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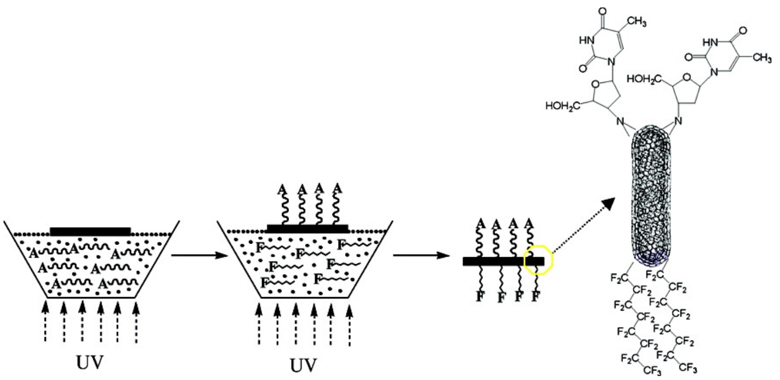

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Asymmetric End-Functionalization of Multi-Walled Carbon Nanotubes

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The use of carbon nanotubes for many practical applications often requires a precision loading of individual nanotubes into various functional structures and devices. In this regard, the synthesis of aligned and/or micropatterned carbon nanotubes has played a critical role in facilitating the integration of carbon nanotubes into certain useful devices (e.g., electron emitters, transistors, etc.).[1] However, a more general self-assembling approach would allow the construction of individual nanotubes into various functional structures with a molecular precision. For this purpose, the site-selective chemical modification of carbon nanotubes is essential. Recently, judicious application of site-selective reactions to nonaligned and aligned carbon nanotubes for selectively modifying nanotube tips, inner walls, and/or outer walls has opened a rich field of carbon nanotube chemistry.[2] It has been demonstrated that the sidewalls of carbon nanotubes are rather unreactive due to the seamless arrangement of hexagon rings without any dangling bonds, and that the fullerene-like tips of carbon nanotubes are more reactive than their sidewalls for chemical attaching with various chemical reagents.[2c] However, the *asymmetric* functionalization of carbon nanotubes with each of their two end-tips attached by different chemical reagents still remains a big challenge. The asymmetric end-functionalization, if realized, should significantly advance the self-assembling of carbon nanotubes into many new functional structures with a molecular-level control.[2c,3]

We have previously prepared large-scale, micropatterned, perpendicularly aligned multi-wall carbon nanotubes (MWNTs) by pyrolyzing iron(II) phthalocyanine (FePc) onto a clean quartz glass plate in a tube furnace at 800−1100 °C under a mixture gas flow of Ar and H_2.[4,5] Subsequently, we found that the as-synthesized aligned carbon nanotube film could be easily separated from the quartz glass as a clean substrate-free film simply by immersing the nanotube-deposited quartz plate into an aqueous hydrofluoric acid solution (ca. 10% w/w), followed by thoroughly washing with pure water.[4] The substrate-free aligned carbon nanotube film thus prepared can float either on a hydrophilic solvent (e.g., water, alcohol) due to its hydrophobic nature[6] or on a high-density solvent (e.g., 1,1,2,2-tetrachloroethane, TCE, $\rho = 1.58$ g/mL) because of the density difference. In both cases, each of the constituent carbon nanotubes within the aligned nanotube film perpendicularly aligned at the air/liquid interface.[4] These findings, together with recent reports on photochemical modification of carbon nanotube sidewalls and tips,[7] enabled us to asymmetrically end-functionalize carbon nanotubes by sequentially floating the substrate-free aligned carbon nanotube film on two different photoreactive solutions with only one side of the nanotube film being contacted with a photoreactive solution and exposed to UV light each time. While the contact between the hydrophobic nanotube sidewall and photoreactive solution via capillary effect is minimal, the photochemical approach allows only the nanotube tips to be modified by UV-irradiating the nanotube film at a normal incidence angle. Here, we report this rational yet simple and effective approach to asymmetric end-functionalization of the two tube-ends of an individual carbon nanotube with different chemical reagents.

