

ASYMMETRIC END-FUNCTIONALIZATION OF CARBON NANOTUBES

The use of carbon nanotubes for many practical applications often requires a precision landing 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.). 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 non-aligned and aligned carbon nanotubes for selectively modifying nanotube tips, inner and/or outer walls has opened a rich field of carbon nanotube chemistry. 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 the sidewalls for chemical attaching with various chemical reagents. However, the asymmetric functionalization of carbon nanotubes with each of their two end-tips attached by different chemical reagents remains a 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.

Therefore, there is a need for asymmetric functionalized carbon nanotubes, and for methods of preparing them.

The present invention meets those needs by providing a method of making an asymmetric end-functionalized carbon nanotube film. The method comprises: providing a carbon nanotube film having a first end and a second end; contacting the first end of the carbon nanotube film with a first reactive medium; reacting the first end of the carbon nanotube film with the first reactive medium by a first physicochemical process; contacting the second end of the carbon nanotube film with a second reactive medium, wherein the first reactive medium is different from the second reactive medium; and reacting the second end of the carbon nanotube film with the second reactive medium by a second physicochemical process.

Figure 1 is a schematic showing the asymmetric end-functionalization reactions of the present invention.

Figure 2 shows dispersions of (a) A-CNTs in H₂O/ethanol (9/1 v/v), (b) F-CNTs in TCE/ethanol (9/1 v/v), and (c) A-CNT-F in a mixture solvent of H₂O/ethanol (9/1 v/v, top) + TCE/ethanol (9/1 v/v, bottom).

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

We prepared large-scale, 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 H₂. We also developed several microfabrication methods for patterning the aligned carbon nanotubes and for patterned/non-patterned transferring such nanotube arrays to various other substrates or as a free-standing film. We found that the as-synthesized aligned carbon nanotube film could be easily separated from the quartz glass as a clean substrate-free film by immersing the nanotube-deposited quartz plate into an aqueous hydrofluoric acid solution (about 10% w/w), followed by thoroughly washing with pure water. 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 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 is perpendicularly aligned at the air/liquid interface.

This led to the development of a novel photochemical approach for asymmetric end-functionalization of 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.

One of the first and second reactive solution can contain hydrophobic reactant(s) and the other hydrophilic reactant(s), both can contain hydrophobic reactants, or both can contain hydrophilic reactants, if desired. The order of the reactions does not matter.

Figure 1 is a representation of a procedure for the asymmetric end-
5 functionalization of a carbon nanotube film.

The carbon nanotube film is generally an aligned carbon nanotube film. The carbon nanotube film is contacted with a first reactive medium. The reactive medium is one which contains a compound which will react to the particular physicochemical process being used. For example, if a photochemical process is being used, a photoreactive
10 solution will be used. If a plasma process is used, the reactive medium will be appropriate monomer vapor(s).

The physicochemical process is then performed with the first medium by exposing the medium and carbon nanotubes to the physicochemical activation source for the particular type of reaction. The reaction occurs between one end of the carbon nanotubes
15 and the medium. The particular physicochemical activation source used will depend on the process being used. For example, in a photochemical reaction, the activation source will be a source of radiation, such as ultraviolet light, infrared light, or visible light. The photochemical reaction will then take place between the photoreactive solution and the carbon nanotubes.

20 The other side of the carbon nanotube film is contacted with a second reactive medium, and the medium is exposed to the activation source for that type of reaction. The first and second reactive media are different.

The physicochemical process can be same for both reactions, or they can be different. If the same process is used for both reactions, the activation sources can be the
25 same or they can be different. For example, with photochemical reactions, ultraviolet radiation can be used for both, or ultraviolet radiation can be used for one, and another radiation source can be used for the other.

Suitable physicochemical processes include, but are not limited to photochemical reactions, plasma activated reactions, adsorption, deposition, coating, ion beam etching,
30 thermal/chemical oxidation, and chemical grafting.

This allows the appropriate selection of physicochemical process and reactive medium depending on the particular chemicals which are to be added to each end of the carbon nanotubes.

5 Example 1

The end-attachment of 3'-Azido-3'-deoxythymidine (AZT) molecules was carried out by UV-irradiating (100 W Hanovia 7825 medium pressure mercury lamp at a lamp-sample distance of 10 cm for 1 hr), through the bottom of the quartz-boat container at a normal incidence angle, with one side of the aligned carbon nanotube film floating on an
10 AZT solution in ethanol. 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 physically-absorbed AZT molecules, if any. Thereafter, the freshly purified, aligned A-CNT film was laid on the top surface of a
15 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 in the same manner as in the case for the AZT attachment. 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
20 atmosphere for subsequent characterization.

