Templated Assembly of Semiconductor and Insulator Nanoparticles at the Surface of Covalently Modified Multiwalled Carbon Nanotubes

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Received May 28, 2004. Revised Manuscript Received July 12, 2004

Reported is the preparation and characterization of phosphonic acid-modified and alkoxy silane-modified multiwalled carbon nanotubes (MWCNTs). Also reported is the use of these modified MWCNTs to template the assembly of titanium dioxide and silica nanoparticles, respectively. Some potential applications of these findings are considered.

Introduction

The demand for integrated circuits that will allow information to be processed at even faster speeds is as great as ever. This is despite the fact that scaling has led to a doubling of the density of the wires and switches that comprise such circuits every 18 months for 4 decades, giving rise to Moore's Law.[1] While it is expected that Moore's Law will continue to hold true for another decade, it is not expected that it will hold true thereafter.[2]

In order for Moore's Law to hold true even for another decade, major advances in existing fabrication and materials technologies will be required. Specifically, the development of new short wavelength light sources, masks and resists, and materials with high and low dielectric constants are all requirements. The scientific and engineering advances, not to mention the investment, which will be required to secure these advances, are very significant.

Even assuming these advances can be secured, and the sizes of the wires and switches that comprise integrated circuits be reduced still further, they will eventually approach sizes where the materials of which they are composed no longer exhibit bulk properties, but exhibit properties that are dominated by surface and confinement effects.

For these reasons it is necessary to contemplate alternative fabrication and materials technologies that offer the prospect of still smaller wires and switches at lower cost and new circuit architectures that can accommodate or even exploit the novel properties exhibited by nanoscale components.

When considering alternative fabrication technologies, one is immediately attracted to the self-assembly in solution and the self-organization at technologically relevant substrates of nanoscale architectures.[3] When considering alternative materials technologies, one is immediately attracted to high information content molecules,[4] and to the growing number of nanomaterials that are becoming available.[5] It is noted that there are a growing number of reports that demonstrate the potential of this and related approaches.[6–10]

One particularly active area has been research into the use of carbon nanotubes (CNTs) as wires and as nanoscale building blocks for switches. Accordingly, there are a growing number of reports that describe the structure-dependent electrical properties of CNTs and that demonstrate their use as wires and as nanoscale building blocks for switches.[11]

A limitation of CNTs, however, is that their electrical properties are very sensitive to the local environment, to the extent that the local environment alters their physical or chemical properties. For example, the purification or modification of CNTs may lead to the introduction of defects, which alter the structure of the CNT and their electronic properties.[12] It is in this context that we have explored the potential of CNTs, not as wires, but as templates for the self-assembly of wires.

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Previously, we have reported the CNT-templated assembly of continuous gold nanowires.[13] Briefly, a suspension of multiwalled carbon nanotubes (MWCNTs) was added to a dispersion of tetraoctylammonium bromide (TOAB) modified gold nanoparticles. The gold nanoparticles were adsorbed at the surface of the MWCNTs. The principal driving force for adsorption is the transfer of electron density from the gold nanoparticles to the continuum of π^* states present in the carbon nanotube. The resulting nanoparticle-modified MWCNTs were annealed in air at 300 °C for up to 120 s, causing the nanoparticles to sinter and to form continuous gold nanowires with an external diameter of approximately 60 nm and a length in excess of 1 μm.

Since then, there have been a large number of reports describing the preparation of metal and metal oxide nanoparticle coated carbon nanotubes.[14] There have also been a large number of reports describing the chemical modification of carbon nanotubes. Initially, these reports focused on the covalent introduction of carboxy groups at the surface of carbon nanotubes.[15] Subsequently, these reports have focused on the covalent coupling of an increasingly wide range of functional molecules and biomolecules to the surface of carboxy-modified carbon nanotubes.[16]

