suggesting that the basic principle of these separations is common. These surfactants have relatively low dispersibilities, which is likely due to their common structural features, i.e., straight alkyl tails and charged head groups, and appeared to enable M- and S-SWCNTs to be distinguished and separated. These surfactants should stimulate research in this field and extend the application of electrically homogeneous SWCNTs not only for electronics but also for biology and medicine.

6.107 A Mechanistic Study of the Selective Retention of SDS-Suspended Single-Wall Carbon Nanotubes on Agarose Gels

Silvera-Batista, C.A., Scott, D.C., McLeod, S.M. and Ziegler, K.J.
J. Phys. Chem. C, ***115****, 9361-9369 (2011)*

Elution chromatography through columns packed with agarose beads has been used to separate metallic from semiconducting single-wall carbon nanotubes (SWCNTs). Prior studies have attributed the separation to either selective adsorption or size-exclusion (due to selective aggregation) of semiconducting SWCNTs. Initial SWCNT suspensions with different aggregation states were prepared to test these competing theories. Retention characteristics of the SWCNT suspensions were not affected by changes to aggregation state, except when the centrifugation time was short and aggregation excessive. On the other hand, selective adsorption of nanotubes on the agarose matrix is confirmed by modifying the surfactant structure around the SWCNTs without changing the aggregation state of the suspension. In addition, salt-modifiers and solvent-modifiers allow systematic changes to the surfactant aggregation number, orientation, and sidewall coverage. The retention characteristics from these modified SWCNT suspensions suggest that surfactant orientation rather than the exposed regions on the surface of the nanotubes is the dominant factor in the adsorption process.

6.108 Selective Polycarboxylation of Semiconducting Single-Walled Carbon Nanotubes by Reductive Sidewall Functionalization

Gebhardt, B., Hof, F., Backes, C., Müller, M., Plocke, t., Maultzsch, J., Thomsen, C., Hauke, F. and Hirsch, A.
J. Am. Chem. Soc., ***133(48)****, 19459-19473 (2011)*

The efficient and controllable synthesis, the detailed characterization, and the chemical postfunctionalization of polycarboxylated single-walled carbon nanotubes SWCNT(COOH)$_n$ are reported. This innovative covalent sidewall functionalization method is characterized by (a) the preservation of the integrity of the entire σ-framework of SWCNTs; (b) the possibility of achieving very high degrees of addition; (c) control of the functionalization degrees by the variation of the reaction conditions (reaction time, ultrasonic treatment, pressure); (d) the identification of conditions for the selective functionalization of semiconducting carbon nanotubes, leaving unfunctionalized metallic tubes behind; (e) the proof that the introduced carboxylic acid functionalities can serve as versatile anchor points for the coupling to functional molecules; and (f) the application of a subsequent thermal degradation step of the functionalized semiconducting tubes leaving behind intact metallic SWCNTs. Functional derivatives have been characterized in detail by means of Raman, UV–vis/nIR, IR, and fluorescence spectroscopy as well as by thermogravimetric analysis combined with mass spectrometry, atomic force microscopy, and zeta-potential measurements.

6.109 Intensity-Dependent Exciton Dynamics of (6,5) Single-Walled Carbon Nanotubes: Momentum Selection Rules, Diffusion, and Nonlinear Interactions

Harrah, D.M., Schneck, J.R., Green, A.A., Hersam, M.C., Ziegler, L.D.a dn Swan, A.K.
ACS Nano, ***5(12)****, 9898-9906 (2011)*

The exciton dynamics for an ensemble of individual, suspended (6,5), single-walled carbon nanotubes revealed by single color E_{22} resonant pump–probe spectroscopy for a wide range of pump fluences are reported. The optically excited initial exciton population ranges from approximately 5 to 120 excitons per ~725 nm nanotube. At the higher fluences of this range, the pump–probe signals are no longer linearly dependent on the pump intensity. A single, predictive model is described that fits all data for two decades of pump fluences and three decades of delay times. The model introduces population loss from the optically active zero momentum E_{22} state to the rest of the E_{22} subband, which is dark due to momentum selection rules. In the single exciton limit, the E_{11} dynamics are well described by a stretched exponential, which is a direct consequence of diffusion quenching from an ensemble of nanotubes of different lengths. The observed change in population relaxation dynamics as a function of increasing pump intensity is attributed to exciton–exciton Auger de-excitation in the E_{11} subband and, to a lesser extent, in the E_{22} subband. From the fit to the model, an average defect density $1/\rho = 150$ nm and diffusion constants $D_{11} = 4$ cm^2/s and $D_{22} = 0.2$ cm^2/s are determined.

6.110 Minimizing Oxidation and Stable Nanoscale Dispersion Improves the Biocompatibility of Graphene in the Lung
Duch, M.C., Budinger, G.R.S., Liang, Y.T., Soberanes, S., Urich, D., Chiarella, S.E., Campochiaro, L.A., Gonzales, A., Chandel, N.S., Hersam, M.C. and Mutlu, G.M.
Nano Lett., ***11(12)***, *5201-5207 (2011)*

To facilitate the proposed use of graphene and its derivative graphene oxide (GO) in widespread applications, we explored strategies that improve the biocompatibility of graphene nanomaterials in the lung. In particular, solutions of aggregated graphene, Pluronic dispersed graphene, and GO were administered directly into the lungs of mice. The introduction of GO resulted in severe and persistent lung injury. Furthermore, in cells GO increased the rate of mitochondrial respiration and the generation of reactive oxygen species, activating inflammatory and apoptotic pathways. In contrast, this toxicity was significantly reduced in the case of pristine graphene after liquid phase exfoliation and was further minimized when the unoxidized graphene was well-dispersed with the block copolymer Pluronic. Our results demonstrate that the covalent oxidation of graphene is a major contributor to its pulmonary toxicity and suggest that dispersion of pristine graphene in Pluronic provides a pathway for the safe handling and potential biomedical application of two-dimensional carbon nanomaterials.

6.111 Design of a Polymer–Carbon Nanohybrid Junction by Interface Modeling for Efficient Printed Transistors
Kim, D.H., Shin, H-J., Lee, H.S., Lee, J., Lee, B-L., Lee, W.H., Lee, J-H., Cho, K., Kim, W-J., Lee, S.Y., Choi, J-Y. and Kim, J.M.
ACS Nano, ***6(1)***, *662-670 (2012)*

Molecularly hybridized materials composed of polymer semiconductors (PSCs) and single-walled carbon nanotubes (SWNTs) may provide a new way to exploit an advantageous combination of semiconductors, which yields electrical properties that are not available in a single-component system. We demonstrate for the first time high-performance inkjet-printed hybrid thin film transistors with an electrically engineered heterostructure by using specially designed PSCs and semiconducting SWNTs (sc-SWNTs) whose system achieved a high mobility of 0.23 $cm^2\ V^{-1}\ s^{-1}$, no V_{on} shift, and a low off-current. PSCs were designed by calculation of the density of states of the backbone structure, which was related to charge transfer. The sc-SWNTs were prepared by a single cascade of the density-induced separation method. We also revealed that the binding energy between PSCs and sc-SWNTs was strongly affected by the side-chain length of PSCs, leading to the formation of a homogeneous nanohybrid film. The understanding of electrostatic interactions in the heterostructure and experimental results suggests criteria for the design of nanohybrid heterostructures.

6.112 Electronic Durability of Flexible Transparent Films from Type-Specific Single-Wall Carbon Nanotubes
Harris, J.M., Iyver, G.R.S., Bernhardt, A.K., Huh, J.Y., Hudson, S.D., Fagan, J.A. and Hobbie, E.E.
ACS Nano, ***6(1)***, *881-887 (2012)*

The coupling between mechanical flexibility and electronic performance is evaluated for thin films of metallic and semiconducting single-wall carbon nanotubes (SWCNTs) deposited on compliant supports. Percolated networks of type-purified SWCNTs are assembled as thin conducting coatings on elastic polymer substrates, and the sheet resistance is measured as a function of compression and cyclic strain through impedance spectroscopy. The wrinkling topography, microstructure and transparency of the films are independently characterized using optical microscopy, electron microscopy, and optical absorption spectroscopy. Thin films made from metallic SWCNTs show better durability as flexible transparent conductive coatings, which we attribute to a combination of superior mechanical performance and higher interfacial conductivity.

6.113 Highly concentrated carbon nanotube admixture for nano-fiber reinforced cementitious materials
Metaxa, Z.S., Seo, J-W.T., Konsta-Gdoutos, M.S., Hersam, M.C. and Shah, S.P.
Cement & Concrete Composites, ***34***, *612-617 (2012)*

The use of effectively dispersed multiwalled carbon nanotube (MWCNT)/aqueous/surfactant suspensions in cement based materials have been shown to substantially improve their mechanical properties. The produced MWCNT suspensions have a high aqueous content, which corresponds to the mixing water. In the present work, a method for preparing highly concentrated MWCNT suspensions is presented, thus reducing the volume of the resulting admixture that is required in cement based materials. A centrifugal process, that uses two different ultracentrifuge rotors, was employed to reduce the quantity of water in the suspensions. Optical absorbance spectroscopy shows that the ultracentrifugation process increases the concentration of the MWCNT suspensions by a factor of 5. Using the highly concentrated MWCNT suspensions following dilution results in nanocomposites with mechanical properties that are comparable to the performance of samples prepared using the non-concentrated suspensions. These results verify that the ultracentrifugation concentration method successfully preserves the solubility of the MWCNT suspensions without affecting the reinforcing properties of the admixture. In this manner, the ultracentrifugation concentration method may constitute an effective preparation step for large-scale implementation of MWCNT admixtures.

6.114 Density gradient ultracentrifugation and stability of SWNT–peptide conjugates

Hartleb, H., Kröker, K. and Hertel, T.
Chem. Phys. Lett., ***535***, *131-135 (2012)*

Density gradient ultracentrifugation was used for preparation of biocompatible single-wall carbon nanotube (SWNT)–peptide conjugates. Aggregate size selected SWNT suspensions were analyzed by absorption and photoluminescence spectroscopy to determine stability and structure of conjugates. The results suggest that conjugates with densities over 1.19 g cm^{-3} consist of SWNT aggregates. More buoyant fractions with $\rho \approx 1.18 \text{ g cm}^{-3}$ contain mostly individual SWNTs. Dilution experiments indicate that equilibration between SWNT-bound and free peptide in solution is approached within a few minutes making excess peptide in solution necessary to prevent peptide–SWNT conjugate aggregation. This has significant implications for the use of SWNT–peptide conjugates in biochemical applications.

6.115 Evidence for Patchy Lipid Layers on Gold Nanoparticle Surfaces

Yang, J.A. and Murphy, C.J.
Langmuir, ***28(12)****, 5404-5416 (2012)*

Gold nanoparticles bearing multiple surface ligands are becoming favored candidates as multifunctional targeting, imaging, and therapeutic vehicles for biomedicine. The question of spatial location of different ligands on nanoparticle surfaces, especially with those of diameters less than 100 nm, is an important one that is difficult to quantitatively address. Here we functionalize the surface of 20, 50, and 90 nm gold nanoparticles with two different lipids, both single and mixed, using two different surface chemical procedures. Mass spectrometry supports the presence of both lipids in the mixed-lipid systems on nanoparticles, while electron microscopy evidence shows domain sizes for one lipid apparently a quarter to a half the projected diameter for 50 and 90 nm particles; but for 20 nm particles, there is no evidence for the existence of patches of the two lipids. Larger gold nanoparticles (90 nm) can be decorated with an array of 12 nm gold nanoparticles by use of a third lipid and antibody–antigen connectors; the display of the 12 nm particles about the 90 nm particles can be controlled to some extent by the initial surface chemistry and is quantified via a new angle analysis procedure.

6.116 Confirmation of K-Momentum Dark Exciton Vibronic Sidebands Using 13C-labeled, Highly Enriched (6,5) Single-walled Carbon Nanotubes

Blackburn, J.L., Holt, J.M., Irurzun, V.M., Resasco, D.E. and Rumbles, G.
Nano Lett., ***12(3)****, 1398-1403 (2012)*

A detailed knowledge of the manifold of both bright and dark excitons in single-walled carbon nanotubes (SWCNTs) is critical to understanding radiative and nonradiative recombination processes. Exciton–phonon coupling opens up additional absorption and emission channels, some of which may “brighten” the sidebands of optically forbidden (dark) excitonic transitions in optical spectra. In this report, we compare ^{12}C and ^{13}C-labeled SWCNTs that are highly enriched in the (6,5) species to identify both absorptive and emissive vibronic transitions. We find two vibronic sidebands near the bright $^1E_{11}$ singlet exciton, one absorptive sideband ∼200 meV above, and one emissive sideband ∼140 meV below, the bright singlet exciton. Both sidebands demonstrate a ∼50 cm^{-1} isotope-induced shift, which is commensurate with exciton–phonon coupling involving phonons of A_1' symmetry (D band, ω ∼1330 cm^{-1}). Independent analysis of each sideband indicates that both sidebands arise from the same dark exciton level, which lies at an energy approximately 25 meV above the bright singlet exciton. Our observations support the recent prediction of, and mounting experimental evidence for, the dark K-momentum singlet exciton lying ∼25 meV (for the (6,5) SWCNT) above the bright Γ-momentum singlet. This study represents the first use of ^{13}C-labeled SWCNTs highly enriched in a single nanotube species to unequivocally confirm these sidebands as vibronic sidebands of the dark K-momentum singlet exciton.

6.117 Unique Origin of Colors of Armchair Carbon Nanotubes
Haroz, E.H., Duque, J.G:, Lu, B.Y., Nikolaev, P., Arepalli, S., Hauge, R.H., Doorn, S.K. and Kono, J.
J. Am. Chem. Soc., ***134(10)****, 4461-4464 (2012)*

The colors of suspended metallic colloidal particles are determined by their size-dependent plasma resonance, while those of semiconducting colloidal particles are determined by their size-dependent band gap. Here, we present a novel case for armchair carbon nanotubes, suspended in aqueous medium, for which the color depends on their size-dependent excitonic resonance, even though the individual particles are metallic. We observe distinct colors of a series of armchair-enriched nanotube suspensions, highlighting the unique coloration mechanism of these one-dimensional metals.

6.118 Unraveling the 13C NMR Chemical Shifts in Single-Walled Carbon Nanotubes: Dependence on Diameter and Electronic Structure
Engtrakul, C., Irurzun, V.M., Gjersing, E.L., Holt, J.M., Larsen, B.A., Resasdco, D.E. and Blackburn, J.L.
J. Am. Chem. Soc., ***134(10)****, 4850-4856 (2012)*

The atomic specificity afforded by nuclear magnetic resonance (NMR) spectroscopy could enable detailed mechanistic information about single-walled carbon nanotube (SWCNT) functionalization as well as the noncovalent molecular interactions that dictate ground-state charge transfer and separation by electronic structure and diameter. However, to date, the polydispersity present in as-synthesized SWCNT populations has obscured the dependence of the SWCNT ^{13}C chemical shift on intrinsic parameters such as diameter and electronic structure, meaning that no information is gleaned for specific SWCNTs with unique chiral indices. In this article, we utilize a combination of ^{13}C labeling and density gradient ultracentrifugation (DGU) to produce an array of ^{13}C-labeled SWCNT populations with varying diameter, electronic structure, and chiral angle. We find that the SWCNT isotropic ^{13}C chemical shift decreases systematically with increasing diameter for semiconducting SWCNTs, in agreement with recent theoretical predictions that have heretofore gone unaddressed. Furthermore, we find that the ^{13}C chemical shifts for small diameter metallic and semiconducting SWCNTs differ significantly, and that the full-width of the isotropic peak for metallic SWCNTs is much larger than that of semiconducting nanotubes, irrespective of diameter.

6.119 Measuring Single-Wall Carbon Nanotubes with Solid-State Nanopores
Hall, A.R., Keegstra, J.M., Duch, M.C., Hersam, M.C. and Dekker, C.
Methods in Mol. Biol., ***870****, 227-239 (2012)*

Solid-state nanopores have been used widely to study biological polymers. Here, we expand the technique to analyze single-wall carbon nanotubes. By wrapping them in an amphiphilic layer, individual tubes can be translocated electrically through a nanopore, resulting in temporary interruptions in the trans-pore current reminiscent of measurements on DNA, RNA, and proteins. The technique may find use in discriminating nanotubes by size and thus electrical structure, facilitating their inclusion in electrical devices.

6.120 Towards Rationally Designed Graphene-Based Materials and Devices
Liang, Y.T. and Hersam, M.C.
Macromol. Chem. Physics, ***213(10-11)****, 1091-1100 (2012)*

With its exceptional charge transport properties, graphene has emerged as a potential replacement material in the electronics industry. For these applications, much effort has been devoted towards the synthesis of large defect-free graphene sheets. However, recent developments have enabled the efficient production of micrometer- and nanometer-sized graphene sheets in the solution phase. These suspensions have stimulated the development of novel materials and devices that more fully exploit the tunability and large specific surface area of pristine graphene. This review highlights advances in the understanding of the defect structure and properties of as-produced graphene as well as strategies for its chemical selection and modification that facilitates its use in functional materials and devices.