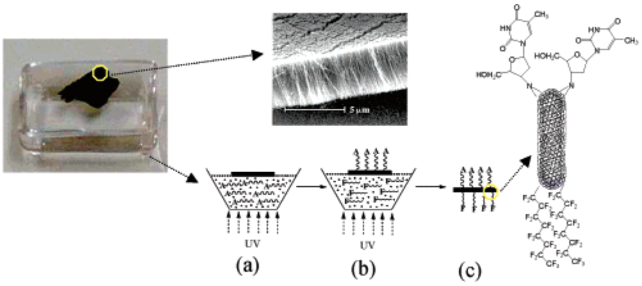

Figure 1. A free-standing film of aligned MWNTs floating on the top surface of (a) an AZT solution in ethanol (2%) for UV irradiation at one side of the nanotube film for 1 h, and (b) a perfluorooctyl iodide solution in TCE (2%) for UV irradiation at the opposite side of the nanotube film for 1.5 h.

Figure 1 shows procedures for the asymmetric end-functionalization of an aligned carbon nanotube film. In a typical experiment, we first carried out the end-attachment of 3′-azido-3′-deoxythymidine (AZT) molecules by UV-irradiating (100 W Hanovia 7825 medium pressure mercury lamp at a lamp-sample distance of 10 cm for 1 h),[7a] through the bottom of the quartz-boat container at a normal incidence angle, one side of the aligned carbon nanotube film floating on an AZT solution in ethanol (Figure 1a). The end-functionalized aligned carbon nanotube film thus-prepared (designated as A-CNT) was then removed from the AZT solution with care and thoroughly washed with pure ethanol to remove any physically absorbed AZT molecules. Thereafter, the freshly purified, aligned A-CNT film was laid on the top surface of a perfluorooctyl iodide solution in TCE (2 wt %) with the unmodified side of the aligned carbon nanotube film in contact with the TCE solution for the end-attachment of perfluorooctyl chains (F-CNT) by UV-irradiation[7b] in the same manner as in the case for the AZT attachment (Figure 1b). The resultant asymmetrically modified aligned carbon nanotube film (designated as A-CNT-F) was then washed by repeatedly rinsing with pure ethanol to completely remove any absorbed perfluorooctyl iodide molecules and dried in an ambient atmosphere for subsequent characterization (Figure 1c).

Among many reagents that can be photochemically attached onto carbon nanotube tips, we chose the *hydrophilic* AZT and *hydrophobic* perfluorooctyl iodide for the asymmetric end-functionalization to demonstrate the potential for self-assembling of the modified carbon nanotubes through the hydrophilic/hydrophobic interactions. In so doing, we first used ultrasonication (Electron Microscopy Science-2510MT) to deliberately destroy the alignment of the A-CNT, F-CNT, and A-CNT-F films and to homogeneously disperse them in H_2O/ethanol (9/1 v/v, Figure 2a), TCE/ethanol (9/1 v/v, Figure 2b), and a mixture solvent of H_2O/ethanol (9/1 v/v) + TCE/ethanol (9/1 v/v) (Figure 2c), respectively. While the relatively small amount of ethanol was used to promote the dispersion of A-CNTs in H_2O, we kept the same amount of ethanol

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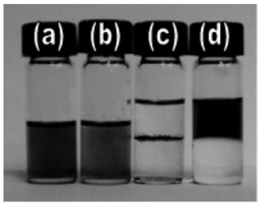

Figure 2. Dispersions of (a) A-CNTs in H_2O/ethanol (9/1 v/v), (b) F-CNTs in TCE/ethanol (9/1 v/v), (c) A-CNT-F in a mixture solvent of H_2O/ethanol (9/1 v/v, top) + TCE/ethanol (9/1 v/v, bottom), and (d) A-CNTs predispersed in H_2O/ethanol (9/1 v/v, top) after adding TCE/ethanol (9/1 v/v, bottom) in a dropwise fashion.

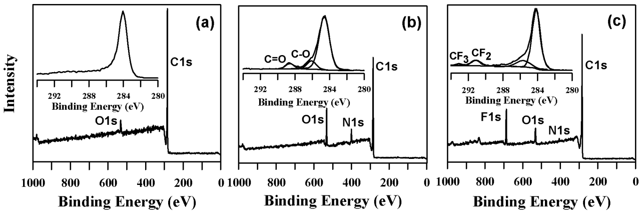

Figure 3. XPS spectra of (a) the pristine aligned carbon nanotube film, (b) the AZT-grafted side, and (c) the perfluorooctyl chain-grafted side of an aligned carbon nanotube film after the asymmetric end-functionalization. Insets show the corresponding high-resolution C 1s spectra.