Building on these capabilities, we have recently reported the preparation of the thiol-modified MWCNTs and their use to template the assembly of conducting gold nanowires in solution.[17] Briefly, a dispersion of dimethyl(4-aminopyridine) (DMAP) modified gold nano-

particles was added to a suspension of thiol-modified MWCNTs. The gold nanoparticles were adsorbed at the surface of the MWCNTs. The driving force for adsorption is both the transfer of electron density from the gold nanoparticles to the continuum of π^* states present in the carbon nanotube and the formation of coordinative covalent bonds between the gold nanoparticles and the thiol-modified MWCNT surface. The resulting nanoparticle-modified MWCNTs were exposed to an electrodeless deposition solution, which caused the nanoparticles to be enlarged and enjoined and to form continuous gold nanowires. Electrical characterization of these nanowires shows them to be ohmic conductors and to have a resistivity of 2×10^{-4} Ωm.

Again, building on these capabilities, we have also recently reported the preparation of dibenzylammonium cation-modified multiwalled carbon nanotubes that were used to template the noncovalent self-assembly in solution of gold nanowires from crown-modified gold nanoparticles.[18] The driving force for self-assembly is formation of the surface-confined pseudorotaxane that results from the electron-poor cation threading the electron-rich crown.

Here, we report on the preparation and characterization of phosphonic acid-modified and alkoxy silane-modified MWCNTs. We also report on the use of these MWCNTs to template the assembly of titanium dioxide and silica nanoparticles, respectively, as shown in Scheme 1.

This extension of our recent work to include the use of modified MWCNTs to template the assembly of semiconductor and insulator nanoparticles represents a potentially significant development and extends the range of possible applications that can be considered.

Experimental Section

All solvents and compounds were used as supplied by the Sigma-Aldrich Chemical Co. Ltd., unless otherwise stated. The MWCNTs used in this study were supplied by MER Corporation. The MWCNTs were the "as-produced cathode deposit" produced during the Kratschmer-Huffman arc process.

All TEMs were obtained using a JEOL 2000 FX TEMscan (at an accelerating voltage of 80 kV) for samples deposited on both uncoated (2000 mesh) and carbon-coated (400 mesh) copper grids. The preparation of samples for TEM analysis involved depositing a drop (20 μL) of the relevant dispersion or suspension onto one of the above grids.

All FT-IR spectra were obtained using a Matteson Galaxy FT-IR spectrometer. Spectra of solids (including MWCNTs) were obtained using KBr pellets (0.05 mg in 100.00 mg of KBr), while spectra of liquids were obtained using a CaF$_2$ solution cell (Specac, Omni-Cell, 50-μm path length).

EDX analysis was performed using a JEOL 5410 SEM equipped with a Phoenix-Pro EDX System supplied by EDAX Inc.

Purification of Unmodified MWCNTs. As-received MWCNTs (3 mg) were suspended by sonication (15 min) in chloroform (20 mL). The resulting suspension was centrifuged (5000 rpm, 15 min) and the supernatant fraction (approximately 75 vol %) retained. This procedure was repeated an additional three times, with the supernatant fraction being retained on each occasion until a clear gray-brown suspension was obtained.