6.121 Narrow Diameter Distributions of Metallic Arc Discharge Single-Walled Carbon Nanotubes via

Dual-Iteration Density Gradient Ultracentrifugation
Tyler, T.P., Shastry, T.A., Leever, B.J: and Hersam, M.C.
*Adv. Mater., **24(35)**, 4765-4768 (2012)*

Dual-iteration density gradient ultracentrifugation isolates nearly single diameters of monodisperse metallic arc discharge SWCNTs. Subsequently fabricated conductive thin films possess distinct colors due to well-defined transmittance windows flanked by sharp optical transitions. Measurements of uniform sheet resistances and work functions confirm the largely invariant electronic properties between metallic arc discharge SWCNT films of differing diameters.

6.122 Probing and Tailoring pH-Dependent Interactions between Block Copolymers and Single-Walled Carbon Nanotubes for Density Gradient Sorting
Antaris, A.L., Jung-Wu. T. Seo., Brock, R.E., Herriman, J.E., Born, M.J., Green, A.A. and Hersam, M.C:
*J. Phys. Chem. C, **116(37)**, 20103-20108 (2012)*

The method by which surfactants selectively interact with particular electronic types of single-walled carbon nanotubes (SWCNTs) and thereby enable the isolation of metallic and semiconducting species is not well understood. While density gradient ultracentrifugation (DGU) has demonstrated its potential as a powerful nanomaterial separation technique, this study utilizes DGU as an analytic tool to probe the interactions between amphiphilic block copolymers, surfactants capable of electronic type extraction, and the SWCNT surface. By modulating the pH during DGU, we find that the linear shaped Pluronic copolymers can extract either metallic or semiconducting SWCNTs at purities in excess of 99%. Furthermore, the first electronic type sorting mechanism is given by which oxygen absorption and subsequent protonation of the SWCNT surface acts to template copolymer adhesion. Detailed characterization reveals the underlying mechanism for pH-shifted DGU and is thus likely to enable future development of more efficient and facile SWCNT electronic type sorting methods.

6.123 Fundamental Performance Limits of Carbon Nanotube Thin-Film Transistors Achieved Using Hybrid Molecular Dielectrics
Sangwan, V.K., Ortiz, R.P., alaboson, J.M.P., Emery, J.D., Bedzyk, M.J., Lauhon, L.J., Marks, T.J. and Hersam, M.C.
*ACS Nano, **6(8)**, 7480-7488 (2012)*

In the past decade, semiconducting carbon nanotube thin films have been recognized as contending materials for wide-ranging applications in electronics, energy, and sensing. In particular, improvements in large-area flexible electronics have been achieved through independent advances in postgrowth processing to resolve metallic *versus* semiconducting carbon nanotube heterogeneity, in improved gate dielectrics, and in self-assembly processes. Moreover, controlled tuning of specific device components has afforded fundamental probes of the trade-offs between materials properties and device performance metrics. Nevertheless, carbon nanotube transistor performance suitable for real-world applications awaits understanding-based progress in the integration of independently pioneered device components. We achieve this here by integrating high-purity semiconducting carbon nanotube films with a custom-designed hybrid inorganic–organic gate dielectric. This synergistic combination of materials circumvents conventional design trade-offs, resulting in concurrent advances in several transistor performance metrics such as transconductance (6.5 μS/μm), intrinsic field-effect mobility (147 $cm^2/(V\ s)$), subthreshold swing (150 mV/decade), and on/off ratio (5×10^5), while also achieving hysteresis-free operation in ambient conditions.

6.124 Manipulating Electron Transfer between Single-Walled Carbon Nanotubes and Diazonium Salts for High Purity Separation by Electronic Type
Do, Y-J., Lee, J-H., CHOI, H., Han, J-H., Chung, C-H., Jeong, M-G., Strano, M.S. and Kim, W-J.
*Chem. Mater, **24(21)**, 4146-4151 (2012)*

Diazonium salts preferentially react with metallic single-walled carbon nanotubes (SWNT) over semiconducting SWNT, enabling the separation of SWNT by electronic type. Therefore, the reaction selectivity of diazonium salts for metallic SWNT is crucial for high purity separation of both metallic and semiconducting SWNT. Herein, we developed an efficient method of increasing the reaction selectivity by manipulating the redox potential of diazonium salts. The electron affinity of diazonium salts is effectively lowered when the para-substituent of the diazonium salts is an electron-donating group, (i.e., 4-hydroxy and 4-propargyloxy) rather than an electron-withdrawing group (i.e., 4-nitro, 4-carboxy, and 4-cholro).

The reduction potential of 4-hydroxyphenyl and 4-propargyloxyphenyl diazonium salt was greater than the oxidation potential of semiconducting SWNT; therefore, the electron transfer reaction between these two reagents was effectively suppressed, leading to a highly selective reaction for metallic SWNT. We confirmed that this highly selective reaction scheme can be used to separate SWNT, and high purity semiconducting SWNT can be obtained via density-induced separation.

6.125 Mild Bromination-Assisted Density-Gradient Ultracentrifugation to Sort Single-Walled Carbon Nanotubes by Metallicity
Wang, W., Mahasin, A.S., Gao, P.Q., Lim, K.H. and Chan-Park, M.B.
J. Phys. Chem. C, ***116(43)****, 23027-23035 (2012)*

Brominated single-walled carbon nanotubes, with bromine covalently attached to the nanotube surface, have been synthesized by a mild reaction using n-bromosuccinimide (NBS). The latter preferentially attacks metallic single walled carbon nanotubes (SWNTs) over semiconducting ones, and the attached Br leads to a significant density differential between reacted and pristine nanotubes. The differential reactivity between semiconducting and metallic SWNTs enhances the density contrast between them, which may be more effectively spatially separated via density gradient ultracentrifugation than unchemically modified SWNTs. The results of optical absorbance, photoluminescence emission, and resonant Raman scattering show that bromination-assisted density gradient ultracentrifugation (hereafter labeled as Br-DGU) preferentially separated semiconducting nanotubes within a certain diameter range (0.829–0.966 nm, specifically (7,6), (8,4), (9,4), and (10,3)). We have applied the semiconducting species enriched SWNTs to prepare solution-processed FET devices with random nanotube network active channels. The devices exhibit stable p-type semiconductor behavior in air with very promising characteristics. The on–off current ratio reaches up to 1730 within a narrow gate voltage (−2 to 2 V) and an estimated hole mobility of 13 $cm^2 V^{-1} s^{-1}$.

6.126 Characterization and Quantitative Analysis of Single-Walled Carbon Nanotubes in the Aquatic Environment Using Near-Infrared Fluorescence Spectroscopy
Schierz, A., Parks, A.N., Washburn, K.M., Chandler, G.T. and Ferguson, P.L.
Environ. Sci. Technol., ***46(22)****, 12262-12271 (2012)*

Near infrared fluorescence (NIRF) spectroscopy is capable of sensitive and selective detection of semiconductive, single-walled carbon nanotubes (SWNT) using the unique electronic bandgap properties of these carbon allotropes. We reported here the first detection and quantitation of SWNT in sediment and biota at environmentally relevant concentrations using NIRF spectroscopy. In addition, we utilized this technique to qualitatively characterize SWNT samples before and after ecotoxicity, bioavailability and fate studies in the aquatic environment. Sample preparation prior to NIRF analysis consisted of surfactant-assisted high power ultrasonication. The bile salt sodium deoxycholate (SDC) enabled efficient extraction and disaggregation of SWNT prior to NIRF analysis. The method was validated using standard-addition experiments in two types of estuarine sediments, yielding recoveries between 66 ± 7% and 103 ± 10% depending on SWNT type and coating used, demonstrating the ability to isolate SWNT from complex sediment matrices. Instrument detection limits were determined to be 15 ng mL^{-1} SWNT in 2% SDC solution and method detection limits (including a concentration step) were 62 ng g^{-1} for estuarine sediment, and 1.0 μg L^{-1} for water. Our work has shown that NIRF spectroscopy is highly sensitive and selective for SWNT and that this technique can be applied to track the environmental and biological fate of this important class of carbon nanomaterial in the aquatic environment.

6.127 Ultrashort Single-Walled Carbon Nanotubes: Density Gradient Separation, Optical Property, and Mathematical Modeling Study
Kuang, Y., Liu, J. and Sun, X.
J. Phys. Chem. C, ***116(46)****, 24770-24776 (2012)*

The density gradient ultracentrifuge separation (DGUS) method for obtaining ultrashort single-walled carbon nanotubes (SWNTs) was systematically investigated. A twice separation was used for further narrowing the length distribution. Investigations on Raman and absorbance spectra evidenced the concomitant chirality separation of the NTs. The length-dependent blue shift recorded on the absorbance spectra confirmed band gap widening on finite semiconductive SWNTs, which showed a linear relationship to the inverse of the length of the NTs. Laser ablation NTs were used to demonstrate DGUS as a general method for separation of different type of SWNTs. A possible vertical sedimentation separation mechanism is proposed, and a mathematical model was set up to give a quantitive description on separation results, which was further demonstrated by time-dependence experiments.

6.128 **Surface-enhanced Raman scattering-active Au/TiO2 films prepared by electrochemical and photochemical methods**
Yang, K-H. and Chang, C-M.
*Materials Research Bulletin, **48**, 372-377 (2013)*

In this work, we report a new strategy for the preparation of surface-enhanced Raman scattering (SERS)-active Au/TiO_2(P25) nanocomposites (NCs), using electrochemical and photochemical methods. First, Au substrates were subjected to electrochemical oxidation–reduction cycles (ORCs) in a deoxygenated aqueous solution containing 0.1 M HCl and 1 mM TiO_2. After the ORC treatment $AuCl_4^-$-adsorbed TiO_2 complexes were produced in the solution. These complex-containing substrates were then irradiated with UV light at 310 nm to synthesize Au/TiO_2 NCs with strong SERS activities for probe molecules of rhodamine 6G (R6G) and conductive polymers of polypyrrole (PPy). Experimental results indicated that the wavelength of UV light and the presence of TiO_2 before and after the ORC procedure during the preparation process both affected the resulting SERS activities.

6.129 **Large-Area, Electronically Monodisperse, Aligned Single-Walled Carbon Nanotube Thin Films Fabricated by Evaporation-Driven Self-Assembly**
Shastry, T.A., Seo, J-W.T., Lopez, J.J., Arnold, H.N., Kelter, J.Z., Sangwan, V.K., Lauhon, L.J., Marks, T.J. and Hersam, M.C.
*Small, **9(1)**, 45-51 (2013)*

By varying the evaporation conditions and the nanotube and surfactant concentrations, large-area, aligned single-walled carbon nanotube (SWCNT) thin films are fabricated from electronically monodisperse SWCNT solutions by evaporation-driven self-assembly with precise control over the thin film growth geometry. Tunability is possible from 0.5 μm stripes to continuous thin films. The resulting SWCNT thin films possess highly anisotropic electrical and optical properties that are well suited for transparent conductor applications.

6.130 **High-Field Transport and Thermal Reliability of Sorted Carbon Nanotube Network Devices**
Behnam, A., Sangwan, V.K., Zhong, X., Lian, F., Estrada, D., Jariwala, d., Hoag, A.J., Lauhon, L.J., Marks, T.J., Hersam, M.C. and Pop, E.
*ACS Nano, **7(1)**, 482-490 (2013)*

We examine the high-field operation, power dissipation, and thermal reliability of sorted carbon nanotube network (CNN) devices, with <1% to >99% semiconducting nanotubes. We combine systematic electrical measurements with infrared (IR) thermal imaging and detailed Monte Carlo simulations to study high-field transport up to CNN failure by unzipping-like breakdown. We find that metallic CNNs carry peak current densities up to an order of magnitude greater than semiconducting CNNs at comparable nanotube densities. Metallic CNNs also appear to have a factor of 2 lower intrinsic thermal resistance, suggesting a lower thermal resistance at metallic nanotube junctions. The performance limits and reliability of CNNs depend on their makeup, and could be improved by carefully engineered heat dissipation through the substrate, contacts, and nanotube junctions. These results are essential for optimization of CNN devices on transparent or flexible substrates which typically have very low thermal conductivity.

6.131 **Single-Walled Carbon Nanotube Surface Control of Complement Recognition and Activation**
Andersen, A.J., Robinson, J.T., Dai, H., Hunter, A.C., Andresen, T. and Moghimi, S.M.
*ACS Nano, **7(2)**, 1108-1119 (2013)*

Carbon nanotubes (CNTs) are receiving considerable attention in site-specific drug and nucleic acid delivery, photodynamic therapy, and photoacoustic molecular imaging. Despite these advances, nanotubes may activate the complement system (an integral part of innate immunity), which can induce clinically significant anaphylaxis. We demonstrate that single-walled CNTs coated with human serum albumin activate the complement system through C1q-mediated classical and the alternative pathways. Surface coating with methoxypoly(ethylene glycol)-based amphiphiles, which confers solubility and prolongs circulation profiles of CNTs, activates the complement system differently, depending on the amphiphile structure. CNTs with linear poly(ethylene glycol) amphiphiles trigger the lectin pathway of the complement through both l-ficolin and mannan-binding lectin recognition. The lectin pathway activation, however, did not trigger the amplification loop of the alternative pathway. An amphiphile with branched poly(ethylene glycol) architecture also activated the lectin pathway but only through l-ficolin recognition. Importantly, this mode of activation neither generated anaphylatoxins nor induced triggering of the effector arm of the complement system. These observations provide a major step toward nanomaterial surface modification with polymers that have the properties to significantly improve innate immunocompatibility by limiting the formation of complement C3 and C5 convertases.

6.132 High-Resolution Length Fractionation of Surfactant-Dispersed Carbon Nanotubes
Khripin, C.Y., Tu, X., Heddleston, J.M., Silvera-Batista, C., Hight Walker, A.R., Fagan, J. and Zheng, M.
Anal. Chem., ***85(3)****, 1382-1388 (2013)*

Length fractionation of colloidal single-wall carbon nanotube (SWCNT) dispersions is required for many studies. Size-exclusion chromatography (SEC) has been developed as a reliable method for high-resolution length fractionation of DNA-dispersed SWCNTs but has not been applied to surfactant-dispersed SWCNTs due to their lower dispersion stability and tendency to adsorb onto SEC stationary phases. Here, we report that SEC length fractionation can be achieved for bile salt dispersed SWCNTs by using porous silica-based beads as the stationary phase and bile salt solution as the mobile phase. We demonstrate that the SEC length sorting method can be combined with existing ultracentrifugation SWCNT sorting methods to produce “orthogonally sorted” samples, including length sorted semiconducting SWCNTs, which are important for electronics applications as well as length sorted empty-core SWCNTs. Importantly, we show that unlike simple length fractionation by SEC or any other method, orthogonal sorting produces samples of consistent quality for different length fractions, with similar UV–vis-nearIR absorption and Raman spectral features.

6.133 Scalable and Effective Enrichment of Semiconducting Single-Walled Carbon Nanotubes by a Dual Selective Naphthalene-Based Azo Dispersant
Sundramoorthy, A.K., Mesgari, S., Wang, J., Kumar, R., Sk, M.A,m Yeap, S.H., Zhang, Q., Sze, S.K., Lim, K.-H. and Chan-Park, M.B.
J. Am. Chem. Soc., ***135(15)****, 5569-5581 (2013)*

Semiconducting single-walled carbon nanotubes (s-SWNTs) have emerged as a promising class of electronic materials, but the metallic (m)-SWNTs present in all as-synthesized nanotube samples must be removed for many applications. A high selectivity and high yield separation method has remained elusive. A separation process based on selective chemistry appears to be an attractive route since it is usually relatively simple, but more effective chemicals are needed. Here we demonstrate the first example of a new class of dual selective compounds based on polycyclic aromatic azo compounds, specifically Direct Blue 71 (**I**), for high-purity separation of s-SWNTs at high yield. Highly enriched (~93% purity) s-SWNTs are produced through the simple process of standing arc-discharge SWNTs with **I** followed by centrifugation. The s-SWNTs total yield is up to 41%, the highest yet reported for a solution-based separation technique that demonstrates applicability in actual transistors. 91% of transistor devices fabricated with these s-SWNTs exhibited on/off ratios of 10^3 to 10^5 with the best devices showing mobility as high as 21.8 cm^2/V s with on/off ratio of 10^4. Raman and X-ray photoelectron spectroscopic shifts and ultraviolet–visible–near-infrared (UV–vis–NIR) show that **I** preferentially complexes with s-SWNTs and preferentially suspends them. Preferential reaction of naphthyl radicals (generated from **I** with ultrasonication) with m-SWNTs is confirmed by changes in the D-band in the Raman spectroscopy, matrix-assisted desorption–ionization time-of-flight mass spectrometry (MALDI-TOF-MS), and molecular simulation results. The high selectivity of **I** stems from its unique dual action as both a selective dispersion agent and the generator of radicals which preferentially attack unwanted metallic species.

