SWNT alignment and placement by meniscus action. Design In this technique, we form a meniscus between two surfaces with an aqueous solution of surfactant-coated SWNTs. We employ a glass capillary array as the top surface, filling them with SWNT solution. After meniscus formation, we drag the meniscus across the substrate with a translation platform, aligning SWNTs on the surface. Results On hydrophilic surfaces like SiO2 and Si3N4, we note that SWNT alignment occurs parallel to the drag direction. With constant timestep Monte Carlo simulation, we find that alignment occurs through mechanical torque by surface roughness pinning. Atomic force microscopy (AFM) analysis shows that for SiO2 the SWNTs align at angles 7.99±10.92°, 5.80±12.97°, and 5.35±17.2° for meniscus velocities of 203, 272, and 543 μm/s, respectively, indicating good alignment in the drag direction. On hydrophobic surfaces like H-Si(111) and positive-tone photoresist, SWNTs longer than 800 nm align perpendicular to the drag direction. We attribute this to hydrophilic-hydrophobic surface energy minimization. In our process, we can place SWNTs in densities of up to ~30 SWNTs/μm², with the density exponentially dependent on the number of meniscus passes. Conclusion Understanding the SWNT interaction on hydrophobic and hydrophilic surfaces allows wafer-scale control of SWNT alignment and placement. We are developing SWNT crossbar memory structures and field-effect transistors with the technique.

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Selective dispersion of carbon nanotubes in polyfluorene solutions studied by optical spectroscopy and molecular dynamics

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The preparation of single walled carbon nanotubes (SWNT) dispersions in several solvents, and using several encapsulating agents, has allowed the study of the properties of individual nanotubes. These dispersions can further be used to separate suspended SWNT by diameter, for instance by ultracentrifugation in a density gradient. It was recently demonstrated that conjugated polymers from the polyfluorene family are able to wrap selectively in nanotubes having high chiral angles, especially when toluene is used as solvent. In the present work we report on the photophysical properties of SWNT suspensions in toluene solutions of poly[9,9-dioctylfluorenyl-2,7-diyl](PFO). Steady-state and time-resolved photoluminescence spectroscopy in the near infrared and visible spectral regions are used to study the interaction of the dispersed SWNT and the wrapped polymer. Molecular dynamics simulations of the PFO-wrapped nanotubes in toluene were carried out to assess the conformation of these systems. The simulated fluorescence spectra in the visible region were obtained by the quantum chemical ZINDO-CI method, using a sampling of structures obtained from the dynamics trajectories. We were able to show that PFO chains adsorb in SWNT surface in basically two conformations. The polymer chains are either aligned along the nanotube axis, where chirality has a minimal effect, or the polymers form helical structures, where a preference for high chiral angles is evidenced. Toluene affects the polymer structure favoring the helical conformation. The most stable hybrid system is the PFO-wrapped (8,6) nanotube, in agreement with the experimentally observed selectivity.

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Surface modification of MWCNTs in the afterglow of a cold atmospheric plasma jet

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Improving the properties of polymers by the addition of carbon nanotubes (CNTs) requires an efficient dispersion and alignment of the CNTs in and interfacial adhesion to the matrix. Surface modification of CNTs is one possibility to influence these three factors. Oxidative functionalization is frequently the first step for further chemical surface modification of CNTs and is typically performed by using strong inorganic acids. We report on the development of a plasma process that modifies the CNT surface in the relaxing afterglow of a non-thermal atmospheric pressure plasma jet. The plasma process can be easily combined with the industrial CVD synthesis of MWCNTs and reduces drastically the amount of waste typically encountered in acidic treatments. In addition, the process requires very short reaction times (milliseconds) and can be scaled up for high throughput (several kg/day). As XPS analysis shows, the plasma treatment incorporates about 8 at% of oxygen into the CNT surface. The formation of different oxygen-containing functional groups is observed, while the degree of functionalization can be controlled by the treatment time. TGA and Raman spectroscopy are used to study the change of CNT structure and the formation of defects. Both seem to be only slightly affected by the plasma treatment. The improvements in dispersability are shown by contact angle and sedimentation measurements. The improvements in matrix adhesion are studied by characterizing CNT/epoxy nanocomposites. These results indicate that the atmospheric plasma process can provide an attractive alternative to wet chemical processing.

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Carbon nanotubes-photosystem I and –hydrogenase biohybrids for energy devices

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Biohybrids take advantage of the evolutionarily optimized function of enzymes in the design of efficient devices for applications such as diagnostics, catalysis or self-assembly. Focusing on alternative energy devices, we chose two redox enzymes: photosystem I (PSI) for photovoltaic cells and hydrogenases for hydrogen fuel cells. The proteins were coupled to carbon nanotubes (CNT)s as nanoelectrodes to collect electrons. PSI is one of the main light harvesting complexes involved in photosynthesis in plants, algae and cyanobacteria. We first incorporated PSI from cyanobacteria into photosensitive CNT transistors to test their stability in electronic, dry devices. The phototransistors showed good robustness and a high sensitivity to light (<10mW/cm²). Covalent coupling of PSI onto CNTs is now under way to control the protein orientation and optimize electron transfer to the nanotube for photocurrent collection. Hydrogenases catalyse hydrogen oxidation in numerous bacteria with a very high activity in solution, which makes it worth testing them as an alternative to platinum catalysts. Covalently coupled hydrogenase-CNT biohybrids were prepared and characterized by AFM, XPS and cyclic voltammetry. The proteins were coupled through their carboxyl groups to allow direct electron transfer from their active site to the CNT. Integration on fuel cell Gas Diffusion Layer is under way to evaluate their catalytic efficiency in a realistic fuel cell system. In spite of their notorious fragility, the proteins are shown to keep their functionalities once integrated with CNTs and they could provide interesting components for energy production.