Next, we demonstrated the potential for self-assembling of the modified carbon nanotubes through the hydrophilic/hydrophobic interactions. We used ultrasonication (Electron Microscopy Science-2510MT) to deliberately destroy the alignment of the A-CNT, F-CNT, and A-CNT-F films and to disperse them homogeneously in H₂O/ethanol
25 (9/1 v/v, Figure 2a), TCE/ethanol (9/1 v/v, Figure 2b), and a mixture solvent of H₂O/ethanol (9/1 v/v) + TCE/ethanol (9/1 v/v) (Figure 2c), respectively. As shown in Figure 2a, a stable homogenous dispersion in the hydrophilic solvent of H₂O/ethanol (9/1 v/v) was obtained (no precipitation about 2 days after the sonication) for the carbon nanotubes end-functionalized with the hydrophilic AZT molecules. Similarly, the
30 hydrophobically-modified F-CNTs in the hydrophobic solvent of TCE/ethanol (9/1 v/v) gave a stable homogenous dispersion (no precipitation about 4 days after the sonication)

(Figure 2b). In contrast, a sonication-induced homogenous dispersion of the asymmetrically-modified A-CNT-F nanotubes in the mixture solvent of H₂O/ethanol (9/1 v/v) + TCE/ethanol (9/1 v/v) rapidly segregated (about 5 min after the sonication) into a two-phase system, where the hydrophilic solvent of H₂O/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. This 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.

We also performed X-ray photoelectron spectroscopic (XPS, VG Microtech ESCA 2000 using monochromatic Mg K α radiation at a power of 300W) measurements on an aligned carbon nanotube film before and after the asymmetric end-functionalization for a more quantitative characterization. Figure 3 shows the survey spectra for (a) the pristine aligned carbon nanotube film, (b) the AZT-grafted side (A-side) and (c) perfluorooctyl chain-grafted side (F-side) of an aligned A-CNT-F film, along with the corresponding high resolution C 1s spectra (insets). Figure 3a shows the expected graphitic C 1s peak at 284.7 eV and a weak signal for O 1s (531 eV), consistent with previously reported results. Although not wishing to be bound by theory, the atomic ratio of O/C = 0.038 deduced from the survey spectrum in Figure 3a could be attributed to possible incorporation of a trace amount of oxygen during the nanotube growth and/or through the post-synthesis adsorption. The C 1s spectrum shown in the inset of Figure 3a is similar to that of HOPG graphite. 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 are attributable to the C-O and C=O bonds, respectively, associated with the AZT moieties. 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 appeared 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

CF₂ peak at 291 eV and a carbon component around 285.6 eV attributable to (nanotube) carbon atoms adjacent to the C-F bonds.

The XPS results indicate that both 3'-Azido-3'-deoxythymidine and perfluorooctyl moieties have been successfully bonded onto the opposite tube-ends of individual carbon nanotubes within the aligned nanotube film. A trivial explanation of the XPS results related to physical adsorption of the photoreactive reagents can be ruled out 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 photochemically-grafted end-groups can be used for further chemical modification via their characteristic reactions, indicating a generic nature of the asymmetric end-functionalization approach developed in the present study for asymmetric chemical modification of carbon nanotubes.

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.

Depending on what and how to activate each of the two nanotube ends, the number of chemical reagents that can be asymmetrically attached onto the nanotube ends is unlimited. In particular, plasma activation can be used to graft each of the two nanotube ends with various functional groups (e.g. -COOH, -COH, -OH, -NH₂, etc.), followed by further chemical modification through reactions characteristic of the plasma-induced functionalities as discussed in Q. Chen, L. Dai, M. Gao, S. Huang, and A.W.H. Mau "Plasma activation of carbon nanotubes for chemical modification" *J. Phys. Chem. B* 105, 618, 2001), which is incorporated herein by reference.

Asymmetric end-functionalization of carbon nanotubes was achieved by sequentially floating a substrate-free aligned carbon nanotube film on two different photoreactive solutions with only one side of the nanotube film being contacted with the photoreactive solution and exposed to UV light each time. The resultant nanotubes with different chemical reagents attached onto their opposite tube-ends should be very useful

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for site-selective self-assembling of carbon nanotubes into many novel functional structures for various potential applications.