6.134 Probing Carbon Nanotube–Surfactant Interactions with Two-Dimensional DOSY NMR
Shastry, T.A., Morris-Cohen, A.J., Weiss, E.A. and hersam, M.C.
J. Am. Chem. Soc., ***135(18)****, 6750-6753 (2013)*

Two-dimensional diffusion ordered spectroscopy (2D DOSY) NMR was used to probe the micellar structure of sodium dodecyl sulfate (SDS) and sodium cholate (SC) in aqueous solutions with and without semiconducting and metallic single-walled carbon nanotubes (SWCNTs). The solutions contain SDS and SC at weight ratios of 1:4 and 3:2, the ratios commonly used to isolate semiconducting and metallic SWCNTs through density gradient ultracentrifugation (DGU). These results show that the coverage of surfactant on the semiconducting and metallic SWCNTs is nearly identical in the 1:4 surfactant mixture, and a lower degree of bundling is responsible for the greater buoyancy of semiconducting SWCNTs. In the

3:2 surfactant mixture, the metallic SWCNTs are only encapsulated in SC while the semiconducting SWCNTs remain encapsulated in a poorly packed two-surfactant micelle, leading to a large buoyant density difference between the electronic species. This work provides insight into future directions to increase the purity of semiconducting and metallic SWCNTs sorted through DGU and demonstrates the utility of 2D DOSY NMR in probing SWCNT–surfactant complexes.

6.135 **Spontaneous Partition of Carbon Nanotubes in Polymer-Modified Aqueous Phases**
Khripin, C.Y., Fagan, J.A. and Zheng, M.
J. Am. Chem. Soc., ***135(18)****, 6822-6825 (2013)*

The distribution of nanoparticles in different aqueous environments is a fundamental problem underlying a number of processes, ranging from biomedical applications of nanoparticles to their effects on the environment, health, and safety. Here, we study distribution of carbon nanotubes (CNTs) in two immiscible aqueous phases formed by the addition of polyethylene glycol (PEG) and dextran. This well-defined model system exhibits a strikingly robust phenomenon: CNTs spontaneously partition between the PEG- and the dextran-rich phases according to nanotube's diameter and metallicity. Thermodynamic analysis suggests that this chirality-dependent partition is determined by nanotube's intrinsic hydrophobicity and reveals two distinct regimes in hydrophobicity-chirality relation: a small diameter (<1 nm) regime, where curvature effect makes larger diameter tubes more hydrophobic than small diameter ones, and a large diameter (>1.2 nm) regime, where nanotube's polarizability renders semiconducting tubes more hydrophobic than metallic ones. These findings reveal a general rule governing CNT behaviors in aqueous phase and provide an extremely simple way to achieve spatial separation of CNTs by their electronic structures.

6.136 **SERS Tags: Novel Optical Nanoprobes for Bioanalysis**
Wang, Y., Yan, B. and Chen, L.
Chemical Reviews, ***113(3)****, 1391-1428 (2013)*

No abstract available.

6.137 **Analyzing Surfactant Structures on Length and Chirality Resolved (6,5) Single-Wall Carbon Nanotubes by Analytical Ultracentrifugation**
Fagan, J.A., Zheng, M., Rastogi, V., Simpson, J.R., Khripin, C.Y., Batista, C.A.S. and Walker, A.R.H.
ASC Nano, ***7(4)****, 3373-3387 (2013)*

The structure and density of the bound interfacial surfactant layer and associated hydration shell were investigated using analytical ultracentrifugation for length and chirality purified (6,5) single-wall carbon nanotubes (SWCNTs) in three different bile salt surfactant solutions. The differences in the chemical structures of the surfactants significantly affect the size and density of the bound surfactant layers. As probed by exchange of a common parent nanotube population into sodium deoxycholate, sodium cholate, or sodium taurodeoxycholate solutions, the anhydrous density of the nanotubes was least for the sodium taurodeoxycholate surfactant, and the absolute sedimentation velocities greatest for the sodium cholate and sodium taurodeoxycholate surfactants. These results suggest that the thickest interfacial layer is formed by the deoxycholate, and that the taurodeoxycholate packs more densely than either sodium cholate or deoxycholate. These structural differences correlate well to an observed 25% increase in fluorescence intensity relative to the cholate surfactant for deoxycholate and taurodeoxycholate dispersed SWCNTs displaying equivalent absorbance spectra. Separate sedimentation velocity experiments including the density modifying agent iodixanol were used to establish the buoyant density of the (6,5) SWCNT in each of the bile salt surfactants; from the difference in the buoyant and anhydrous densities, the largest hydrated diameter is observed for sodium deoxycholate. Understanding the effects of dispersant choice and the methodology for measurement of the interfacial density and hydrated diameter is critical for rationally advancing separation strategies and applications of nanotubes.

6.138 **Ultra-Low Doses of Chirality Sorted (6,5) Carbon Nanotubes for Simultaneous Tumor Imaging and Photothermal Therapy**
Antaris, A.L., Robinson, J.T., Yaghi, O.K., Hong, g., Diao, S., Luong, R. and Dai, H.
ACS Nano, ***7(4)****, 3644-3652 (2013)*

Single-walled carbon nanotubes (SWCNTs) exhibit intrinsic fluorescence and strong optical absorption in the near-infrared (NIR) biological window (0.7–1.4 μm), rendering them ideal for *in vivo* imaging and photothermal therapy. Advances in SWCNT sorting have led to improved nanoelectronics and are promising for nanomedicine. To date, SWCNTs used *in vivo* consist of heterogeneous mixtures of nanotubes and only a small subset of chirality nanotubes fluoresces or heats under a NIR laser. Here, we demonstrate that separated (6,5) SWCNTs exchanged into a biocompatible surfactant, C_{18}-PMH-mPEG, are more than 6-fold brighter in photoluminescence on the per mass basis, afford clear tumor imaging, and reach requisite photothermal tumor ablation temperatures with a >10-fold lower injected dose than as-synthesized SWCNT mixtures while exhibiting relatively low (6,5) accumulation in the reticuloendothelial system. The intravenous injection of ~4 μg of (6,5) SWCNTs per mouse (0.254 mg/kg) for dual imaging/photothermal therapy is, by far, the lowest reported dose for nanoparticle-based *in vivo* therapeutics.

6.139 Ultrafast Charge Photogeneration in Semiconducting Carbon Nanotubes
Soavi, G., Scotognella, F., Brida, D., Hefner, ST., Späth, f., Antognazza, M.R., Hertel, T., Lanzani, G. and Cerullo, G.
J. Phys. Chem. C., ***117(20)****, 10849-10855 (2013)*

We show that excitons are not the unique outcome of photoexcitation in single-walled carbon nanotubes (SWNTs). Our experiments of transient photoinduced absorption suggest that charge carriers are formed with quantum yield of a few percent and that such species strongly affect the long-lived transient spectrum. Photogenerated charge carriers induce strong local electric fields that shift by the Stark effect the second subband exciton absorption in SWNTs, resulting in a characteristic derivative shape of the transient absorption spectra.

6.140 Aerosol Jet Printed, Low Voltage, Electrolyte Gated Carbon Nanotube Ring Oscillators with Sub-5 μs Stage Delays
Ha, M., Seo, J-W.T., Prabhumirashi, P.L., Zhang, W., Geier, M.L., Renn, M.J., Kim, C.H., Hersam, M.C. and Frisbie, C.D.
Nano Lett., ***13(3)****, 954-960 (2013)*

A central challenge for printed electronics is to achieve high operating frequencies (short transistor switching times) at low supply biases compatible with thin film batteries. In this report, we demonstrate partially printed five-stage ring oscillators with >20 kHz operating frequencies and stage delays <5 μs at supply voltages below 3 V. The fastest ring oscillator achieved 1.2 μs delay time at 2 V supply. The inverter stages in these ring oscillators were based on ambipolar thin film transistors (TFTs) employing semiconducting, single-walled carbon nanotube (CNT) networks and a high capacitance (~1 $\mu F/cm^2$) ion gel electrolyte as the gate dielectric. All materials except the source and drain electrodes were aerosol jet printed. The TFTs exhibited high electron and hole mobilities (~20 $cm^2/(V\ s)$) and ON/OFF current ratios (up to 10^5). Inverter switching times *t* were systematically characterized as a function of transistor channel length and ionic conductivity of the gel dielectric, demonstrating that both the semiconductor and the ion gel play a role in switching speed. Quantitative scaling analysis suggests that with suitable optimization low voltage, printed ion gel gated CNT inverters could operate at frequencies on the order of 1 MHz.

6.141 Separation of graphene oxide by density gradient centrifugation and study on their morphology-dependent electrochemical properties
Li, S., Zhu, F., Meng, F., Li, H., Wang, L., Zhao, J., Yue, Q., Liu, J. and Jia, J.
J. Electroanal. Chem., ***703****, 135-145 (2013)*

Graphene oxide (GO) made from graphite oxidation by Hummer's method is a mixture of GO sheets with different size and thickness. Previous work has shown that these GO sheets have different electrophoretic properties and can be separated via capillary electrophoresis according to their surface charge (J. Zhao et al., Anal. Chem. 83 (2011) 9100–9106). Herein, the GO sheets were separated by density gradient centrifugation to achieve preparation of bulk GO materials. GO sheets were separated by their thicknesses and the as-obtained sheets were characterized for their spectroscopic, electronic and electrochemical properties. After treated by hydrazine, GO was derivatized with N element and become active toward oxygen reduction reaction. The thin layer GO sheets incorporated with more hydrazine and the atomic ratio of N/C was higher than thick layer GO sheets. This work suggested that the physicochemical properties of GO sheets were N of layer related and it is necessary to separate GO sheets to prepare suitable materials for device fabrication or catalysts use.

6.142 **Nanoparticles as macromolecules**
Miller, J.B. and Hobbie, E.K.
*J. Polymer Science Part B, **51**, 1195-1208 (2013)*

A review of recent trends in the dispersion, purification, and assembly of colloidal nanoparticles highlights a number of growing analogies with ideas borrowed from polymer science. Beyond the similar scales of size, several key concepts lying at the foundation of polymer physics—such as polydispersity, fractionation, phase ordering, and viscoelasticity—are taking on new and unique significance in the contemporary realm of nanotechnology. Leveraging “soft matter” at the nanoscale to simplify materials processing and improve material performance is becoming a reality, with potentially profound implications for a number of emerging technologies.

6.143 **Sorting Nanoparticles by Centrifugal Fields in Clean Media**
Bonaccorso, F., Zerbetto, M., Ferrari, A.C. and Amendola, V.
*J. Phys. Chem. C, **117(25)**, 13217-13229 (2013)*

The on-demand availability of nanomaterials with selected size and well-defined chemical/physical properties is of fundamental importance for their widespread application. We report two clean, rapid, and non-destructive approaches for nanoparticle (NP) size selection in centrifugal fields. The first exploits rate zonal separation in a high viscosity gradient. The second exploits selective sedimentation of NPs with different sizes. These methods are here applied to metallic nanoparticles (MNPs) with different compositions and surface chemistry, dispersed either in water or organic solvents. The approach is general and can also be exploited for the separation of NPs of any material. We selectively sort both Au and AgNPs with sizes in the 10–30 nm range, achieving chemical-free MNPs with low polydispersivity. We do not use solutes, thus avoiding contamination, and only require low centrifugal fields, easily achievable in benchtop systems.

6.144 **Raman Spectroscopic Investigation of Individual Single-Walled Carbon Nanotubes Helically Wrapped by Ionic, Semiconducting Polymers**
Bonhommeau, S., Deria, P., Glesner, M.G., Talaga, D., Najjar, S., Belin, C., Auneau, L., trainini, S., Therien, M.J. and Rodriguez, V.
*J. Phys. Chem. C, **117(28)**, 14840-14849 (2013)*

Raman-active vibrational modes of (6,5) chirality-enriched single-walled carbon nanotubes (SWNTs), helically wrapped by semiconducting poly[2,6-{1,5-bis(3-propoxysulfonic acid sodium salt)}naphthylene]ethynylene (PNES), are described in great detail. At an irradiation wavelength of 568.2 nm, the extent to which the environment impacts the nanotube vibrational signature can be probed; in particular, the absence of a G band shift for PNES–[(6,5) SWNT] samples relative to benchmark surfactant-coated nanotubes indicates the lack of any significant charge transfer between the PNES strand and the SWNT skeleton, but electronic spectra provide compelling evidence for polymer-to-SWNT energy transfer. At an irradiation wavelength of 457.9 nm, vibrational modes associated with PNES chains that wrap (6,5) SWNTs are conspicuously enhanced. Under 514.5 nm irradiation, PNES–[(6,5) SWNTs] are not excited in resonance but G and G′ bands associated with these nanohybrids are strongly enhanced, reflecting the excitation of a multiphonon-mediated vibronic transition of the (6,5) SWNT backbone. At a 488.0 nm irradiation wavelength, Raman spectral signatures of both the PNES polymer and the vibronically excited (6,5) SWNT skeleton through one-phonon-assisted processes are pronounced, demonstrating that a specific SWNT chirality and the corresponding semiconducting polymer helically wrapped about its surface can be probed using an excitation wavelength that does not resonantly excite the SWNT structure.

6.145 **Solution-processable exfoliated zeolite nanosheets purified by density gradient centrifugation**
Agrawal, K.V., Topuz, B., Jiang, Z., Nguenkam, K., Elyassi, B., Francis, L.F. and Tsapatsis, M.
*AICHE J., **59(9)**, 3458-3467 (2013)*

Highly crystalline exfoliated MFI-nanosheets can pave the way for large-scale deployment of sub-500-nm zeolite membranes due to their processing and packing advantages. Exfoliated MFI-nanosheets prepared by melt compounding contain a large amount of polymer and unexfoliated particles which are detrimental to the fabrication of ultrathin zeolite membranes. Complete removal of polystyrene from the nanosheet suspension in toluene is demonstrated by centrifugation of the suspension across chlorobenzene as confirmed by thermogravimetric analysis (TGA) data and transmission electron microscopy (TEM) images.

Rate-zonal centrifugation in a nonlinear density gradient fractionated exfoliated MFI-nanosheets from unexfoliated particles. The purified nanosheets were highly crystalline as indicated by high-resolution TEM (HRTEM) and electron diffraction (ED). Coating of purified MFI-nanosheets on a smooth α-alumina support, fabricated by filtration of α-alumina suspension, led to a compact, b-oriented, 80-nm-thick film. A mild hydrothermal treatment of the film led to a 200-nm-thick membrane, which demonstrated molecular sieving properties.

6.146 **Diameter Refinement of Semiconducting Arc Discharge Single-Walled Carbon Nanotubes via Density Gradient Ultracentrifugation**
Seo, J-W.T., Yoder, N.L., Shastry, T.A., Humes, J.J., Johns, J.E., Green, A.A. and hersam, M.C.
J. Phys. Chem. Lett., ***4(17)****, 2805-2810 (2013)*

Arc discharge single-walled carbon nanotubes (SWCNTs) possess superlative optical and electronic properties that are of high interest for technologically important applications including fiber optic communications, biomedical imaging, and field-effect transistors. However, as-grown arc discharge SWCNTs possess a mixture of metallic and semiconducting species in addition to a wide diameter distribution (1.2 to 1.7 nm) that limit their performance in devices. While previous postsynthetic sorting efforts have achieved separation by electronic type and diameter refinement for metallic arc discharge SWCNTs, tight diameter distributions of semiconducting arc discharge SWCNTs have not yet been realized. Herein, we present two advances in density gradient ultracentrifugation that enable the isolation of high purity (>99%) semiconducting arc discharge SWCNTs with narrow diameter distributions centered at ~1.6 and ~1.4 nm. The resulting diameter-refined populations of semiconducting arc discharge SWCNTs possess monodisperse characteristics that are well-suited for high-performance optical and electronic technologies.

6.147 **Centrifugal Shape Sorting and Optical Response of Polyhedral Gold Nanoparticles**
Shin, Y.J., Ringe, E., Personick, M.L., Cardinal, M.F., Mirkin, C.A., Marks, L.D., Van Duyne, R.P. and Hersam, M.C.
Adv. Mater., ***25(29)****, 4023-4027 (2013)*

A centrifugal route for separating small {110}-faceted gold nanostructures, namely rhombic dodecahedra (RD) and triangular bipyramids (BPs), which form simultaneously during synthesis and cannot be separated by means of conventional filtration methods, is presented. The centrifuged solution shows two distinct bands: i) RD and ii) BPs, as verified in the corresponding scanning electron microscopy images. The sorted BPs show a refractive index dependence 2.5 times that of the as-synthesized, unsorted mixture.

6.148 **Growth of carbon nanotubes via twisted graphene nanoribbons**
Lim, H.E., Miyata, Y., Kitaura, R., Nishimura, Y., Nishimoto, Y., Irle, S.A., Warner, J.H., Kataura, H. and Shinohara, H.
Nature Communications, ***4****:2485 (2013)*

Carbon nanotubes have long been described as rolled-up graphene sheets. It is only fairly recently observed that longitudinal cleavage of carbon nanotubes, using chemical, catalytical and electrical approaches, unzips them into thin graphene strips of various widths, the so-called graphene nanoribbons. In contrast, rolling up these flimsy ribbons into tubes in a real experiment has not been possible. Theoretical studies conducted by Kit *et al*. recently demonstrated the tube formation through twisting of graphene nanoribbon, an idea very different from the rolling-up postulation. Here we report the first experimental evidence of a thermally induced self-intertwining of graphene nanoribbons for the preferential synthesis of (7, 2) and (8, 1) tubes within parent-tube templates. Through the tailoring of ribbon's width and edge, the present finding adds a radically new aspect to the understanding of carbon nanotube formation, shedding much light on not only the future chirality tuning, but also contemporary nanomaterials engineering.