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Designing Density Gradient Ultracentrifugation Recipes for Desired Separation of Single-Walled Carbon Nanotubes

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The density gradient ultracentrifugation (DGU) method adapted to SWNTs is considered one of the most promising and effective for achieving good SWNT selectivity. We used this method to sort surfactant-dispersed single-walled carbon nanotubes (SWNTs) by their diameters or electronic types. As to diameter separation, a controllable multicolored expansion was obtained in which the average SWNT diameter increased in each successive colored layer. By adjusting the concentration and types of surfactants, as well as choosing a suitable density gradient profile, this expansion can be further expanded or contracted. Furthermore, tuning the surfactant concentrations can result in electronic type separation, or even a simultaneous isolation of (6,5) nanotubes in addition to separation by electronic type. Investigating the experimental conditions yielding these different results allowed us to investigate the mechanism behind this surfactant-assisted separation. We find that the addition of bile salts such as sodium deoxycholate (DOC) or sodium cholate (SC) are used in combination with sodium dodecyl sulfate (SDS), their hydration conditions,activation energies with SWNTs, and surrounding environments will determine how they adsorb onto the nanotube surfaces, which will further determine the density of the formed surfactant-SWNT micelles. This model can not only explain these results but also make predictions based on the DGU starting recipes.

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Molecularly engineered “peapods”: tuning the electro-optical response of SWNTs

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Despite carbon nanotubes are characterized by high electrical and thermal conductivity, they do not absorb light in the visible region (350-800 nm) extensively. In order to exploit single-walled carbon nanotubes (SWNTs) as functional materials in such application as photoelectrochemical cells, photodetectors and organic light-emitting diodes, it is necessary to design supramolecular structures responsive to visible light. Indeed, the engineering of the properties of carbon nanotube is possible by encapsulating organic photoactive molecules to obtain supramolecular entities, usually referred as “peapods”, that combine the electrical and thermal conductivity of SWNTs and the optical properties of the guest. In this work we encapsulated suitable polycyclic aromatic hydrocarbons (such as pyrene and coronene) in shortened purified SWNTs by nano-extraction, vapor-phase technique and using supercritical carbon dioxide. We studied the novel peapods by means of steady-state and time-resolved UV-vis spectroscopy, Raman spectroscopy, thermogravimetric analysis, and HRTEM. All the results point out that we did succeed in the encapsulation processes. Moreover, the spectral fingerprints of the peapods are markedly different from those of the isolated compounds, suggesting an efficient guest-host coupling to form interacting supramolecular assemblies. In conclusion, we were able to design, synthesize and characterize novel SWNT-based peapods to be incorporated in functional materials exhibiting improved electro-optical response over the visible spectrum.

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Properties of Phenyl- and Methylene- Functionalized Carbon Nanotubes

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Covalent functionalization of carbon nanotubes (CNT) appears nowadays as one of the most important chemical tools enabling the processing, manipulation and assembly of CNT from solution. However, little is known about the effect of the chemical reaction on the electronic properties of the CNTs and about the thermal stability of the functionalized derivatives. Here, we compare the repercussions and the stability of monovalent and bivalent adducts grafted on CNT. The first case studied involves phenyl adducts attached by a covalent bonding to a single site of the sidewall. The second case involves methylene adducts that bridge two carbon sites of CNT. We analyzed the decrease of conductivity and light absorption induced by these functionalizations. We also determined the thermal stability of the CNT derivatives using temperature desorption spectroscopy (TDS). The results show that the methylene moities are detached from the sidewalls at ~500 K while, under the same experimental conditions, the phenyls are removed at ~600 K. In addition, we observed no influence from the helicity and diameter distributions of the different samples of CNT studied (mean diameter: 0,81 nm versus 0,93 nm). Moreover we proved that the detachment of the phenyl adducts occurs through a phenyl-phenyl coupling at the sidewall. The advantages of the covalent functionalization for applications in nanoelectronics will be discussed.

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High-Yield Purification of Double-Walled Carbon Nanotubes for Optical Modulation

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Transparent and conductive thin films were prepared from purified double-walled carbon nanotubes (DWNTs). Purification of the as-received soot was achieved in a two-step process: The key step is a high temperature endothermic oxidation in a pure CO2 gas flow according to the Boudouard reaction which is combined with a standard reflux in concentrated nitric acid. This treatment provides fast oxidation of amorphous carbon and removal of other impurities without affecting the carbon nanotubes. Parameterization of the high temperature reaction was explored to selectively remove single-wall NT and highly-damaged DWNTs. AFM, TEM, XPS, UV-vis-IR absorption and Raman spectroscopy analyses reveal that the films are composed of high quality DWNTs (micrometer long nanotubes, very low impurity concentration, high Raman IG/ID ratios). The films were then used as electrodes for light modulating devices using a polyelectrolyte to induce charge injection doping. Those devices give an effective modulation of the absorption of the first optical transition of the semiconducting outer walls.

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Biotin molecules on the surface of nitrogen-doped carbon nanotubes enhance the anchoring and formation Ag nanoparticles

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A simple, efficient and innovative method for anchoring Ag nanoparticles on the surface of nitrogen-doped multi-walled carbon nanotubes (CNx-MWNTs) is reported. The process involves the attachment of an important bio-molecule, biotin