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that
5 various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims

CLAIMS

1. A method of making an asymmetric end-functionalized carbon nanotube film,
5 comprising:
 providing a carbon nanotube film having a first end and a second end;
 contacting the first end of the carbon nanotube film with a first reactive medium;
 reacting the first end of the carbon nanotube film with the first reactive medium by
a first physicochemical process;
10 contacting the second end of the carbon nanotube film with a second reactive
medium, wherein the first reactive medium is different from the second reactive medium;
and
 reacting the second end of the carbon nanotube film with the second reactive
medium by a second physicochemical process.
15
2. The method of claim 1 wherein contacting the first or second end of the carbon
nanotube film with the first or second reactive medium comprises floating the carbon
nanotube film on a first or second reactive solution.
- 20 3. The method of claim 1 wherein the physicochemical process is selected from
photochemical processes, plasma processes, adsorption processes, deposition processes,
coating processes, ion beam etching processes, thermal/chemical oxidation processes, and
chemical grafting processes.
- 25 4. The method of claim 1 wherein the first or second physicochemical process is a
photochemical process and wherein reacting the first or second end of the carbon nanotube
film with the first or second reactive medium comprises exposing the first or second end
of the carbon nanotube film to a source of radiation selected from ultraviolet radiation,
infrared radiation, or visible light.
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5. The method of claim 4 wherein the source of radiation is perpendicular to the carbon nanotube film.
6. The method of claim 4 wherein the first reactive medium is a solution containing
5 3'-azido-3'-deoxythymidine and the second reactive medium is a solution containing perfluorooctyl iodide.
7. The method of claim 1 wherein the first reactive medium contains a hydrophilic reactant and the second reactive medium contains a hydrophobic reactant.
- 10 8. The method of claim 1 wherein the carbon nanotube film comprises carbon nanotubes selected from single-wall carbon nanotubes or multi-wall carbon nanotubes.
9. The method of claim 1 wherein the carbon nanotube film is aligned.
- 15 10. The method of claim 1 wherein the first and second physicochemical processes are the same.
11. A method of making an asymmetric end-functionalized carbon nanotube film,
20 comprising:
 providing a carbon nanotube film having a first end and a second end;
 floating the first end of the aligned carbon nanotube film on a first photoreactive solution;
 exposing the first end of the aligned carbon nanotube film to ultraviolet radiation
25 so that the first end of the aligned carbon nanotube film reacts with the first photoreactive solution;
 floating the second end of the aligned carbon nanotube film on a second photoreactive solution, wherein the first photoreactive solution is different from the second photoreactive solution; and

exposing the second end of the aligned carbon nanotube film to ultraviolet radiation so that the second end of the aligned carbon nanotube film reacts with the second photoreactive solution.

- 5 12. The method of claim 11 wherein the ultraviolet radiation is perpendicular to the aligned carbon nanotube film.
13. The method of claim 11 wherein the first photoreactive solution contains a hydrophilic reactant and the second photoreactive solution contains a hydrophobic
10 reactant.
14. The method of claim 11 wherein the first photoreactive solution contains 3'-azido-3'-deoxythymidine and the second photoreactive solution contains perfluorooctyl iodide.
- 15 15. The method of claim 11 wherein the carbon nanotube film comprises carbon nanotubes selected from single-wall carbon nanotubes or multi-wall carbon nanotubes.
16. The method of claim 11 wherein the carbon nanotube film is aligned.
- 20 17. The method of claim 11 wherein the first and second physicochemical processes are the same.
18. An asymmetric end-functionalized carbon nanotube film, comprising:
a carbon nanotube film having a first end and a second end;
25 a first end group attached to the first end of the aligned carbon nanotube film,
wherein the first end group is the reaction product of a first reactive solution and the carbon nanotube film; and
a second end group attached to the second end of the carbon nanotube film,
wherein the second end group is the reaction product of a second reactive solution and the
30 carbon nanotube film, wherein the first and second end groups are different.

19. The asymmetric end-functionalized carbon nanotube film of claim 18 wherein the first end group is hydrophilic and the second end group is hydrophobic.
20. The asymmetric end-functionalized carbon nanotube film of claim 18 wherein the
5 first end group is 3'-azido-3'-deoxythymidine and the second end group is perfluorooctyl iodide.
21. The asymmetric end-functionalized carbon nanotube film of claim 18 wherein the carbon nanotube film comprises carbon nanotubes selected from single-wall carbon
10 nanotubes and multi-wall carbon nanotubes.
22. The asymmetric end-functionalized carbon nanotube film of claim 18 wherein the carbon nanotube film is aligned.