6.149 **Subnanowatt Carbon Nanotube Complementary Logic Enabled by Threshold Voltage Control**
Geier, M.L., Prabhumirashi, P., McMorrow, J.J., Xu, W., Seo, J-W.T., Everaerts, K., Kim, C.H., Marks, T.J. and Hersam, M.C.
Nano Lett., ***13(10)****, 4810-4814 82013)*

In this Letter, we demonstrate thin-film single-walled carbon nanotube (SWCNT) complementary metal-oxide-semiconductor (CMOS) logic devices with subnanowatt static power consumption and full rail-to-rail voltage transfer characteristics as is required for logic gate cascading. These results are enabled by a local metal gate structure that achieves enhancement-mode p-type and n-type SWCNT thin-film transistors (TFTs) with widely separated and symmetric threshold voltages. These complementary SWCNT TFTs are integrated to demonstrate CMOS inverter, NAND, and NOR logic gates at supply voltages as low as 0.8 V with ideal rail-to-rail operation, subnanowatt static power consumption, high gain, and excellent noise immunity. This work provides a direct pathway for solution processable, large area, power efficient SWCNT advanced logic circuits and systems.

6.150 **Plasmonic Nature of the Terahertz Conductivity Peak in Single-Wall Carbon Nanotubes**
Zhang, Q., Haroz, E.H., Jin, Z., Ren, L., Wang, X., Arvidson, R.S., Lüttge, A. and Kono, J.
*Nano Lett., **13(12)**, 5991-5996 (2013)*

Plasmon resonance is expected to occur in metallic and doped semiconducting carbon nanotubes in the terahertz frequency range, but its convincing identification has so far been elusive. The origin of the terahertz conductivity peak commonly observed for carbon nanotube ensembles remains controversial. Here we present results of optical, terahertz, and direct current (DC) transport measurements on highly enriched metallic and semiconducting nanotube films. A broad and strong terahertz conductivity peak appears in both types of films, whose behaviors are consistent with the plasmon resonance explanation, firmly ruling out other alternative explanations such as absorption due to curvature-induced gaps.

6.151 **Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes**
Rohringer, P., Shi, L., Liu, X., Yanagi, K. and Pichler, T.
*Carbon, **74**, 282-290 (2014)*

We studied the effect of varying sonication and centrifugation parameters on double-walled carbon nanotubes (DWCNT) by measuring optical absorption and photoluminescence (PL) of the samples. We found that by using a low sonication intensity before applying density gradient ultracentrifugation (DGU), only inner tube species with a diameter $\leqslant\leqslant 0.8$ nm can be identified in absorption measurements. This is in stark contrast to the result after sonicating at higher intensities, where also bigger inner tubes can be found. Furthermore, by comparing PL properties of samples centrifugated either with or without a gradient medium, we found that applying DGU greatly enhances the PL intensity, whereas centrifugation at even higher speeds but without a gradient medium results in lower intensities. This can be explained by extraction of inner tubes from their host outer tubes in a two-stage process: the different shearing forces from the sonication treatments result in some DWCNT to be opened, whereas others stay uncut. A subsequent application of DGU leads to the extraction of the inner tubes or not if the host nanotube stayed uncut or no gradient medium was used. This work shows a pathway to avoid this phenomenon to unravel the intrinsic PL from inner tubes of DWCNT.

6.152 **Influence of Electronic Type Purity on the Lithiation of Single-Walled Carbon Nanotubes**
Jaber-Ansari, L., Iddir, H., Curtiss, L.A. and Hersam, M.C.
*ACS Nano, **8(3)**, 2399-2409 (2014)*

Single-walled carbon nanotubes (SWCNTs) have emerged as one of the leading additives for high-capacity nanocomposite lithium ion battery electrodes due to their ability to improve electrode conductivity, current collection efficiency, and charge/discharge rate for high power applications. However, since as-grown SWCNTs possess a distribution of physical and electronic structures, it is of high interest to determine which subpopulations of SWCNTs possess the highest lithiation capacity and to develop processing methods that can enhance the lithiation capacity of underperforming SWCNT species. Toward this end, SWCNT electronic type purity is controlled *via* density gradient ultracentrifugation, enabling a systematic study of the lithiation of SWCNTs as a function of metal *versus* semiconducting content. Experimentally, vacuum-filtered freestanding films of metallic SWCNTs are found to accommodate lithium with an order of magnitude higher capacity than their semiconducting counterparts, which is consistent with *ab initio* molecular dynamics and density functional theory calculations in the limit of isolated SWCNTs. In contrast, SWCNT film densification leads to the enhancement of the lithiation capacity of semiconducting SWCNTs to levels comparable to metallic SWCNTs, which is corroborated by theoretical calculations that show increased lithiation of semiconducting SWCNTs in the limit of small SWCNT–SWCNT spacing. Overall, these results will inform ongoing efforts to utilize SWCNTs as conductive additives in nanocomposite lithium ion battery electrodes.

6.153 Etching of Surfactant from Solution-Processed, Type-Separated Carbon Nanotubes and Impact on Device Behavior
Kane, A.A., Ford, A.C., Nissen, A., Krafcik, K.L. and Leonard, F.
*ACS Nano, **8(3)**, 2477-2485 (2014)*

Semiconducting single-walled carbon nanotubes (SWCNTs) have great potential for use in electronic and optoelectronic devices. However, methods for synthesizing SWCNTs produce a mixture of metallic and semiconducting materials, which require additional processing to separate by electronic type. Purification and enrichment of the semiconducting fraction is readily achieved by using the centrifugation of aqueous suspensions of SWCNTs with the help of surfactants, but this leaves residual surfactant on the SWCNT surface that can impact their electronic and optical properties. Here, we present a detailed study of the sodium taurodeoxycholate (STDC) surfactant removal process during vacuum annealing, showing that it occurs through fragmentation of the surfactant, and that complete removal requires exceedingly high temperatures, which indicates strong binding to the SWCNTs. We then present an approach based on air oxidation and mild annealing to completely remove the surfactant while maintaining the SWCNT properties. Using this approach, we compare single SWCNT electronic devices with and without STDC and show that, despite the very strong surfactant binding, it does not affect device performance substantially.

6.154 Rod Hydrodynamics and Length Distributions of Single-Wall Carbon Nanotubes Using Analytical Ultracentrifugation
Batista, C.A.S., Zheng, M., Khripin, C.Y., Tu, X. and Fagan, J.A.
*Langmuir, **30(17)**, 4895-4904 (2014)*

Because of their repetitive chemical structure, extreme rigidity, and the separability of populations with varying aspect ratio, SWCNTs are excellent candidates for use as model rodlike colloids. In this contribution, the sedimentation velocities of length and density sorted single-wall carbon nanotubes (SWCNTs) are compared to predictions from rod hydrodynamic theories of increasing complexity over a range of aspect ratios from <50 to >400. Independently measuring all contributions to the sedimentation velocity besides the shape factor, excellent agreement is found between the experimental findings and theoretical predictions for numerically calculated hydrodynamic radius values and for multiterm analytical expansion approximations; values for the hydrodynamic radii in these cases are additionally found to be consistent with the apparent hydrated particle radius determined independently by buoyancy measurements. Lastly, we utilize this equivalency to calculate the apparent distribution of nanotube lengths in each population from their sedimentation coefficient distribution without adjustable parameters, achieving excellent agreement with distributions from atomic force microscopy. The method developed herein provides an alternative for the ensemble measurement of SWCNT length distributions and others rodlike particles.

6.155 Structure-Dependent Mitochondrial Dysfunction and Hypoxia Induced with Single-Walled Carbon Nanotubes
Wang, L-R., Xue, X., Hu, X-M., Wei, M-Y., Zhang, C-Q., Ge, G-L. and Liang, X-J.
*Small, **10(14)**, 2859-2869 (2014)*

Cytotoxicity of nanomaterials on living systems is known to be affected by their size, shape, surface chemistry, and other physicochemical properties. Exposure to a well-characterized subpopulation of specific nanomaterials is therefore desired to reveal more detailed mechanisms. This study develops scalable density gradient ultracentrifugation sorting of highly dispersed single-walled carbon nanotubes (SWNTs) into four distinct bands based on diameter, aggregation, and structural integrity, with greatly improved efficiency, yield, and reproducibility. With guarantee of high yield and stability of four SWNT fractions, it is possible for the first time, to investigate the structure-dependent bioeffects of four SWNT fractions. it is possible Among these, singly-dispersed integral SWNTs show no significant effects on the mitochondrial functions and hypoxia. The aggregated integral SWNTs show more significant effects on the mitochondrial dysfunction and hypoxia compared to the aggregated SWNTs with poor structure integrity. Then, it is found that the aggregated integral SWNTs induced the irregular mitochondria respiratory and pro-apoptotic proteins activation, while aggregated SWNTs with poor structure integrity greatly enhanced reactive oxygen species (ROS) levels. This work supports the view that control of the distinct structure characteristics of SWNTs helps establish clearer structure-bioeffect correlation and health risk assessment. It is also hoped that these results can help in the design of nanomaterials with higher efficiency and accuracy in subcellular translocation.

6.156 High-Yield, Single-Step Separation of Metallic and Semiconducting SWCNTs Using Block Copolymers at Low Temperatures

Homenick, C.M., Rousina-Webb, A., Cheng, F., Jakubinek, M.B., Malenfant, P.R.L. and Simard, b.
J. Phys. Chem. C, 118(29), 16156-16164 (2014)

Electronic type separation of SWCNT material is necessary to facilitate the development of carbon nanotube electronics. A convenient, high-yield, single-step separation of metallic and semiconducting SWCNTs has been developed using block copolymers and density gradient ultracentrifugation. In particular by varying the centrifugation temperature and dissolved oxygen content under acidic conditions, extraction efficiencies of up to 65% were achieved with both metallic and semiconducting SWCNT electronic purity exceeding 99% as determined by absorption spectroscopy. It was demonstrated that lowering the temperature during the DGU separation, which is expected to increase the difference in densities between metallic and semiconducting nanotube complexes, results in higher purity and yield. Semiconducting and metallic bands are separated simply with a disposable pipet such that specialized fractioning equipment is not required for effective isolation of enriched SWCNTs.

6.157 Top-Down Patterning and Self-Assembly for Regular Arrays of Semiconducting Single-Walled Carbon Nanotubes

Wu, J., Antaris, A., Gong, M. and Dai, H.
Adv. Mater., ***26(35)****, 6151-6156 (2014)*

Highly pure semiconducting single-walled carbon nanotubes (SWNTs), sorted by density-gradient ultracentrifugation, undergo self-assembly using depletion attraction forces into rafts along lithographically defined patterns of narrow pitch (100 or 200 nm). The arrays demonstrate high pattern fidelity and channel filling, along with large-scale homogeneity. Field-effect transistors made from these arrays exhibit high performance at on/off ratios > 1000.

6.158 Fringing-field dielectrophoretic assembly of ultrahigh-density semiconducting nanotube arrays with a self-limited pitch

Cao, Q., Han, S-j. and Tulevski, G.
Nature Communications, ***5****:5071 (2014)*

One key challenge of realizing practical high-performance electronic devices based on single-walled carbon nanotubes is to produce electronically pure nanotube arrays with both a minuscule and uniform inter-tube pitch for sufficient device-packing density and homogeneity. Here we develop a method in which the alternating voltage-fringing electric field formed between surface microelectrodes and the substrate is utilized to assemble semiconducting nanotubes into well-aligned, ultrahigh-density and submonolayered arrays, with a consistent pitch as small as 21±6 nm determined by a self-limiting mechanism, based on the unique field focusing and screening effects of the fringing field. Field-effect transistors based on such nanotube arrays exhibit record high device transconductance (>50 μS μm^{-1}) and decent on current per nanotube (~1 μA per tube) together with high on/off ratios at a drain bias of −1 V.

6.159 Thickness sorting of two-dimensional transition metal dichalcogenides via copolymer-assisted density gradient ultracentrifugation

Kang, J., Seo, J-W.T., Alducin, D., Ponce, A., Yacaman, M.J. and Hersam, M.C.
Nature Communications, ***5****:5478 (2014)*

Two-dimensional transition metal dichalcogenides have emerged as leading successors to graphene due to their diverse properties, which depend sensitively on sample thickness. Although solution-based exfoliation methods hold promise for scalable production of these materials, existing techniques introduce irreversible structural defects and/or lack sufficient control over the sample thickness. In contrast, previous work on carbon nanotubes and graphene has shown that isopycnic density gradient ultracentrifugation can produce structurally and electronically monodisperse nanomaterial populations. However, this approach cannot be directly applied to transition metal dichalcogenides due to their high intrinsic buoyant densities when encapsulated with ionic small molecule surfactants. Here, we overcome this limitation and thus demonstrate thickness sorting of pristine molybdenum disulfide (MoS_2) by employing a block copolymer dispersant composed of a central hydrophobic unit flanked by hydrophilic chains that effectively reduces the overall buoyant density in aqueous solution. The resulting solution-processed monolayer MoS_2 samples exhibit strong photoluminescence without further chemical treatment.

6.160 High Precision Fractionator for Use with Density Gradient Ultracentrifugation

Kadria-Vili, Y., Canning, g., Bachilo, S.M. and Weisman, R.B.
*Anal. Chem., **86(22)**, 11018-11023 (2014)*

The recent application of density gradient ultracentrifugation (DGU) for structural sorting of single-walled carbon nanotube samples has created a need for highly selective extraction of closely spaced layers formed in the centrifuged tube. We describe a novel computer-controlled device designed for this purpose. Through the use of fine needles, systematic needle motions, and slow flow rates, multiple sample layers can be aspirated under program control with minimal cross contamination between layers. The fractionator's performance is illustrated with DGU-sorted samples of single-walled carbon nanotubes.

6.161 Diameter dependence of the optoelectronic properties of single walled carbon nanotubes determined by ellipsometry

Battie, Y., Broch, L., En Naciri, A., Lauret, J-S., Guezo, M. and Loiseau, A.
*Carbon, **83**, 32-39 (2015)*

We report ellipsometric measurement on single walled carbon nanotube (SWCNT) films performed in a large spectral range from 0.07 to 4.97 eV. The complex dielectric functions of SWCNTs are correlated to their diameter distribution extracted from transmission electron microscopy. Here we show that the transition energies between Van Hove singularities are directly related to the strong one dimensional confinement. In the infrared spectral range, the real part of the dielectric function becomes negative. The electronic properties of SWCNTs are extracted from ellipsometry by using a Drude model. The mobility and the mean free path of charge carriers are limited by the high number of SWCNT contacts. In accordance with tight binding simulation, the conductivity and the charge carrier concentration increase with the SWCNT diameter. Finally, we demonstrate that the π-plasmon energy depends on the charge carrier concentration.

6.162 Separation of colloidal two dimensional materials by density gradient ultracentrifugation

Kuang, Y., Song, S., Huang, J. and Sun, X.
*J. Solid State Chem., **224**, 120-126 (2015)*

Two-dimensional (2D) materials have been made through various approaches but obtaining monodispersed simply by synthesis optimization gained little success, which highlighted the need for introducing nanoseparation methods. Density gradient ultracentrifugation method has emerged as a versatile and scalable method for sorting colloidal 2D nanomaterials. Isopycnic separation was applied on thickness-dependent separation of graphene nanosheets. And rate-zonal separation, as a more versatile separation method, demonstrated its capability in sorting nanosheets of chemically modified single layered graphene, layered double hydroxide, and even metallic Ag. Establishing such density gradient ultracentrifugation method not only achieves monodispersed nanosheets and provides new opportunities for investigation on size dependent properties of 2D materials, but also makes the surface modification possible by introducing "reaction zones" during sedimentation of the colloids.

6.163 Determination of the Lateral Dimension of Graphene Oxide Nanosheets Using Analytical Ultracentrifugation

Walter, J., Nacken, T.J., Damm, C., Thajudeen, T., Eigler, S. and Peukert, W.
*Small, **11(7)**, 814-825 (2015)*

In this paper, a method to determine the lateral dimensions of 2D nanosheets directly in suspension by analytical ultracentrifugation (AUC) is shown. The basis for this study is a well-characterized and stable dispersion of graphene oxide (GO) monolayers in water. A methodology is developed to correlate the sedimentation coefficient distribution measured by AUC with the lateral size distribution of the 2D GO nanosheets obtained from atomic force microscopy (AFM). A very high accuracy can be obtained by virtue of counting several thousand sheets, thereby minimizing any coating effects or statistical uncertainties. The AFM statistics are further used to fit the lateral size distribution obtained from the AUC to determine the unknown hydrodynamic sheet thickness or density. It is found that AUC can derive nanosheet diameter distributions with a relative error of the mean sheet diameter of just 0.25% as compared to the AFM analysis for 90 mass% of the particles in the distribution. The standard deviation of the size-dependent error for the total distribution is found to be 3.25%. Based on these considerations, an expression is given to calculate the cut size of 2D nanosheets in preparative centrifugation experiments.