in all of the solutions for consistency. As indicated by Figure 2a, a stable homogeneous dispersion in the *hydrophilic* solvent of H_2O/ethanol (9/1 v/v) was obtained (no precipitation about 2 days after the sonication) for the hydrophilically modified A-CNTs, as were for the *hydrophobically modified* F-CNTs in the *hydrophobic* solvent of TCE/ethanol (9/1 v/v) (no precipitation even about 4 days after the sonication) (Figure 2b). In contrast, a sonication-induced homogeneous dispersion of the asymmetrically modified A-CNT-F nanotubes in the mixture solvent of H_2O/ethanol (9/1 v/v) + TCE/ethanol (9/1 v/v) rapidly segregated (ca. 5 min after the sonication) into a two-phase system, where the hydrophilic solvent of H_2O/ethanol (9/1 v/v, top in Figure 2c) equilibrated immiscibly with the hydrophobic solvent of TCE/ethanol (9/1 v/v, bottom in Figure 2c), with the A-CNT-F nanotubes self-assembling at the interface. Furthermore, the A-CNTs predispersed in a H_2O/ethanol (9/1 v/v) solution did not fall out of dispersion upon the addition of the hydrophobic solvent (i.e., TCE/ethanol, 9/1 v/v), as shown in Figure 2d. The above observation is consistent with the asymmetric end-functionalization reactions schematically shown in Figure 1, indicating a possible control of the dispersion stability and self-assembling process by regulating the nature and size of the chemical moieties attached onto the nanotube tips.

For a more quantitative characterization, we performed X-ray photoelectron spectroscopic (XPS, VG Microtech ESCA 2000 using monochromatic Mg Kα radiation at a power of 300 W) measurements on an aligned carbon nanotube film before and after the asymmetric end-functionalization. Figure 3 shows the survey spectra for (a) the pristine aligned carbon nanotube film, (b) the AZT-grafted side (A-side), and (c) the perfluorooctyl chain-grafted side (F-side) of an aligned A-CNT-F film, along with the corresponding high-resolution C 1s spectra (insets). Consistent with previously reported results,[6] Figure 3a shows the expected HOPG graphite-like C 1s peak at 284.7 eV and a weak signal for O 1s (531 eV, O/C = 0.038), due largely to physically absorbed oxygen.[6,8] The XPS survey spectrum for the A-side of the aligned A-CNT-F film (Figure 3b) shows a N 1s peak at 399 eV with a concomitant increase in the atomic ratio of O/C from 0.038 to 0.15 due to the attachment of AZT molecules. The appearance of new peaks at about 286.5 and 288.6 eV in the corresponding high-resolution C 1s spectrum given in the inset of Figure 3b is attributable to the C−O and C═O bonds, respectively, associated with the AZT moieties (see Figure 1). On the other hand, XPS measurements on the F-side of the aligned A-CNT-F film revealed a new peak at 685 eV attributable to F 1s with its Auger features appearing around 850 eV (Figure 3c). Apart from the graphitic C 1s peak at 284.7 eV, the corresponding high-resolution C 1s spectrum (inset, Figure 3c) shows the CF_n peaks around 291 eV and a carbon component around 285.6 eV attributable to (nanotube) carbon atoms adjacent to the C−F bonds.[9]

These XPS results clearly indicate that both the AZT and perfluorooctyl moieties have been successfully bonded onto the opposite tube-ends of individual carbon nanotubes within the aligned nanotube film as no obvious change was observed for XPS spectra recorded from the aligned carbon nanotube film after the same treatments but without the UV exposure. The reported photochemically grafted end-groups can be used for further chemical modification via their characteristic reactions.[7a,10]

In summary, we have successfully developed a simple but effective method for grafting different chemical reagents onto the opposite tube-ends of individual carbon nanotubes, as confirmed by X-ray photoelectron spectroscopic measurements. It was also demonstrated that the asymmetrically modified carbon nanotubes with the hydrophilic 3′-azido-3′-deoxythymidine molecules chemically attached onto one tube-end and the hydrophobic perfluorooctyl moieties on the other could effectively self-assemble at the hydrophilic/hydrophobic interface in a two-phase solvent system. This work, together with the recent breakthroughs in the aligned growth of single-wall carbon nanotubes (SWNTs),[11] could lead to site-selective self-assembling of both MWNTs and SWNTs into a large variety of novel functional systems with highly controllable structures for various potential applications.

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Supporting Information Available: High-resolution peaks of A-CNT-F. This material is available free of charge via the Internet at http://pubs.acs.org.

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