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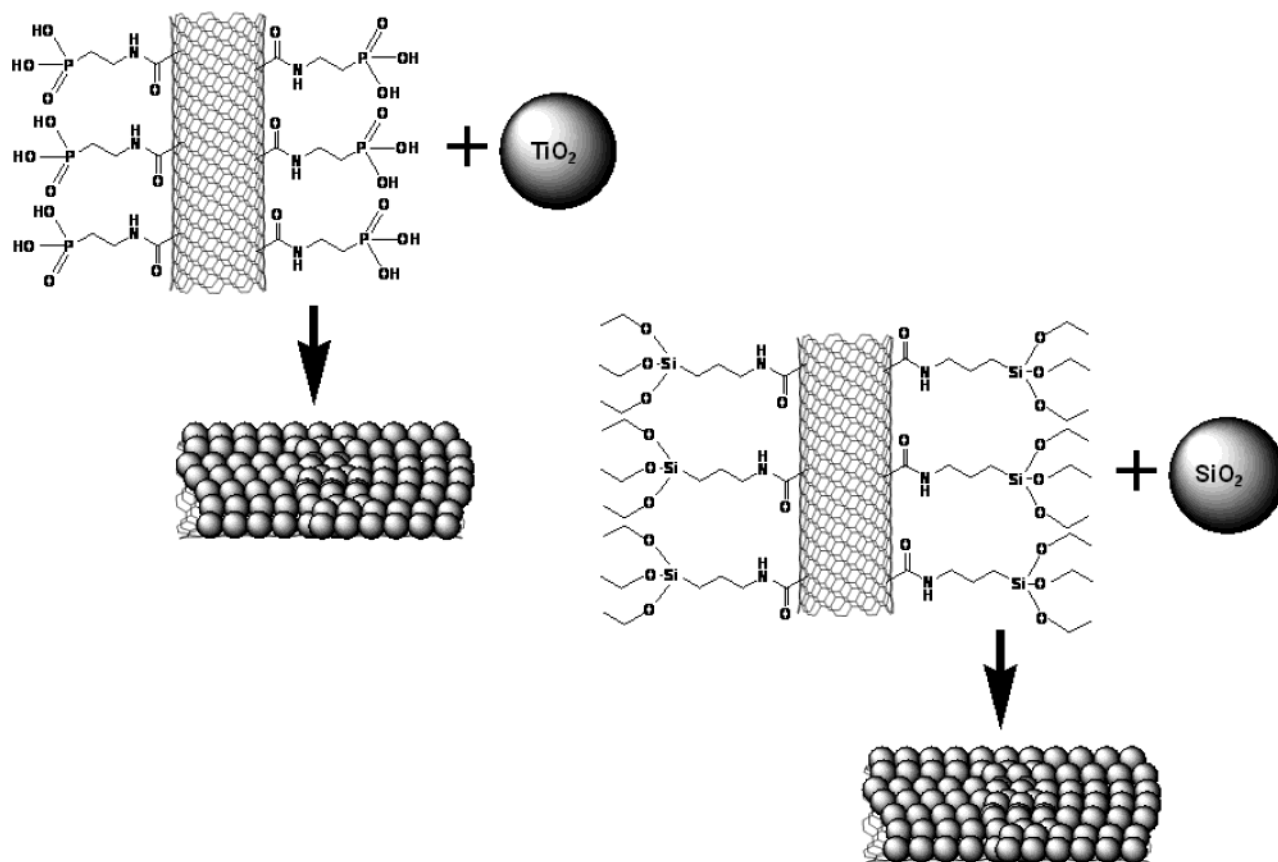
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Scheme 1. Templated Self-assembly of TiO₂ and SiO₂ Nanoparticles at the Surface of AEPA-Modified and APTES-Modified MWCNTs, Respectively

Preparation of Carboxy-Modified MWCNTs. MWCNTs were modified as outlined below in order to introduce carboxy groups at the surface of the nanotubes.[15] The MWCNTs were refluxed in nitric acid in order to produce hydroxyl, carbonyl, and carboxy groups at defects in the carbon atom lattice. The above hydroxyl and carbonyl groups were further oxidized to carboxy groups by treatment with potassium permanganate and perchloric acid as described below. A detailed experimental methodology has recently been reported.[18]

Preparation of 2-Aminoethylphosphonic Acid-Modified MWCNTs. Preparation of 2-aminoethylphosphonic acid (AEPA) modified MWCNTs involved 1-[3-(dimethylamino)-propyl]-3-ethylcarbodiimide hydrochloride (EDAC) mediated amide formation between carboxy-modified MWCNTs and AEPA as described below.

AEPA (50 mg) was added to a suspension of carboxy-modified MWCNTs (3 mg) in deionized-distilled water (10 mL), followed by EDAC (91 mg) and 4-(dimethylamino)pyridine (DMAP, 3 mg). The solution was stirred for 12 h, filtered through a polycarbonate membrane filter (Whatman-UK 0.2 μm pore diameter) and washed with deionized-distilled water (1 L). The AEPA-modified MWCNTs, denoted AEPA-MWCNTs, were resuspended in water (200 mL) by sonication. The resulting suspension was sonicated for an additional 15 min. The above suspension of AEPA-modified MWCNTs was filtered through a polycarbonate membrane filter (Whatman-UK 0.2 μm pore diameter) and washed with deionized-distilled water (1 L). The AEPA-modified MWCNTs were finally resuspended in deionized-distilled water (10 mL) by sonication.