6.164 High energetic excitons in carbon nanotubes directly probe charge-carriers
Soavi, G., Scotognella, F., Viola, D., Hefner, T., Hertel, T., Cerullo, G. and Lanzani, G.
*Scientific Reports, **5**:9681 (2015)*

Theory predicts peculiar features for excited-state dynamics in one dimension (1D) that are difficult to be observed experimentally. Single-walled carbon nanotubes (SWNTs) are an excellent approximation to 1D quantum confinement, due to their very high aspect ratio and low density of defects. Here we use ultrafast optical spectroscopy to probe photogenerated charge-carriers in (6,5) semiconducting SWNTs. We identify the transient energy shift of the highly polarizable S_{33} transition as a sensitive fingerprint of charge-carriers in SWNTs. By measuring the coherent phonon amplitude profile we obtain a precise estimate of the Stark-shift and discuss the binding energy of the S_{33} excitonic transition. From this, we infer that charge-carriers are formed instantaneously (<50 fs) even upon pumping the first exciton, S_{11}. The decay of the photogenerated charge-carrier population is well described by a model for geminate recombination in 1D.

6.165 Double-Walled Carbon Nanotube Processing
Moore, K.E., Tune, D.D. and Flavel, B.S.
*Advanced Materials, **27(20)**, 3105-3137 (2015)*

Single-walled carbon nanotubes (SWCNTs) have been the focus of intense research, and the body of literature continues to grow exponentially, despite more than two decades having passed since the first reports. As well as extensive studies of the fundamental properties, this has seen SWCNTs used in a plethora of applications as far ranging as microelectronics, energy storage, solar cells, and sensors, to cancer treatment, drug delivery, and neuronal interfaces. On the other hand, the properties and applications of double-walled carbon nanotubes (DWCNTs) have remained relatively under-explored. This is despite DWCNTs not only sharing many of the same unique characteristics of their single-walled counterparts, but also possessing an additional suite of potentially advantageous properties arising due to the presence of the second wall and the often complex inter-wall interactions that arise. For example, it is envisaged that the outer wall can be selectively functionalized whilst still leaving the inner wall in its pristine state and available for signal transduction. A similar situation arises in DWCNT field effect transistors (FETs), where the outer wall can provide a convenient degree of chemical shielding of the inner wall from the external environment, allowing the excellent transconductance properties of the pristine nanotubes to be more fully exploited. Additionally, DWCNTs should also offer unique opportunities to further the fundamental understanding of the inter-wall interactions within and between carbon nanotubes. However, the realization of these goals has so far been limited by the same challenge experienced by the SWCNT field until recent years, namely, the inherent heterogeneity of raw, as-produced DWCNT material. As such, there is now an emerging field of research regarding DWCNT processing that focuses on the preparation of material of defined length, diameter and electronic type, and which is rapidly building upon the experience gained by the broader SWCNT community. This review describes the background of the field, summarizing some relevant theory and the available synthesis and purification routes; then provides a thorough synopsis of the current state-of-the-art in DWCNT sorting methodologies, outlines contemporary challenges in the field, and discusses the outlook for various potential applications of the resulting material.

6.166 Bench-top aqueous two-phase extraction of isolated individual single-walled carbon nanotubes
Subbaiyan, N.K., Parra-Vasquez, A.N.G., Cambre, S., Cordoba, M.A.S., Yalcin, S.E:, Hamilton, C.E., Mack, N.H., Blackburn, J.L., Doom, S.K. and Duque, J.G.
*Nano Res., **8(5)**, 1755-1769 (2015)*

Isolation and purification of single-walled carbon nanotubes (SWCNTs) are prerequisites for their implementation in various applications. In this work, we present a fast (~5 min), low-cost, and easily scalable bench-top approach to the extraction of high-quality isolated SWCNTs from bundles and impurities in an aqueous dispersion. The extraction procedure, based on aqueous two-phase (ATP) separation, is widely applicable to any SWCNT source (tested on samples up to 1.7 nm in diameter) and independent of defect density, purity, diameter, and length. The extracted dispersions demonstrate that the removal of large aggregates, small bundles, and impurities is comparable to that by density gradient ultracentrifugation, but without the need for high-end instrumentation. Raman and fluorescence-excitation spectroscopy, single-nanotube fluorescence imaging, atomic force and transmission electron microscopy, and thermogravimetric analysis all confirm the high purity of the isolated SWCNTs. By predispersing the SWCNTs without sonication (only gentle stirring), full-length, pristine SWCNTs can be isolated (tested up to 20 µm). Hence, this simple ATP method will find immediate application in the generation of SWCNT materials for all levels of nanotube research and applications, from fundamental studies to high-performance devices.

6.167 Gold Nanoparticles Stabilized with MPEG-Grafted Poly(l-lysine): in Vitro and in Vivo Evaluation of a Potential Theranostic Agent
Bogdanov, A.A., Gupta, S., Koshkina, N., Corr, S.J., Zhang, S., Curley, S.A. and Han, G.
Bioconjugate Chem., ***26(1)***, *39-50 (2015)*

As the number of diagnostic and therapeutic applications utilizing gold nanoparticles (AuNPs) increases, so does the need for AuNPs that are stable in vivo, biocompatible, and suitable for bioconjugation. We investigated a strategy for AuNP stabilization that uses methoxypolyethylene glycol-*graft*-poly(l-lysine) copolymer (MPEG-gPLL) bearing free amino groups as a stabilizing molecule. MPEG-gPLL injected into water solutions of $HAuCl_4$ with or without trisodium citrate resulted in spherical (Z_{av} = 36 nm), monodisperse (PDI = 0.27), weakly positively charged nanoparticles (AuNP3) with electron-dense cores (diameter: 10.4 ± 2.5 nm) and surface amino groups that were amenable to covalent modification. The AuNP3 were stable against aggregation in the presence of phosphate and serum proteins and remained dispersed after their uptake into endosomes. MPEG-gPLL-stabilized AuNP3 exhibited high uptake and very low toxicity in human endothelial cells, but showed a high dose-dependent toxicity in epithelioid cancer cells. Highly stable radioactive labeling of AuNP3 with ^{99m}Tc allowed imaging of AuNP3 biodistribution and revealed dose-dependent long circulation in the blood. The minor fraction of AuGNP3 was found in major organs and at sites of experimentally induced inflammation. Gold analysis showed evidence of a partial degradation of the MPEG-gPLL layer in AuNP3 particles accumulated in major organs. Radiofrequency-mediated heating of AuNP3 solutions showed that AuNP3 exhibited heating behavior consistent with 10 nm core nanoparticles. We conclude that PEG-pPLL coating of AuNPs confers “stealth” properties that enable these particles to exist in vivo in a nonaggregating, biocompatible state making them suitable for potential use in biomedical applications such as noninvasive radiofrequency cancer therapy.

6.168 Solubilization of Single-Walled Carbon Nanotubes Using a Peptide Aptamer in Water below the Critical Micelle Concentration
Li, Z., Kameda, T., Isoshima, T., Kobatake, E., Tanaka, T., Ito, y. and Kawamoto, M.
Langmuir, ***31(11)***, *3482-3488 (2015)*

The solubilizing ability of single-walled carbon nanotubes (SWCNTs) in water with several dispersants was investigated. Among the dispersants, including low-molecular-weight surfactants, peptides, DNA, and a water-soluble polymer, the peptide aptamer, A2 (IFRLSWGTYFS), exhibited the highest dispersion capability below the critical micelle concentration at a concentration of 0.02 w/v%. The dispersion of supernatant aqueous solution of SWCNTs containing aptamer A2 was essentially unchanged for several months after high-speed ultracentrifugation and gave rise to an efficient and stable dispersion of the SWCNTs in water. From the results of isothermal titration calorimetry and molecular dynamics simulations, the effective binding capability of A2 was due to π–π interaction between aromatic groups in the peptide aptamer and the side walls of SWCNTs. Interestingly, the peptide aptamer showed the possibility of diameter separation of semiconducting SWCNTs using a uniform density gradient ultracentrifuge. These phenomena are encouraging results toward an effective approach to the dispersion and separation of SWCNTs.

6.169 Isolation of >1 nm Diameter Single-Wall Carbon Nanotube Species Using Aqueous Two-Phase Extraction
Fagan, J.A., haroz, E.H., Ihly, R., Gui, H., Blackburn, J.L., Simpson, J.R., Lam, S., Walker, A.R.H., Doorn, S.K. and Zheng, M.
ACS Nano, ***9(5)***, *5377-5390 (2015)*

In this contribution we demonstrate the effective separation of single-wall carbon nanotube (SWCNT) species with diameters larger than 1 nm through multistage aqueous two-phase extraction (ATPE), including isolation at the near-monochiral species level up to at least the diameter range of SWCNTs synthesized by electric arc synthesis (1.3–1.6 nm). We also demonstrate that refined species are readily obtained from both the metallic and semiconducting subpopulations of SWCNTs and that this methodology is effective for multiple SWCNT raw materials. Using these data, we report an empirical function for the necessary surfactant concentrations in the ATPE method for separating different SWCNTs into either the lower or upper phase as a function of SWCNT diameter. This empirical correlation enables predictive separation design and identifies a subset of SWCNTs that behave unusually as compared to other species. These results not only dramatically increase the range of SWCNT diameters to which species selective separation can be achieved but also demonstrate that aqueous two-phase separations can be designed across experimentally accessible ranges of surfactant concentrations to controllably separate SWCNT populations of very small (∼0.62 nm) to very large diameters (>1.7 nm). Together, the results reported here indicate that total separation of all SWCNT species is likely feasible by the ATPE method, especially given future development of multistage automated extraction techniques.

6.170 Semiconducting enrichment of arc discharge single-walled carbon nanotubes by density gradient ultracentrifugation
Scharfenberg, L. and Mertig, M.
Phys. Status Solidi A, ***6**, 1395-1398 (2015)*

Due to their intrinsic properties, single-walled carbon nanotubes (SWCNTs) are promising candidates for source-drain channels in field-effect transistors (FETs). However, their application in transistors requires semiconducting tubes, and thus, sorting of SWCNTs according to those. The basis for an efficient sorting is the dispersion of the material that usually includes but is not limited to applying tip sonication in the presence of appropriate amphiphilic molecules. We present a high semiconducting enrichment of surfactant-wrapped arc discharge SWCNTs via sorting according to electronic type by applying density gradient ultracentrifugation (DGU). We utilized a common combination of anionic surfactants, but optimized the sonication time during the dispersion step of the SWCNTs and the duration of performing DGU. Furthermore, we used UV–Vis spectroscopy to determine the differences in the content of metallic (m) and semiconducting (sc) SWCNTs of different samples. By the refinement of the conditions, we have achieved an enrichment of sc-SWCNTs up to 98% in two sorting steps.

6.171 Bright Fraction of Single-Walled Carbon Nanotubes through Correlated Fluorescence and Topography Measurements
Nogaj, L.J., Smyder, J.A., Leach, K.E., Tu, X., Zheng, M. and Krauss, T.D.
J. Phys. Chem. Lett., ***6(14)**, 2816-2821 (2015)*

Correlated measurements of fluorescence and topography were performed for individual single-walled carbon nanotubes (SWNTs) on quartz using epifluorescence confocal microscopy and atomic force microscopy (AFM). Surprisingly, only ∼11% of all SWNTs in DNA-wrapped samples were found to be highly emissive on quartz, suggesting that the ensemble fluorescence quantum yield is low because only a small population of SWNTs fluoresces strongly. Qualitatively similar conclusions were obtained from control studies using a sodium cholate surfactant system. To accommodate AFM measurements, excess surfactant was removed from the substrate. Though individual SWNTs on nonrinsed and rinsed surfaces displayed differences in fluorescence intensities and line widths, arising from the influence of the local environment on individual SWNT optical measurements, photoluminescence data from both samples displayed consistent trends.

6.172 Sorting Semiconducting Single-Walled Carbon Nanotubes by Water-Soluble Polyfluorene Assisted Electrophoresis and Its Application in Field-effect Transistors
Zhu, H. and Wang, W.
Chin. J. Chem., ***33**, 756-764 (2015)*

We report a considerably promising method based on agarose gel electrophoresis (AGE) to separate single-walled carbon nanotubes by adding a water-soluble polyfluorene (w-PFO) as surfactant into the agarose gel. In this effective method, the AGE/w-PFO gel network will trap more semiconducting single-walled carbon nanotubes (SWNTs) with the assistance of w-PFO, for the strong interaction between w-PFO and semiconducting species. The optical absorbance, photoluminescence emission and resonant Raman scattering characterization were used to verify the separation effect. The purity of separated semiconducting species is as high as (98±1)%. The demonstrated field effect transistors give the on/off ratio and mobility about 27000 and 10.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$, respectively.

6.173 High-work-function metal/carbon nanotube/low-work-function metal hybrid junction photovoltaic

device
Chen, C., Jin, T., Wei, L., Li, Y., Liu, X., Wang, Y., Zhang, L., Liao, C., Hu, N., Song, C. and Zhang, Y.
*NPG Asia Materials, **7**, e220 (2015)*

Photovoltaic devices based on nanotechnology have attracted much attention because of their great potential for application in electronic and energy fields. Here, a photovoltaic device based on a high-work-function metal/single-walled carbon nanotube (SWNT)/low-work-function metal hybrid junction was investigated. In the device, asymmetric metal electrodes (palladium and aluminum) were fabricated on opposite ends of a single semiconducting SWNT, which was used as the photosensitive material. This structure allowed a strong built-in electric field to be generated in the SWNT to efficiently separate photogenerated electron-hole pairs and achieve good photovoltaic effect. In the dark, the device behaved as a gate-dependent Schottky diode and exhibited the electrical characteristics of a rectifier. The SWNT diameter (band gap) was found to have a significant effect on the device characteristics. For the device fabricated with a 1.4-nm-diameter SWNT, a high rectification ratio ($I_{forward}/I_{reverse}$) of $>10^3$ could be achieved in the dark. Under monochromatic illumination, this device had an open-circuit voltage of 0.15 V and a high quantum efficiency of ~75%.

6.174 **Solution-Processed Dielectrics Based on Thickness-Sorted Two-Dimensional Hexagonal Boron Nitride Nanosheets**
Zhu, J., Kang, J., Kang, J.,Jjariwala, D., Wood, J.D., Seo, J-W.T., Chen, K-S., marks, T.J. and hersam, M.C.
*Nano Lett., **15(10)**, 7029-7036 (2015)*

Gate dielectrics directly affect the mobility, hysteresis, power consumption, and other critical device metrics in high-performance nanoelectronics. With atomically flat and dangling bond-free surfaces, hexagonal boron nitride (h-BN) has emerged as an ideal dielectric for graphene and related two-dimensional semiconductors. While high-quality, atomically thin h-BN has been realized via micromechanical cleavage and chemical vapor deposition, existing liquid exfoliation methods lack sufficient control over h-BN thickness and large-area film quality, thus limiting its use in solution-processed electronics. Here, we employ isopycnic density gradient ultracentrifugation for the preparation of monodisperse, thickness-sorted h-BN inks, which are subsequently layer-by-layer assembled into ultrathin dielectrics with low leakage currents of 3×10^{-9} A/cm^2 at 2 MV/cm and high capacitances of 245 nF/cm^2. The resulting solution-processed h-BN dielectric films enable the fabrication of graphene field-effect transistors with negligible hysteresis and high mobilities up to 7100 cm^2 V^{-1} s^{-1} at room temperature. These h-BN inks can also be used as coatings on conventional dielectrics to minimize the effects of underlying traps, resulting in improvements in overall device performance. Overall, this approach for producing and assembling h-BN dielectric inks holds significant promise for translating the superlative performance of two-dimensional heterostructure devices to large-area, solution-processed nanoelectronics.

6.175 **Optical detection of individual ultra-short carbon nanotubes enables their length characterization down to 10 nm**
Gao, Z., Oudjedi, L., Faes, R., Morote, F., Jaillet, C., Poulin, P., Lounis, B. and Cognet, L.
*Scientific Reports, **5**:17093 (2015)*

Ultrashort single-walled carbon nanotubes, i.e. with length below ~30 nm, display length-dependent physical, chemical and biological properties that are attractive for the development of novel nanodevices and nanomaterials. Whether fundamental or applicative, such developments require that ultrashort nanotube lengths can be routinely and reliably characterized with high statistical data for high-quality sample production. However, no methods currently fulfill these requirements. Here, we demonstrate that photothermal microscopy achieves fast and reliable optical single nanotube analysis down to ~10 nm lengths. Compared to atomic force microscopy, this method provides ultrashort nanotubes length distribution with high statistics, and neither requires specific sample preparation nor tip-dependent image analysis.