Preparation of 3-Aminopropyltriethoxysilane-Modified MWCNTs. Preparation of 3-aminopropyltriethoxysilane (APTES) modified MWCNTs involved the formation of an amide link between acid-chloride-modified MWCNTs and APTES as described below.

Carboxy-modified MWCNTs (3 mg) were suspended by sonication in SOCl₂ (15 mL) and heated to 70 °C for 24 h. The unreacted SOCl₂ and the SO₂ and HCl byproducts were

removed by rotary evaporation under reduced pressure, followed by drying using a Schlenk apparatus for 6 h.

APTES (10 mL) was added to the dry acid-chloride-modified MWCNTs, and the mixture was sonicated for 15 min to ensure resuspension of the MWCNTs in the APTES. The resulting suspension was stirred for 12 h, with sonication for 5 min at 1 h intervals. The APTES-modified MWCNTs, denoted APTES-MWCNTs, were filtered through an alumina membrane filter (Anodisc, Whatman-UK 0.2 μm pore diameter) and washed with anhydrous ethanol (200 mL). The APTES-modified MWCNTs were then resuspended in anhydrous ethanol (200 mL) by sonicating the filter membrane. The resulting suspension was sonicated for an additional 15 min to ensure any unreacted APTES was dissolved. The above APTES-modified MWCNT suspension was filtered through an alumina membrane filter (Anodisc, Whatman-UK 0.2 μm pore diameter) and washed with anhydrous ethanol (200 mL). The APTES-modified MWCNTs were finally resuspended in anhydrous ethanol (10 mL) by sonicating the membrane filter.

Preparation of Propylamine-Modified MWCNTs. Preparation of propylamine (PA) modified MWCNTs involved the formation of an amide link between acid-chloride-modified MWCNTs and PA as described below.

Carboxy-modified MWCNTs (3 mg) were suspended by sonication in SOCl₂ (15 mL) and heated to 70 °C for 24 h. The unreacted SOCl₂ and the SO₂ and HCl byproducts were removed by rotary evaporation under reduced pressure, followed by drying using a Schlenk apparatus for 6 h.

PA (10 mL) was then added to the dry acid-chloride-modified MWCNT material, and the mixture was sonicated for 15 min to ensure complete resuspension of the MWCNTs. The suspension was stirred for 12 h, with sonication for 5 min at 1 h intervals. The PA-modified MWCNTs, denoted PA-MWCNTs, were then filtered through an alumina membrane filter (Anodisc, Whatman-UK 0.2 μm pore diameter) and washed with ethanol (200 mL). The PA-MWCNTs were then resuspended in ethanol (200 mL) by sonication of the membrane

filter. The resulting suspension was sonicated for an additional 15 min to ensure any remaining unreacted PA was dissolved. The above PA-modified MWCNT suspension was then filtered through an alumina membrane filter (Anodisc, Whatman-UK 0.2 μm pore diameter) and washed with ethanol (200 mL) and chloroform (200 mL). The PA-modified MWCNTs were sonicated off the membrane filter into ethanol (5 mL). The ethanol was removed by rotary evaporation, followed by drying using a Schlenk apparatus (2 h). The dry PA-modified MWCNTs were resuspended in chloroform (10 mL) by sonication (10 min).

Preparation of Aqueous Titanium Dioxide Nanoparticle Dispersions. Stable aqueous dispersions of titanium dioxide nanoparticles were prepared using a method similar to that described by Barbe et al.[19] and based on the arrested hydrolysis of titanium isopropoxide. Briefly, a solution of titanium isopropoxide (1.0 mL) and 2-propanol (1.0 mL) was added dropwise to deionized-distilled water (20 mL) with vigorous stirring at room temperature. After 10 min, nitric acid (70%, 0.130 mL) was added to the milky white suspension, which was stirred for an additional 10 min. The suspension was heated to 80 °C for 8 h in order to peptize the agglomerates of titania formed following hydrolysis. The resulting dispersion was filtered using filter paper and also using a syringe filter (Whatman-UK Anotop 0.02 μm) and the volume of the solution adjusted to 20 mL with deionized-distilled water. The dispersion was characterized by TEM following dilution by deionized-distilled water (1:1000) and evaporation of a drop (20 μL) onto a carbon-coated copper TEM grid. The particle concentration was found to be 5×10^{16} nanoparticles mL^{-1}, based on a determination of the mean particle diameter of 5 ± 2 nm (analysis of 200 nanoparticles from TEM image) and the dry mass of TiO$_2$ in 1 mL of the dispersion.

Preparation of Chloroformic Titanium Dioxide Nanoparticle Dispersions. Stable chloroformic dispersions of titanium dioxide nanoparticles were prepared using a method similar to that described by Kotov et al.[20] based on the arrested hydrolysis of titanium isopropoxide. Briefly, a solution of titanium isopropoxide (0.5 mL) in 1-propanol (4.5 mL) was added to a solution of hexadecyltrimethylammonium bromide (CTAB, 0.153 g) in deionized-distilled water (0.02 mL), chloroform (60 mL), and 1-propanol (40 mL) under vigorous stirring. The resulting mixture was refluxed at 90 °C for 2 h, yielding a straw-yellow dispersion of stabilized TiO$_2$ nanoparticles. The dispersion was cooled and filtered using filter paper and a syringe filter (Whatman-UK Anotop 0.02 μm). The dispersion was characterized by TEM following dilution by chloroform (1:1000) and evaporation of a drop (20 μL) onto a carbon-coated copper TEM grid. The particle concentration was found to be 2×10^{16} nanoparticles mL^{-1}, based on a determination of the mean particle diameter of 4 ± 2 nm (analysis of 200 nanoparticles by TEM) and a determination of the dry mass of TiO$_2$ in 1 mL of the dispersion.

Preparation of Ethanolic Silicon Dioxide Nanoparticles Dispersions. A stable ethanolic dispersion of silicon dioxide nanoparticles was prepared using a procedure similar to that originally developed by Stöber et al.[21] and modified by van Blaaderen and Vrij.[22] This procedure involved the hydrolysis and condensation of tetraethyl orthosilicate in ethanolic solution in the presence of ammonia.

Briefly, tetraethyl orthosilicate (320 mg) was added to anhydrous ethanol (9.44 mL) followed after 10 s by ammonia (190 mg, 28% aqueous solution). The solution was vigorously stirred for 24 h. The dispersion was characterized by TEM following dilution by anhydrous ethanol (1:1000) and evaporation of a drop (20 μL) onto a carbon-coated copper TEM grid. The particle concentration was found to be 2×10^{16} nanopar-ticles mL^{-1}, based on a determination of the mean particle diameter of 7 ± 3 nm (analysis of 200 nanoparticles by TEM) and a determination of the dry mass of SiO$_2$ in 1 mL of the dispersion.

Templated Assembly of TiO$_2$ Nanoparticles at the Surface of AEPA-Modified MWCNTs. An aliquot of an aqueous suspension of AEPA-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was added to deionized-distilled water (0.8 mL) and sonicated for 3 min to ensure they were fully dispersed. An aliquot of an aqueous dispersion of TiO$_2$ nanoparticles (0.01 mL, 5×10^{16} nanoparticles mL^{-1}) was added to the above suspension. The suspension was allowed to equilibrate for 24 h, after which time a drop (20 μL) of the suspension was sampled and evaporated on a copper 2000 square mesh grid for analysis by TEM.