6.176 **Single Chirality (6,4) Single-Walled Carbon Nanotubes for Fluorescence Imaging with Silicon Detectors**
Antaris, A.L., Yaghi, O.K., Hong, G., Diao, S., Zhang, B., Yang, J., Chew, L. and Dai, H.
*Small, **11(47)**, 6325-6330 (2015)*

Postsynthetic single-walled carbon nanotube (SWCNT) sorting methods such as density gradient ultracentrifugation, gel chromatography, and electrophoresis have all been inspired by established biochemistry separation techniques designed to separate subcellular components. Biochemistry separation techniques have been refined to the degree that parameters such as pH, salt concentration, and temperature are necessary for a successful separation, yet these conditions are only now being applied to SWCNT separation methodologies. Slight changes in pH produce radically different behaviors of SWCNTs inside a density gradient, allowing for the facile separation of ultrahigh purity (6,4) SWCNTs from as-synthesized carbon nanotubes. The (6,4) SWCNTs are novel fluorophores emitting below ≈900 nm and can be easily detected with conventional silicon-based charge-coupled device detectors without the need for specialized InGaAs cameras. The (6,4) SWCNTs are used to demonstrate their potential as a clinically relevant NIR-I fluorescence stain for the immunohistochemical staining of cells and cancer tissue sections displaying high endothelial growth factor receptor levels

6.177 Comprehensive spectroscopic characterization of high purity metallicity-sorted single-walled carbon nanotubes

Kharlamova, M.V., Kramberger, C., Sauer, M., Yanagi, K. and Pichler, T.
*Phys. Status Sollidi B, **252(11)**, 2512-2518 (2015)*

We have performed a thorough characterization of 1.4 nm-diameter single-walled carbon nanotubes (SWCNTs) separated according to their metallicity by optical absorption (OAS), X-ray photoelectron (XPS), ultraviolet photoelectron (UPS), and multifrequency Raman spectroscopy. The OAS, XPS, and UPS data prove a high purity (≳99%) of SWCNTs. The C 1s core level XPS spectra of the separated nanotubes show different spectral widths, asymmetry, and peak positions. The UPS spectra of the samples demonstrate clearly defined van Hove singularities. Significant differences are observed in the Raman spectra of the separated nanotubes. Our findings suggest that for further advances in SWCNT metallicity sorting, Raman spectroscopy has to be applied to assess purity levels beyond the detection limits of OAS, XPS, and UPS.

6.178 Solution-processed carbon nanotube thin-film complementary static random access memory

Geier, M.L., McMorrow, J.J., Xu, W., Zhu, J., Kim, C.H., Marks, T.J. and Hersam, M.C.
*Nature Nanotechnol. Lett., **10**, 944-948 (2015)*

Over the past two decades, extensive research on single-walled carbon nanotubes (SWCNTs) has elucidated their many extraordinary properties[1, 2, 3], making them one of the most promising candidates for solution-processable, high-performance integrated circuits[4, 5]. In particular, advances in the enrichment of high-purity semiconducting SWCNTs[6, 7, 8] have enabled recent circuit demonstrations including synchronous digital logic[9], flexible electronics[10, 11, 12, 13, 14] and high-frequency applications[15]. However, due to the stringent requirements of the transistors used in complementary metal–oxide–semiconductor (CMOS) logic as well as the absence of sufficiently stable and spatially homogeneous SWCNT thin-film transistors[16, 17, 18], the development of large-scale SWCNT CMOS integrated circuits has been limited in both complexity and functionality[19, 20, 21]. Here, we demonstrate the stable and uniform electronic performance of complementary p-type and n-type SWCNT thin-film transistors by controlling adsorbed atmospheric dopants and incorporating robust encapsulation layers. Based on these complementary SWCNT thin-film transistors, we simulate, design and fabricate arrays of low-power static random access memory circuits, achieving large-scale integration for the first time based on solution-processed semiconductors.

6.179 Recent Progress in Obtaining Semiconducting Single-Walled Carbon Nanotubes for Transistor Applications

Islam, A.E., Rogers, J.A. and Alam, M.A.
*Adv. Mater., **27(48)**, 7908-7937 (2015)*

High purity semiconducting single-walled carbon nanotubes (s-SWCNTs) with a narrow diameter distribution are required for high-performance transistors. Achieving this goal is extremely challenging because the as-grown material contains mixtures of s-SWCNTs and metallic- (m-) SWCNTs with wide diameter distributions, typically inadequate for integrated circuits. Since 2000, numerous ex situ methods have been proposed to improve the purity of the s-SWCNTs. The majority of these techniques fail to maintain the quality and integrity of the s-SWCNTs with a few notable exceptions. Here, the progress in realizing high purity s-SWCNTs in as-grown and post-processed materials is highlighted. A comparison of transistor parameters (such as on/off ratio and field-effect mobility) obtained from test structures establishes the effectiveness of various methods and suggests opportunities for future improvements.

6.180 **Misorientation-angle-dependent electrical transport across molybdenum disulfide grain boundaries**
Ly, T.H., Perello, D.J., Zhao, J., Deng, Q., Kim, H., Han, G.H., Chae, S.H., Jeong, H.Y. and Lee, Y.H.
*Nature Communications, **7**:10426 (2016)*

Grain boundaries in monolayer transition metal dichalcogenides have unique atomic defect structures and band dispersion relations that depend on the inter-domain misorientation angle. Here, we explore misorientation angle-dependent electrical transport at grain boundaries in monolayer MoS_2 by correlating the atomic defect structures of measured devices analysed with transmission electron microscopy and first-principles calculations. Transmission electron microscopy indicates that grain boundaries are primarily composed of 5–7 dislocation cores with periodicity and additional complex defects formed at high angles, obeying the classical low-angle theory for angles <22°. The inter-domain mobility is minimized for angles <9° and increases nonlinearly by two orders of magnitude before saturating at ~16 $cm^2\ V^{-1}\ s^{-1}$ around misorientation angle≈20°. This trend is explained via grain-boundary electrostatic barriers estimated from density functional calculations and experimental tunnelling barrier heights, which are ≈0.5 eV at low angles and ≈0.15 eV at high angles (≥20°).

6.181 **Performance Enhancement of Polymer-Free Carbon Nanotube Solar Cells via Transfer Matrix Modeling**
Pfohl, M., Glaser, K., Ludwig, J., Tune, D.F.D., Dehm, S., Kayser, C., Colsmann, A., Krupke, R. and Flavel, B.S.
*Advanced Energy Materials, **6**, 1501345 (2016)*

Polymer-free (6,5) single-walled carbon nanotubes (SWCNTs) prepared using the gel permeation approach are integrated into SWCNT:C_{60} solar cells. Evaporation-driven self-assembly is used to form large-area SWCNT thin films from the surfactant-stabilized aqueous suspensions. The thicknesses of various layers within the solar cell are optimized by theoretical modeling using transfer matrix calculations, where the distribution of the electric field within the stack is matched to light absorption by the SWCNTs through either their primary (S_{11}) or secondary (S_{22}) absorption peaks, or a combination thereof. The validity of the model is verified experimentally through a detailed parameter study and then used to develop SWCNT:C_{60} solar cells with high open-circuit voltage (0.44 V) as well as a cutting-edge internal quantum efficiency of up to 86% through the nanotube S_{11} transition, over an active area of 0.105 cm^2.

6.182 **Resonance Raman Optical Activity Spectra of Single-Walled Carbon Nanotube Enantiomers**
Magg, M., Kadria-Vili, Y., Oulevey, P., Weismann, R.B. and Bürgi, T.
*J. Phys. Chem. Lett., **7**, 221-225 (2016)*

We present experimental Raman optical activity (ROA) spectra of enantio-enriched single-walled carbon nanotubes (SWCNTs). Enantiomeric samples of (6,5) SWCNTs were prepared using nonlinear density gradient ultracentrifugation (DGU). Upon excitation at 2.33 eV, remarkably strong G-band signals are obtained due to strong resonance enhancement with the E_{22}^S transition of (6,5) SWCNTs. Enhancement allows measuring the vibrational optical activity (VOA) at unusually low concentrations. The obtained results are in good agreement with the single-excited-state theory (SES). To our knowledge, these are the first experimental VOA spectra of SWCNTs.

6.183 **Synthesis and Testing of Modular Dual-Modality Nanoparticles for Magnetic Resonance and Multispectral Photoacoustic Imaging**
Bogdanov, Jr, A.A., Dixon, A.J., Gupta, S., Zhang, L., Zheng, s., Shazeeb, M.S., Zhang, S. and Klibanov, A.L.
*Bioconjugate Chem., **27**, 383-390 (2016)*

Magnetic resonance (MR) and photoacoustic (PA) imaging are currently being investigated as complementing strategies for applications requiring sensitive detection of cells in vivo. While combined MR/PAI detection of cells requires biocompatible cell labeling probes, water-based synthesis of dual-modality MR/PAI probes presents significant technical challenges. Here we describe facile synthesis and characterization of hybrid modular dextran-stabilized gold/iron oxide (Au-IO) multimetallic nanoparticles (NP) enabling multimodal imaging of cells. The stable association between the IO and gold NP was achieved by priming the surface of dextran-coated IO with silver NP resulting from silver(I) reduction by aldehyde groups, which are naturally present within the dextran coating of IO at the level of 19–23 groups/particle. The Au-IO NP formed in the presence of silver-primed Au-IO were stabilized by using partially thiolated MPEG5-gPLL graft copolymer carrying residual amino groups. This stabilizer served as a carrier of near-infrared fluorophores (e.g., IRDye 800RS) for multispectral PA imaging. Dual modality imaging experiments performed in capillary phantoms of purified Au-IO-800RS NPs showed that these NPs were detectible using 3T MRI at a concentration of 25 µM iron. PA imaging achieved approximately 2.5-times higher detection sensitivity due to strong PA signal emissions at 530 and 770 nm, corresponding to gold plasmons and IRDye integrated into the coating of the hybrid NPs, respectively, with no "bleaching" of PA signal. MDA-MB-231 cells prelabeled with Au-IO-800RS retained plasma membrane integrity and were detectable by using both MR and dual-wavelength PA at 49 ± 3 cells/imaging voxel. We believe that modular assembly of multimetallic NPs shows promise for imaging analysis of engineered cells and tissues with high resolution and sensitivity.

6.184 Large scale, selective dispersion of long single-walled carbon nanotubes with high photoluminescence quantum yield by shear force mixing

Graf, A., Zakharko, Y., Schiessl, S.P., Backs, C., Pfohl, M., Flavel, B.S. and Zaumseil, J.
*Carbon, **105**, 593-599 (2016)*

Selective dispersion of semiconducting single-walled carbon nanotube (SWCNTs) with conjugated polymers typically involves harsh sonication methods that damage and shorten the nanotubes. Here, we use simple high speed shear force mixing (SFM) to disperse nearly monochiral (6,5) SWCNTs with poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt-co*-(6,6′-{2,2′-bipyridine})] (PFO-BPy) in toluene with high yield and in large volumes. This highly scalable process disperses SWCNTs of exceptional quality with an average tube length of 1.82 µm and an ensemble photoluminescence quantum yield (PLQY) of 2.3%. For the first time for SWCNTs, we describe and apply absolute PLQY measurements, without the need for any reference emitter. We directly compare values for average SWCNT length, PLQY, linewidth and Stokes shift to other dispersion methods, including bath and tip sonication, as well as other sorting methods such as gel chromatography. We find that SFM results in dispersions of longer SWCNT with higher average PLQY than any other technique, thus making it an ideal method for sorting large amounts of long, high quality and purely semiconducting SWCNTs.

6.185 Characterizing the Effect of Salt and Surfactant Concentration on the Counterion Atmosphere around Surfactant Stabilized SWCNTs Using Analytical Ultracentrifugation

Lam, S., Zheng, M. and Fagan, J.A.
*Langmuir, **32(16)**, 3926-3936 (2016)*

Accurate characterization of dispersed-phase nanoparticle properties such as density, size, solvation, and charge is necessary for their utilization in applications such as medicine, energy, and materials. Herein, analytical ultracentrifugation (AUC) is used to quantify bile salt surfactant adsorption on length sorted (7,6) single-wall carbon nanotubes (SWCNTs) as a function of bulk surfactant concentration and in the presence of varying quantities of a monovalent salt—sodium chloride. These measurements provide high precision adsorbed surfactant density values in the literature for only the second SWCNT structure to date and report the quantity of adsorbed surfactant across a broad range of bulk surfactant concentrations utilized in SWCNT dispersion processing. Second, the measurements presented herein unambiguously demonstrate, via AUC, a direct relation between the size of the counterion cloud around a surfactant-stabilized SWCNT and solution ionic strength. The results show that changes in the size of the counterion cloud around surfactant-stabilized SWCNT are attributable to electrostatic phenomenon and not to changes in the quantity of adsorbed surfactant with salt addition. These results provide important reference values for projecting SWCNT dispersion behavior as a function of solution conditions and extend the range of nanoparticle properties measurable via AUC.

6.186 Competitive Impact of Nanotube Assembly and Contact Electrodes on the Performance of CNT-based FETs

Toader, M., Hermann, S., Scharfenberg, L., Hartmann, M., Mertig, M., Schulz, S.E. and Gessner, T.
*J. Phys. Chem. C, **120(18)**, 10020-10026 (2016)*

We report the fabrication and characterization of highly dense field-effect-transistor (FET) arrays based on single-walled carbon nanotubes (SWCNTs). The nanotubes were sorted according to the electronic type by using density gradient ultracentrifugation (DGU). By employing dielectrophoresis (DEP), SWCNTs with enriched semiconducting (sc) content were systematically integrated as active elements into FETs. The performance of air-operating FETs was addressed via an extended statistic study involving both electrical and structural analyses. The competitive impact of nanotube purity and assembly as well as the metal electrode composition and a thermal treatment on the final device performance was shown. Regardless of the used sc-content, the device-to-device consistency was improved via employing annealing up to 250 °C for 1 h in a vacuum. The observed clockwise hysteresis, known so far only in connection with CNT–FETs built on ferroelectric substrates as well as electrolyte gated CNT–FETs, was found to reverse upon annealing. Moreover, a simple approach in producing air-stable ambipolar transistors is pointed out only via change of the adhesion layer for the Pd electrodes. The annealing study, repeated on such systems, supports the previous results and provides complementary information via a reliable monitoring of the off-state. Indications for a doping-like effect, which partially compromises the device performance in terms of threshold voltage shifts and increased off-state currents, are revealed and discussed.

6.187 Aggregated single-walled carbon nanotubes attenuate the behavioural and neurochemical effects of methamphetamine in mice
Xue, X. et al
Nature Nanotechnology, ***11(7)****, 613-620 (2016)*

Methamphetamine (METH) abuse is a serious social and health problem worldwide. At present, there are no effective medications to treat METH addiction[1]. Here, we report that aggregated single-walled carbon nanotubes (aSWNTs) significantly inhibited METH self-administration, METH-induced conditioned place preference and METH- or cue-induced relapse to drug-seeking behaviour in mice. The use of aSWNTs alone did not significantly alter the mesolimbic dopamine system, whereas pretreatment with aSWNTs attenuated METH-induced increases in extracellular dopamine in the ventral striatum. Electrochemical assays suggest that aSWNTs facilitated dopamine oxidation. In addition, aSWNTs attenuated METH-induced increases in tyrosine hydroxylase or synaptic protein expression. These findings suggest that aSWNTs may have therapeutic effects for treatment of METH addiction by oxidation of METH-enhanced extracellular dopamine in the striatum.

6.188 13 nm Exciton Size in (6,5) Single-Wall Carbon Nanotubes
Mann, C. and Hertel, T.
Phys. Chem. Lett., ***7(12)****, 2276-2280 (2016)*

Electron–hole correlation lengths, also termed exciton size, for (6,5) single-wall carbon nanotubes (SWNTs) are determined using femtosecond time-resolved pump–probe spectroscopy. The phase space filling model is used to obtain the sizes of the first subband exciton in samples of isolated and of bundled SWNTs. The experiments indicate that the exciton size of (13 ± 3) nm is a factor of 6 higher than previous experimental estimates and theoretical predictions for vacuum suspended SWNTs. This surprising result may be attributed at least in part to the effect of the dielectric environment on exciton sizes and supports recent theoretical findings predicting that screening in SWNTs may enhance rather than reduce electron–hole interactions for separations larger than the tube diameter. Thereby, the work also points to the unique nature of screening and electronic correlations in one-dimensional semiconductors.

6.189 Toxicological Profiling of Highly Purified Metallic and Semiconducting Single-Walled Carbon Nanotubes in the Rodent Lung and E. coli
Wang, X., Mansukhani, N.D., Guiney, L.M., Lee, J-H., Li, R., Sun, B., Liao, Y-P., Chang, C.H., Ji, Z., Xia, T., Hersam, M.C. and Nel, A.E.
ACS Nano, ***10(6)****, 6008-6019 (2016)*

The electronic properties of single-walled carbon nanotubes (SWCNTs) are potentially useful for electronics, optics, and sensing applications. Depending on the chirality and diameter, individual SWCNTs can be classified as semiconducting (S-SWCNT) or metallic (M-SWCNT). From a biological perspective, the hazard profiling of purified metallic *versus* semiconducting SWCNTs has been pursued only in bacteria, with the conclusion that aggregated M-SWCNTs are more damaging to bacterial membranes than S-SWCNTs. However, no comparative studies have been performed in a mammalian system, where most toxicity studies have been undertaken using relatively crude SWCNTs that include a M:S mix at 1:2 ratio. In order to compare the toxicological impact of SWCNTs sorted to enrich them for each of the chirality on pulmonary cells and the intact lung, we used density gradient ultracentrifugation and extensive rinsing to prepare S- and M-SWCNTs that are >98% purified. *In vitro* screening showed that both tube variants trigger similar amounts of interleukin 1β (IL-1β) and transforming growth factor (TGF-β1) production in THP-1 and BEAS-2B cells, without cytotoxicity. Oropharyngeal aspiration confirmed that both SWCNT variants induce comparable fibrotic effects in the lung and abundance of IL-1β and TGF-β1 release in the bronchoalveolar lavage fluid. There was also no change in the morphology, membrane integrity, and viability of *E. coli*, in contradistinction to the previously published effects of aggregated tubes on the bacterial membrane. Collectively, these data indicate that the electronic properties and chirality do not independently impact SWCNT toxicological impact in the lung, which is of significance to the safety assessment and incremental use of purified tubes by industry.