Templated Assembly of SiO$_2$ Nanoparticles at the Surface of APTES-Modified MWCNTs. An aliquot of an ethanolic suspension of APTES-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was added to anhydrous ethanol (0.8 mL) and sonicated for 3 min to ensure they were fully dispersed. An aliquot of an ethanolic dispersion of SiO$_2$ nanoparticles (0.010 mL, 2×10^{16} nanoparticles mL^{-1}) was added to the above suspension. The suspension was allowed to equilibrate for 24 h, after which time a drop (20 μL) of the suspension was sampled and evaporated on a copper 2000 square mesh grid for analysis by TEM.

Control I: AEPA-Modified MWCNTs with PPA-Modified TiO$_2$ Nanoparticles. An aliquot of an aqueous dispersion of titanium dioxide nanoparticles (0.01 mL, 5×10^{16} nanoparticles mL^{-1}) was added to a solution of propylphosphonic acid (PPA, 2 mg) in deionized-distilled water (0.8 mL) and sonicated for 10 min. The resulting dispersion was allowed equilibrate for 6 h. Excess PPA molecules were removed by centrifugation of the nanoparticle dispersion and disposal of the supernatant. The nanoparticle precipitate was made up to 0.8 mL once more by the addition of deionized-distilled water and sonication for 3 min. Centrifugation and disposal of the supernatant was repeated an additional three times to ensure the complete removal of excess PPA. This was to ensure that the pH of the nanoparticle AEPA-modified MWCNTs suspension was between 4 and 6. This was, in turn, to ensure optimum conditions for adsorption of PPA and to avoid hydrolysis of the amide-bound AEPA.

An aliquot of an aqueous suspension of AEPA-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was added to the above dispersion of PPA-modified TiO$_2$ nanoparticles and the suspension allowed to equilibrate for 24 h, after which time a drop (20 μL) of the suspension was sampled and evaporated on a carbon-coated copper 400 square mesh grid for analysis by TEM.

Control II: PA-Modified MWCNTs with Unmodified TiO$_2$ Nanoparticles. An aliquot of a chloroformic suspension of PA-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was diluted by the addition of chloroform (0.8 mL) and sonicated for 3 min. An aliquot of the chloroformic dispersion of CTAB-modified TiO$_2$ nanoparticles (0.012 mL, 2×10^{16} nanoparticles mL^{-1}) was added to the above suspension of PA-modified MWCNTs and allowed to equilibrate for 24 h, after which time a drop (20 μL) of the suspension was sampled and evaporated on a carbon-coated copper 400 square mesh grid for analysis by TEM.

Control III: Purified Unmodified MWCNTs with Unmodified TiO$_2$ Nanoparticles. An aliquot of a chloroformic suspension of purified unmodified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was diluted by the addition of chloroform (0.8 mL) and sonicated for 3 min. An aliquot of an aqueous dispersion of TiO$_2$ nanoparticles (0.010 mL, 5×10^{16} nanoparticles mL^{-1}) was added to the above suspension of MWCNTs and sonicated for 15 min. The resulting suspension was allowed to equilibrate for 24 h, after which time a drop (20 μL) of the suspension was sampled and evaporated on a carbon-coated copper 400 square mesh grid for analysis by TEM.

Control IV: APTES-Modified MWCNTs with APTES-Modified SiO$_2$ Nanoparticles. APTES (0.079 mL) was added to a dispersion of an aliquot of SiO$_2$ nanoparticles (0.30 mL, 2

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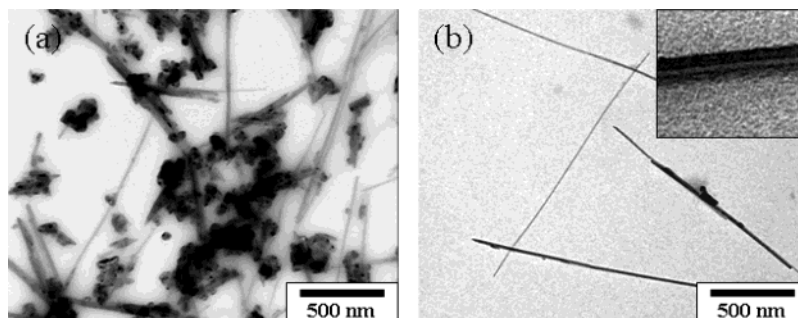
Figure 1. (a) TEM image of the as-received MWCNTs. (b) TEM image of the sample in (a) following purification.

$\times 10^{16}$ nanoparticles mL^{-1}) in anhydrous ethanol (10 mL) and the dispersion was sonicated for 5 min. The dispersion was heated to 80 °C for 15 min and the volume reduced to 2 mL using a rotary evaporator. The volume was then made up to 10 mL using anhydrous ethanol. This procedure was repeated an additional eight times in order to drive the condensation reaction between the APTES molecules and the silanol groups at the surface of the silica nanoparticles and to remove the water produced. The dispersion of APTES-modified SiO$_2$ nanoparticles was centrifuged (15 min, 5500 rpm) in order to precipitate the nanoparticles. The supernatant liquid containing excess APTES was disposed of and the volume of the concentrated dispersion made up to 10 mL. This procedure was repeated an additional four times to ensure as little APTES as possible remained.

An aliquot (1 mL) of the APTES-modified SiO$_2$ nanoparticles (0.030 mL, 2×10^{16} nanoparticles mL^{-1}) was added to a freshly sonicated suspension of APTES-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) and the suspension allowed to equilibrate for 24 h. A drop (20 μL) of the suspension was sampled and evaporated on a copper 400 square mesh grid for analysis by TEM.

Control V: PA-Modified MWCNTs with Unmodified SiO$_2$ Nanoparticles. An aliquot of a chloroformic suspension of PA-modified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was diluted by the addition of chloroform (0.8 mL) and sonicated for 3 min. An aliquot of an ethanolic dispersion of unmodified SiO$_2$ nanoparticles (0.0.30 mL, 1.60×10^{16} nanoparticles mL^{-1}) was added to the above suspension of PA-modified MWCNTs and allowed to equilibrate for 24 h. A drop (20 μL) of the suspension was sampled and evaporated on a copper 400 square mesh grid for analysis by TEM.
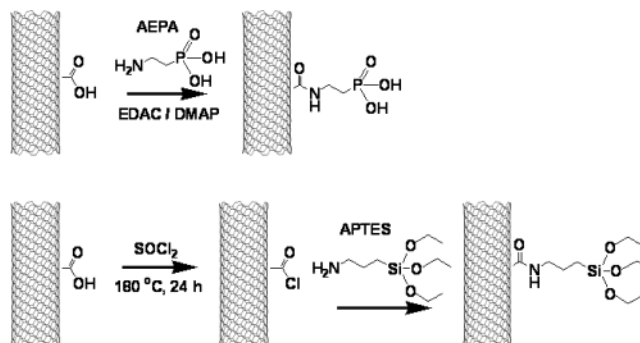
Control VI: Purified Unmodified MWCNTs with Unmodified SiO$_2$ Nanoparticles. An aliquot of a chloroformic suspension of purified unmodified MWCNTs (0.2 mL, 3×10^{-4} g mL^{-1}) was diluted by the addition of chloroform (0.8 mL) and sonicated for 3 min. An aliquot of an ethanolic dispersion of unmodified SiO$_2$ nanoparticles (0.030 mL, 1.60×10^{16} nanoparticles mL^{-1}) was added to the above suspension of purified unmodified MWCNTs and allowed to equilibrate for 24 h. A drop (20 μL) of the suspension was sampled and evaporated on a copper 400 square mesh grid for analysis by TEM.

EDX Analysis. An aqueous suspension of AEPA-modified MWCNTs (3 mg, 10 mL) was diluted to 500 mL with deionized-distilled water and sonicated for 20 min to ensure their complete dispersion. The suspension was filtered using a membrane filtration apparatus, followed by washing with deionized-distilled water (1 L). The AEPA-modified MWCNTs were retained on the membrane, which was then dried using a Schlenk apparatus and mounted for EDX analysis on an aluminum stub using conductive carbon tape. A similar washing procedure was adopted for the analysis of carboxy-modified MWCNTs and purified unmodified MWCNTs using water and chloroform, respectively.