6.190 Bioaccumulation of Multiwall Carbon Nanotubes in Tetrahymena thermophila by Direct Feeding or Trophic Transfer
Mortimer, M., Petersen, E.J., Buchholz, B.A., Orias, E. and Holden, P.A.
Environ. Sci. Technol., ***50(16)****, 8876-8885 (2016)*

Consumer goods contain multiwall carbon nanotubes (MWCNTs) that could be released during product life cycles into the environment, where their effects are uncertain. Here, we assessed MWCNT bioaccumulation in the protozoan *Tetrahymena thermophila* via trophic transfer from bacterial prey (*Pseudomonas aeruginosa*) versus direct uptake from growth media. The experiments were conducted using ^{14}C-labeled MWCNT (^{14}C-MWCNT) doses at or below 1 mg/L, which proved subtoxic since there were no adverse effects on the growth of the test organisms. A novel contribution of this study was the demonstration of the ability to quantify MWCNT bioaccumulation at low (sub µg/kg) concentrations accomplished by employing accelerator mass spectrometry (AMS). After the treatments with MWCNTs at nominal concentrations of 0.01 mg/L and 1 mg/L, *P. aeruginosa* adsorbed considerable amounts of MWCNTs: (0.18 ± 0.04) µg/mg and (21.9 ± 4.2) µg/mg bacterial dry mass, respectively. At the administered MWCNT dose of 0.3 mg/L, *T. thermophila* accumulated up to (0.86 ± 0.3) µg/mg and (3.4 ± 1.1) µg/mg dry mass by trophic transfer and direct uptake, respectively. Although MWCNTs did not biomagnify in the microbial food chain, MWCNTs bioaccumulated in the protozoan populations regardless of the feeding regime, which could make MWCNTs bioavailable for organisms at higher trophic levels.

6.191 Stable aqueous dispersions of optically and electronically active phosphorene
Kang, J., Wells, S., Wood, J.D., Lee, J-H., Liu, X., Ryder, C.R., Zhu, J., Guest, J.R., Husko, C.A. and Hersam, M.C.
PNAS, ***113(42)*** *11688-11693 (2016)*

Understanding and exploiting the remarkable optical and electronic properties of phosphorene require mass production methods that avoid chemical degradation. Although solution-based strategies have been developed for scalable exfoliation of black phosphorus, these techniques have thus far used anhydrous organic solvents in an effort to minimize exposure to known oxidants, but at the cost of limited exfoliation yield and flake size distribution. Here, we present an alternative phosphorene production method based on surfactant-assisted exfoliation and postprocessing of black phosphorus in deoxygenated water. From comprehensive microscopic and spectroscopic analysis, this approach is shown to yield phosphorene dispersions that are stable, highly concentrated, and comparable to micromechanically exfoliated phosphorene in structure and chemistry. Due to the high exfoliation efficiency of this process, the resulting phosphorene flakes are thinner than anhydrous organic solvent dispersions, thus allowing the observation of layer-dependent photoluminescence down to the monolayer limit. Furthermore, to demonstrate preservation of electronic properties following solution processing, the aqueous-exfoliated phosphorene flakes are used in field-effect transistors with high drive currents and current modulation ratios. Overall, this method enables the isolation and mass production of few-layer phosphorene, which will accelerate ongoing efforts to realize a diverse range of phosphorene-based applications.

6.192 Photoluminescence Dynamics of Aryl sp3 Defect States in Single-Walled Carbon Nanotubes
Hartmann, N.F., Velizhanin, K.A., Haroz, E.H., Kim, M., Ma, X., Wang, Y., Htoon, H. and Doorn, S.K.
ACS Nano, ***10(9)****, 8355-8365 (2016)*

Photoluminescent defect states introduced by sp^3 functionalization of semiconducting carbon nanotubes are rapidly emerging as important routes for boosting emission quantum yields and introducing new functionality. Knowledge of the relaxation dynamics of these states is required for understanding how functionalizing agents (molecular dopants) may be designed to access specific behaviors. We measure photoluminescence (PL) decay dynamics of sp^3 defect states introduced by aryl functionalization of the carbon nanotube surface. Results are given for five different nanotube chiralities, each doped with a range of aryl functionality. We find that the PL decays of these sp^3 defect states are biexponential, with both components relaxing on time scales of ∼100 ps. Exciton trapping at defects is found to increases PL lifetimes by a factor of 5–10, in comparison to those for the free exciton. A significant chirality dependence is observed in the decay times, ranging from 77 ps for (7,5) nanotubes to >600 ps for (5,4) structures. The strong correlation of time constants with emission energy indicates relaxation occurs *via* multiphonon decay processes, with close agreement to theoretical expectations. Variation of the aryl dopant further modulates decay times by 10–15%. The aryl defects also affect PL lifetimes of the free E_{11} exciton. Shortening of the E_{11} bright state lifetime as defect density increases provides further confirmation that defects act as exciton traps. A similar shortening of the E_{11} dark exciton lifetime is found as defect density increases, providing strong experimental evidence that dark excitons are also trapped at such defect sites.

6.193 Electron Excess Doping and Effective Schottky Barrier Reduction on the MoS2/h-BN Heterostructure

Joo, M-K., Moon, B.H., Ji, H., Han, G.H., Kim, H., Lee, G., Lim, S.C., Suh, D., and Lee, Y.H.
Nano Lett., ***16****, 6383-6389 (2016)*

Layered hexagonal boron nitride (*h*-BN) thin film is a dielectric that surpasses carrier mobility by reducing charge scattering with silicon oxide in diverse electronics formed with graphene and transition metal dichalcogenides. However, the *h*-BN effect on electron doping concentration and Schottky barrier is little known. Here, we report that use of *h*-BN thin film as a substrate for monolayer MoS_2 can induce $\sim 6.5 \times 10^{11}\ \mathrm{cm}^{-2}$ electron doping at room temperature which was determined using theoretical flat band model and interface trap density. The saturated excess electron concentration of MoS_2 on *h*-BN was found to be $\sim 5 \times 10^{13}\ \mathrm{cm}^{-2}$ at high temperature and was significantly reduced at low temperature. Further, the inserted *h*-BN enables us to reduce the Coulombic charge scattering in MoS_2/*h*-BN and lower the effective Schottky barrier height by a factor of 3, which gives rise to four times enhanced the field-effect carrier mobility and an emergence of metal–insulator transition at a much lower charge density of $\sim 1.0 \times 10^{12}\ \mathrm{cm}^{-2}$ ($T = 25$ K). The reduced effective Schottky barrier height in MoS_2/*h*-BN is attributed to the decreased effective work function of MoS_2 arisen from *h*-BN induced *n*-doping and the reduced effective metal work function due to dipole moments originated from fixed charges in SiO_2.

6.194 Substrate-Mediated Cooperative Adsorption of Sodium Cholate on (6,5) Single-Wall Carbon Nanotubes

Bergler, F.F., Stahl, S., Goy, A., Schöppler, F. and Hertel, T.
Langmuir, ***32****, 9598-9603 (2016)*

The interaction of sodium cholate (NaC) with (6,5) single-wall carbon nanotubes (SWNTs) is investigated using photoluminescence spectroscopy. Dilution of SWNT-NaC suspensions is accompanied by changes in the exciton PL quantum yield and peak emission energy. An abrupt change of the exciton emission peak energy at NaC concentrations between 10 and 14 mM indicates strongly cooperative formation of a micellar phase on (6,5) SWNT surfaces with a Hill coefficient of $n_H = 65 \pm 6$. This is in contrast to the formation of free NaC micelles with aggregation numbers of only about 4 and suggests that the cooperativity of NaC micelle formation on nanotube surfaces is strongly substrate-enhanced. The temperature dependence of this previously unobserved transition is used for a determination of $\Delta_{\mathrm{mic}}G^{\ominus}/(1 + \beta) = -(11.4 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$ which, for typical Na^+ counterion binding with $\beta \approx 0.2$, yields a free SWNT-NaC micellization enthalpy $\Delta_{\mathrm{mic}}G^{\ominus}$ of $-13.7\ \mathrm{kJ \cdot mol^{-1}}$.

6.195 A simple quantitative estimate of the number of functional groups on the surfaces of single-walled carbon nanotubes

Ngoc, Q.B.V., Choi, M-S. and Kim, W-J.
RSC Adv., ***6****, 6451-6458 (2016)*

We develop a quantitative analytical method to estimate the number of functional groups on single-walled carbon nanotube (SWNT) surfaces by simply measuring the Raman features of functionalized SWNTs. We use diazonium chemistry to attach functional groups to the SWNT surfaces and calculate the number of functional groups on the SWNTs by measuring their densities and using the analytical method developed in this study. We successfully establish a linear relationship between the independently estimated number of functional groups per carbon atom and the area ratio of the disorder mode (D peak, 1289 cm^{-1}) to the tangential mode (G peak, 1582 cm^{-1}) from the Raman measurements. From this study, we find that the injected reagents do not completely react with SWNT after 0.0263 functional groups per carbon atom are already attached to SWNT surfaces, ***e.g.***, 2.354 functional groups per nm (6, 5) of SWNT, therefore above this range, there is no linear relationship between the number of functional groups on SWNTs estimated from injected reagent concentration and the D to G area ratio ($\boldsymbol{A}_{D/G}$) of the Raman features. However, the number of functional groups per carbon atom ($\boldsymbol{n}_f$) estimated using the analytical method developed in this study linearly depends on the area ratio of D to G peaks of the Raman spectrum even above this range ($\boldsymbol{n}_\mathrm{f} = 0.02\boldsymbol{A}_\mathrm{D/G}$), therefore this simple and quick estimation scheme can provide an analytical basis for a variety of SWNT applications. We take into account the decrease of the number of surfactants by the coverage of functional groups on SWNTs in this scheme, and also verified that this relation is valid irrespective of SWNT diameter distributions.

6.196 Plasmonic nanostructures for surface enhanced spectroscopic methods

Jahn, M., Patze, S., Hidi, I.J., Knipper, R., Radu, A.I., Mühlig, A., Yüksel, S., Peksa, V., Weber, K., Mayerhöfer, T., Cialla-May, D. and Popp, J.
*Analyst, **141**, 756-793 (2016)*

A comprehensive review of theoretical approaches to simulate plasmonic-active metallic nano-arrangements is given. Further, various fabrication methods based on bottom-up, self-organization and top-down techniques are introduced. Here, analytical approaches are discussed to investigate the optical properties of isotropic and non-magnetic spherical or spheroidal particles. Furthermore, numerical methods are introduced to research complex shaped structures. A huge variety of fabrication methods are reviewed, ***e.g.*** bottom-up preparation strategies for plasmonic nanostructures to generate metal colloids and core–shell particles as well as complex-shaped structures, self-organization as well as template-based methods and finally, top-down processes, ***e.g.*** electron beam lithography and its variants as well as nanoimprinting. The review article is aimed at beginners in the field of surface enhanced spectroscopy (SES) techniques and readers who have a general interest in theoretical modelling of plasmonic substrates for SES applications as well as in the fabrication of the desired structures based on methods of the current state of the art.

6.197 (n,m)-Specific Absorption Cross Sections of Single-Walled Carbon Nanotubes Measured by Variance Spectroscopy

Sanchez, S.R., bachilo, S.M., kadria-Vili, Y., Lin, C-W. and Weisman, R.B.
*Nano Lett., **16(11)**, 6903-6909 (2016)*

A new method based on variance spectroscopy has enabled the determination of absolute absorption cross sections for the first electronic transition of 12 (*n*,*m*) structural species of semiconducting single-walled carbon nanotubes (SWCNTs). Spectrally resolved measurements of fluorescence variance in dilute bulk samples provided particle number concentrations of specific SWCNT species. These values were converted to carbon concentrations and correlated with resonant components in the absorbance spectrum to deduce (*n*,*m*)-specific absorption cross sections (absorptivities) for nanotubes ranging in diameter from 0.69 to 1.03 nm. The measured cross sections per atom tend to vary inversely with nanotube diameter and are slightly greater for structures of *mod 1* type than for *mod 2*. Directly measured and extrapolated values are now available to support quantitative analysis of SWCNT samples through absorption spectroscopy.

6.198 Layer-by-Layer Sorting of Rhenium Disulfide via High-Density Isopycnic Density Gradient Ultracentrifugation

Kang, J., Sangwan, V.K., Wood, J.D., Liu, X., balla, I., Lam, D. and hersam, M.C.
*Nano Lett., **16(11)**, 7216-7223 (2016)*

Isopycnic density gradient ultracentrifugation (iDGU) has been widely applied to sort nanomaterials by their physical and electronic structure. However, the commonly used density-gradient medium iodixanol has a finite maximum buoyant density that prevents the use of iDGU for high-density nanomaterials. Here, we overcome this limit by adding cesium chloride (CsCl) to iodixanol, thus increasing its maximum buoyant density to the point where the high-density two-dimensional nanomaterial rhenium disulfide (ReS_2) can be sorted in a layer-by-layer manner with iDGU. The resulting aqueous ReS_2 dispersions show photoluminescence at ∼1.5 eV, which is consistent with its direct bandgap semiconductor electronic structure. Furthermore, photocurrent measurements on thin films formed from solution-processed ReS_2 show a spectral response that is consistent with optical absorbance and photoluminescence data. In addition to providing a pathway for effective solution processing of ReS_2, this work establishes a general methodology for sorting high-density nanomaterials via iDGU.

6.199 Intramolecular p-i-n junction photovoltaic device based on selectively doped carbon nanotubes

Chen, C., Song, C., Yang, J., Chen, D., Zhu, W., Liao, C., Dong, X., Liu, X., Wei, L., Hu, N., He, R. and

Zhang, Y.
*Nano Energy, **32**, 280-286 (2017)*

Photovoltaic devices show promising applications in detection and energy fields as well as in next-generation optoelectronic circuits. The use of the ideal photosensitive material and device design are critical for achieving a high-performance photovoltaic device. Here, an intramolecular p-i-n junction photovoltaic device based on selectively doped carbon nanotubes is investigated. In this kind of device, the opposite ends of an individual single-walled carbon nanotube (SWCNT) channel are doped selectively by triethyloxonium hexachloroantimonate (OA) and polyethylene imine (PEI) to obtain stable p- and n- type SWCNT segments respectively, while the middle segment of the SWCNT is kept intrinsic, causing the formation of an intra-tube p-i-n junction for the efficient separation of photogenerated electron-hole pairs. The optical-absorption and electrical testing demonstrate that the OA and PEI can dope the SWCNTs into the stable *p-* and *n-* types, respectively. In the dark, the prepared p-i-n junction device behaves as a diode with a high rectification ratio $>10^3$ that can be tuned by the gate voltage. Under a 1550-nm monochromatic illumination, the device exhibits a good photovoltaic effect with a large open-circuit voltage of 0.41 V and an external power conversion efficiency of ~4.2%. The quantum efficiency of the device is estimated to be as high as ~73%.

6.200 Assessing Inhomogeneity in Sorted Samples of Single-Walled Carbon Nanotubes through Fluorescence and Variance Spectroscopy
Kadria-Vili, Y., Sanchez, S.R., bachilo, WS.M. and Weisman, R.B.
*ECS J. Solid State Sci. Technol., **6(6)**, M3097-M3102 (2017)*

Detailed spectroscopic analysis has been used to study the homogeneity of single-walled carbon nanotube fractions carefully prepared by nonlinear density gradient ultracentrifugation sorting. Two distinct colored bands containing (6,5) enantiomers were subdivided into several extracted fractions that were separately diluted with sodium cholate surfactant and characterized by fluorescence, absorption, and variance spectroscopy. Values were measured for emission and absorption peak positions, Stokes shifts, emission peak widths, and emissive quantum yields. In addition, variance data were used to find relative emission per nanotube and to plot covariance slices representing homogeneous emission spectra. It was found that emission from SWCNTs within the upper enantiomer band shifts to shorter wavelengths with increasing depth in the centrifuge tube. In the lower enantiomer band such spectral shifts were not observed, but the emissive quantum yields decreased with depth. Variance analysis revealed spectral differences among SWCNTs within the same fraction of the same band. It is concluded that current methods for density gradient ultracentrifugation sorting produce samples that retain measurable structural and spectral inhomogeneities.

6.201 Separation of double-wall carbon nanotubes by electronic type and diameter
Streit, J.K., Lam, S., Piao, L.Y., Walker, A.R.H., Fagan, J.A. and Zheng, M.
*Nanoscale, **9**, 2531-2540 (2017)*

We introduce a new procedure for the efficient isolation and subsequent separation of double-wall carbon nanotubes (DWCNTs). A simplified, rate zonal ultracentrifugation (RZU) process is first applied to obtain samples of highly-enriched DWCNTs from a raw carbon nanotube material that has both single- and double-wall carbon nanotubes. Using this purified DWCNT suspension, we demonstrate for the first time that DWCNTs can be further processed using aqueous two-phase extraction (ATPE) for sequential separation by electronic structure and diameter. Additionally, we introduce analytical ultracentrifugation (AUC) as a new method for DWCNT characterization to assess DWCNT purity in separated samples. Results from AUC analysis are utilized to compare two DWCNT separation schemes. We find that RZU processing followed by sequential bandgap and diameter sorting ***via*** ATPE provides samples of highest DWCNT enrichment, whereas single-step redox sorting of the same raw material through ATPE yields SWCNT/DWCNT mixtures of similar diameter and electronic character. The presented methods offer significant advancement in DWCNT processing and separation while also providing a promising alternative for DWCNT sample analysis.

6.202 K-Channel: A Multifunctional Architecture for Dynamically Reconfigurable Sample Processing in Droplet Microfluidics
Doonan, S.R. and Bailey, R.C:
*Anal. Chem., **89(7)**, 4091-4099 (2017)*

By rapidly creating libraries of thousands of unique, miniaturized reactors, droplet microfluidics provides a powerful method for automating high-throughput chemical analysis. In order to engineer in-droplet assays, microfluidic devices must add reagents into droplets, remove fluid from droplets, and perform other necessary operations, each typically provided by a unique, specialized geometry. Unfortunately, modifying device performance or changing operations usually requires re-engineering the device among these specialized geometries, a time-consuming and costly process when optimizing in-droplet assays. To address this challenge in implementing droplet chemistry, we have developed the "K-channel," which couples a cross-channel flow to the segmented droplet flow to enable a range of operations on passing droplets. K-channels perform reagent injection (0–100% of droplet volume), fluid extraction (0–50% of droplet volume), and droplet splitting (1:1–1:5 daughter droplet ratio). Instead of modifying device dimensions or channel configuration, adjusting external conditions, such as applied pressure and electric field, selects the K-channel process and tunes its magnitude. Finally, interfacing a device-embedded magnet allows selective capture of 96% of droplet-encapsulated superparamagnetic beads during 1:1 droplet splitting events at ~400 Hz. Addition of a second K-channel for injection (after the droplet splitting K-channel) enables integrated washing of magnetic beads within rapidly moving droplets. Ultimately, the K-channel provides an exciting opportunity to perform many useful droplet operations across a range of magnitudes without requiring architectural modifications. Therefore, we envision the K-channel as a versatile, easy to use microfluidic component enabling diverse, in-droplet (bio) chemical manipulations.

6.203 Colloidal 2D nanosheets of MoS2 and other transition metal dichalcogenides through liquid-phase exfoliation

Grayfer, E.D., Kozlova, M.N. and Fedorov, V.E.
Adv. Colloid Interface Sci., ***245***, *40-61 (2017)*

This review focuses on the exfoliation of transition metal dichalcogenides MQ_2 (TMD, M = Mo, W, etc., Q = S, Se, Te) in liquid media, leading to the formation of 2D nanosheets dispersed in colloids. Nowadays, colloidal dispersions of MoS_2, $MoSe_2$, WS_2 and other related materials are considered for a wide range of applications, including electronic and optoelectronic devices, energy storage and conversion, sensors for gases, catalysts and catalyst supports, biomedicine, etc. We address various methods developed so far for transferring these materials from bulk to nanoscale thickness, and discuss their stabilization and factors influencing it. Long-time known exfoliation through Li intercalation has received renewed attention in recent years, and is recognized as a method yielding highest dispersed concentrations of single-layer MoS_2 and related materials. Latest trends in the intercalation/exfoliation approach include electrochemical lithium intercalation, experimenting with various intercalating agents, multi-step intercalation, etc. On the other hand, direct sonication in solvents is a much simpler technique that allows one to avoid dangerous reagents, long reaction times and purifying steps. The influence of the solvent characteristics on the colloid formation was closely investigated in numerous recent studies. Moreover, it is being recognized that, besides solvent properties, sonication parameters and solvent transformations may affect the process in a crucial way. The latest data on the interaction of MoS_2 with solvents evidence that not only solution thermodynamics should be employed to understand the formation and stabilization of such colloids, but also general and organic chemistry. It appears that due to the sonolysis of the solvents and cutting of the MoS_2 layers in various directions, the reactive edges of the colloidal nanosheets may bear various functionalities, which participate in their stabilization in the colloidal state. In most cases, direct exfoliation of MQ_2 into colloidal nanosheets is conducted in organic solvents, while a small amount of works report low-concentrated colloids in pure water. To improve the dispersion abilities of transition metal dichalcogenides in water, various stabilizers are often introduced into the reaction media, and their interactions with nanosheets play an important role in the stabilization of the dispersions. Surfactants, polymers and biomolecules usually interact with transition metal dichalcogenide nanosheets through non-covalent mechanisms, similarly to the cases of graphene and carbon nanotubes. Finally, we survey covalent chemical modification of colloidal MQ_2 nanosheets, a special and different approach, consisting in the functionalization of MQ_2 surfaces with help of thiol chemistry, interaction with electrophiles, or formation of inorganic coordination complexes. The intentional design of surface chemistry of the nanosheets is a very promising way to control their solubility, compatibility with other moieties and incorporation into hybrid structures. Although the scope of the present review is limited to transition metal dichalcogenides, the dispersion in colloids of other chalcogenides (such as NbS_3, VS_4, Mo_2S_3, etc.) in many ways follows similar trends. We conclude the review by discussing current challenges in the area of exfoliation of MoS_2 and its related materials.

6.204 Solution-Based Processing of Monodisperse Two-Dimensional Nanomaterials
Kang, J., Sangwan, V.K., Wood, J.D. and Hersam, M.C.
Acc. Chem. Res., ***50(4)****, 943-951 (2017)*

Exfoliation of single-layer graphene from bulk graphite and the subsequent discovery of exotic physics and emergent phenomena in the atomically thin limit has motivated the isolation of other two-dimensional (2D) layered nanomaterials. Early work on isolated 2D nanomaterial flakes has revealed a broad range of unique physical and chemical properties with potential utility in diverse applications. For example, the electronic and optical properties of 2D nanomaterials depend strongly on atomic-scale variations in thickness, enabling enhanced performance in optoelectronic technologies such as light emitters, photodetectors, and photovoltaics. Much of the initial research on 2D nanomaterials has relied on micromechanical exfoliation, which yields high-quality 2D nanomaterial flakes that are suitable for fundamental studies but possesses limited scalability for real-world applications. In an effort to overcome this limitation, solution-processing methods for isolating large quantities of 2D nanomaterials have emerged. Importantly, solution processing results in 2D nanomaterial dispersions that are amenable to roll-to-roll fabrication methods that underlie lost-cost manufacturing of thin-film transistors, transparent conductors, energy storage devices, and solar cells. Despite these advantages, solution-based exfoliation methods typically lack control over the lateral size and thickness of the resulting 2D nanomaterial flakes, resulting in polydisperse dispersions with heterogeneous properties. Therefore, post-exfoliation separation techniques are needed to achieve 2D nanomaterial dispersions with monodispersity in lateral size, thickness, and properties.

In this Account, we survey the latest developments in solution-based separation methods that aim to produce monodisperse dispersions and thin films of emerging 2D nanomaterials such as graphene, boron nitride, transition metal dichalcogenides, and black phosphorus. First, we motivate the need for precise thickness control in 2D nanomaterials by reviewing thickness-dependent physical properties. Then we present a succinct survey of solution-based exfoliation methods that yield 2D nanomaterial dispersions in organic solvents and aqueous media. The Account subsequently focuses on separation methods, including a critical analysis of their relative strengths and weaknesses for 2D nanomaterials with different buoyant densities, van der Waals interactions, and chemical reactivities. Specifically, we evaluate sedimentation-based density gradient ultracentrifugation (sDGU) and isopycnic DGU (iDGU) for post-exfoliation 2D nanomaterial dispersion separation. The comparative advantages of sedimentation and isopycnic methods are presented in both aqueous and nonaqueous media for 2D nanomaterials with varying degrees of chemical reactivity. Finally, we survey methods for forming homogeneous thin films from 2D nanomaterial dispersions and emerging technologies that are likely to benefit from these structures. Overall, this Account provides not only an overview of the present state-of-the-art but also a forward-looking vision for the field of solution-processed monodisperse 2D nanomaterials.

6.205 Conjugates between photosystem I and a carbon nanotube for a photoresponse device
Nii, D., Miyachi, M., Shimada, Y., Nozawa, Y., Ito, M., Homma, Y., Ikehira, S., Yamanoi, Y., Nishihara, H. and Tomo, T.
Photosynth. Res., ***133(1-3)****, 155-162 (2017)*

Photosystem I (PS I) is a large pigment–protein complex embedded in the thylakoid membranes that performs light-driven electron transfer across the thylakoid membrane. Carbon nanotubes exhibit excellent electrical conductivities and excellent strength and stiffness. In this study, we generated PSI–carbon nanotube conjugates dispersed in a solution aimed at application in artificial photosynthesis. PS I complexes in which a carbon nanotube binding peptide was introduced into the middle of the PsaE subunit were conjugated on a single-walled carbon nanotube, orienting the electron acceptor side to the nanotube. Spectral and photoluminescence analysis showed that the PS I is bound to a single-walled carbon nanotube, which was confirmed by transmission electron microscopy. Photocurrent observation proved that the photoexcited electron originated from PSI and transferred to the carbon nanotube with light irradiation, which also confirmed its orientated conjugation. The PS I–carbon nanotube conjugate will be a useful nano-optoelectronic device for the development of artificial systems.

6.206 Edge Delamination of Monolayer Transition Metal Dichalcogenides
Ly, T.H., Yun, S.J., Thi, Q.H. and Zhao, J.
ACS Nano, ***11(7)****, 7534-7541 (2017)*

Delamination of thin films from the supportive substrates is a critical issue within the thin film industry. The emergent two-dimensional, atomic layered materials, including transition metal dichalcogenides, are highly flexible; thus buckles and wrinkles can be easily generated and play vital roles in the corresponding physical properties. Here we introduce one kind of patterned buckling behavior caused by the delamination from a substrate initiated at the edges of the chemical vapor deposition synthesized monolayer transition metal dichalcogenides, led by thermal expansion mismatch. The atomic force microscopy and optical characterizations clearly showed the puckered structures associated with the strain, whereas the transmission electron microscopy revealed the special sawtooth-shaped edges, which break the geometrical symmetry for the buckling behavior of hexagonal samples. The condition of the edge delamination is in accordance with the fracture behavior of thin film interfaces. This edge delamination and buckling process is universal for most ultrathin two-dimensional materials, which requires more attention in various future applications.

6.207 3D-printed smartphone-based point of care tool for fluorescence- and magnetophoresis-based cytometry
Knowlton, S., Joshi, A., Syrrist, P., Coskun, A.F. and Tasoglu, S.
Lab on a Chip, ***17****, 2839-2851 (2017)*

In developing countries, there are often limited resources available to provide important medical diagnostics, which severely limits our ability to diagnose conditions and administer proper treatment, leading to high mortality rates for treatable conditions. Here, we propose a multiplex tool capable of density-based cell sorting *via* magnetic focusing in parallel with fluorescence imaging to provide highly specific clinical assays. While many cell sorting techniques and fluorescence microscopes generally are costly and require extensive user training, limiting accessibility and usability in developing countries, this device is compact, low-cost, and portable. The device can separate cells on the basis of density, which can be used to identify cell type and cell activity, and image the cells in either brightfield, darkfield, or fluorescent imaging modes using the built-in smartphone camera. The combination of these two powerful and versatile techniques – magnetic focusing and fluorescence imaging – will make this platform broadly applicable to a range of biomedical assays. Clinical applications include cell cytometry and immunocytochemistry-based assays in limited-resource settings, which can ultimately help to improve worldwide accessibility to medical diagnostics.

6.208 Skewness Analysis in Variance Spectroscopy Measures Nanoparticle Individualization
Sanchez, S.R., Bachilo, S.M., Kadria-Vili, Y. and Weisman, R.B.
J. Phys. Chem. Lett., ***8****, 2924-2929 (2017)*

An important enabling step in nanoparticle studies is the sorting of heterogeneous mixtures to prepare structurally homogeneous samples. It is also necessary to detect and monitor aggregation of the individual nanoparticles. Although variance spectroscopy provides a simple optical method for finding low concentrations of heteroaggregates in samples such as single-walled carbon nanotube dispersions, it cannot detect the homoaggregates that are relevant for well-sorted samples. Here we demonstrate that variance spectral data can be further analyzed to find third moments of intensity distributions (skewness), which reveal the presence of emissive homoaggregates. Using experimental measurements on variously processed nanotube dispersions, we deduce a simple numerical standard for recognizing aggregation in the highly sorted samples that are increasingly available to nanoscience researchers.

6.209 A Low Energy Route to DNA-Wrapped Carbon Nanotubes via Replacement of Bile Salt Surfactants
Streit, J.K., Fagan, J.A. and Zheng, M.
Anal. Chem., ***89****, 10496-1+503 (2017)*

DNA-wrapped carbon nanotubes are a class of bionano hybrid molecules that have enabled carbon nanotube sorting, controlled assembly, and biosensing and bioimaging applications. The current method of synthesizing these hybrids via direct sonication of DNA/nanotube mixtures is time-consuming and not suitable for high-throughput synthesis and combinatorial sequence screening. Additionally, the direct sonication method does not make use of nanotubes presorted by extensively developed surfactant-based methods, is not effective for large diameter (>1 nm) tubes, and cannot maintain secondary and tertiary structural and functional domains present in certain DNA sequences. Here, we report a simple, quick, and robust process to produce DNA-wrapped carbon nanotube hybrids with nanotubes of broad diameter range and DNA of arbitrary sequence. This is accomplished by exchanging strong binding bile salt surfactant coating with DNA in methanol/water mixed solvent and subsequent precipitation with isopropyl alcohol.

The exchange process can be completed within 10 min and converts over 90% nanotubes into the DNA wrapped form. Applying the exchange process to nanotubes presorted by surfactant-based methods, we show that the resulting DNA-wrapped carbon nanotubes can be further sorted to produce nanotubes with defined handedness, helicity, and endohedral filling. The exchange method greatly expands the structural and functional variety of DNA-wrapped carbon nanotubes and opens possibilities for DNA-directed assembly of structurally sorted nanotubes and high-throughput screening of properties that are controlled by the wrapping DNA sequences.

6.210 Determination of the Absolute Enantiomeric Excess of the Carbon Nanotube Ensemble by Symmetry Breaking Using the Optical Titration Method
Sim, J., Kim, S., Jang, M., Park, M., Oh, H. and Ju, S-Y.
*Langmuir, **33**, 11000-11109 (2017)*

Symmetry breaking of single-walled carbon nanotubes (SWNTs) has profound effects on their optoelectronic properties that are essential for fundamental study and applications. Here, we show that isomeric SWNTs that exhibit identical photoluminescence (PL) undergo symmetry breaking by flavin mononucleotide (FMN) and exhibit dual PLs and different binding affinities (K_a). Increasing the FMN concentration leads to systematic PL shifts of SWNTs according to structural modality and handedness due to symmetry breaking. Density gradient ultracentrifugation using a FMN–SWNT dispersion displays PL shifts and different densities according to SWNT handedness. Using the optical titration method to determine the PL-based K_a of SWNTs against an achiral surfactant as a titrant, left- and right-handed SWNTs display two-step PL inflection corresponding to respective K_a values with FMN, which leads to the determination of the enantiomeric excess (ee) of the SWNT ensemble that was confirmed by circular dichroism measurement. Decreasing the FMN concentration for the SWNT dispersion leads to enantiomeric selection of SWNTs. The titration-based ee determination of the widely used sodium cholate-based SWNT dispersion was also demonstrated by using FMN as a cosurfactant.

6.211 Separation of Nickelocene-Filled Single-Walled Carbon Nanotubes by Conductivity Type and Diameter
Kharlamova, M.V., Kramberger, C., Yanagi, K., Sauer, M., Saito, T. and Pichler, T.
*Phys. Status Solidi B., **254**, 1700178 (2017)*

We have performed the separation of nickelocene-filled single-walled carbon nanotubes (SWCNTs) with a mean diameter of 1.7 nm by conductivity type and diameter using density gradient ultracentrifugation. The separated nanotube fractions were characterized by optical absorption spectroscopy (OAS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The OAS investigation of the separated samples showed the absence of optical absorption bands of semiconducting tubes in metallic sample and *vice versa*, which proved a high purity of the nanotube fractions. The XPS investigation of the separated samples showed different positions, spectral widths and asymmetry of the C 1*s* core level spectra. The multifrequency Raman spectroscopy investigation of the separated samples allowed performing an analysis of the diameter range of nanotubes. The demonstrated successful separation of the filled SWCNTs by conductivity type and diameter enables demanding applications of ultra pure SWCNTs with tailored properties.