Results and Discussion

Preparation of Modified Multiwalled Carbon Nanotubes. In this work, the as-received MWCNTs

Scheme 2. Preparation of AEPA-Modified and APTES-Modified MWCNTs

were purified by sonication in chloroform to fully disperse the material and by centrifugation of the resulting suspension in order to precipitate less soluble graphitic impurities. The supernatant suspension was decanted, the volume made-up again, and the process repeated an additional three times. The recovered MWCNTs were readily dispersed in chloroform and found to be largely free of graphitic impurities; see Figure 1. The purified unmodified MWCNTs were determined to possess an average diameter of 24 nm and an average length of 2.0 μm from an analysis of the TEM images of 50 individual MWCNTs.

The oxidation of MWNTs under strongly acidic conditions results in the introduction of carboxylic, hydroxyl, and carbonyl groups at defect sites on the surface of the MWNT in the approximate ratio 4:2:1 [**15a,b,c,d**]. To maximize the number of functional groups suitable for covalent modification, the above hydroxy and carbonyl groups were subsequently oxidized to carboxy groups [**15e**].

The extent of surface oxidation has been calculated to be of the order of 10^{21} carboxy functional groups (g^{-1}) [**15f**]. This value corresponds to 2% of all carbon atoms. Studies have indicated that approximately 15% of the carbon atoms are found at the outer wall of a MWCNT [**15a**]. If the oxidation is predominantly of the outer walls, this corresponds to 13% of the carbon atoms at the surface being oxidized. The scope for surface covalent chemistry is, therefore, significant.

Modification of MWCNTs with a molecule incorporating a terminal phosphonic acid group, namely, AEPA, or a molecule incorporating a terminal alkoxy-silane group, namely, APTES, was achieved by covalently coupling these molecules via the amine functional group present in each, to the carboxy groups at the surface of MWCNTs. AEPA was coupled to carboxy-modified MWCNTs under aqueous conditions by EDAC-mediated
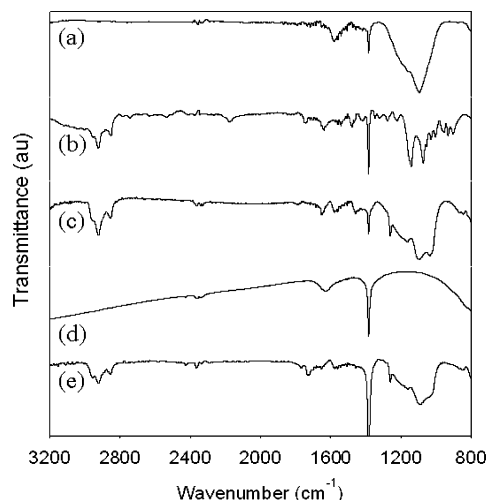
Figure 2. FT-IR spectrum of (a) carboxy-modified MWCNTs, (b) AEPA, (c) AEPA-modified MWCNTs, (d) TiO_2 nanoparticles, and (e) TiO_2 nanoparticles assembled at AEPA-modified MWCNTs.

amide formation as shown in Scheme 2. APTES was coupled to carboxy-modified MWCNTs by first converting the carboxy groups to acid-chloride groups by treatment with thionyl chloride as also shown in Scheme 2. This was followed by the combination of liquid APTES with the acid-chloride-modified MWCNTs and the formation of an amide. TEMs of the AEPA-modified and APTES-modified MWCNTs confirmed that their average diameters and lengths remained unchanged. They also confirmed that they remained well-dispersed.

Clearly, two different coupling strategies were required. EDAC-mediated coupling under aqueous conditions was required for AEPA. A large excess of AEPA and EDAC were used to ensure efficient coupling. Acid-chloride-mediated coupling under nonaqueous conditions was required for APTES. Coupling under nonaqueous conditions was required to prevent APTES hydrolysis. A large excess of APTES was also required, but clearly this was assured by dispersing the acid-chloride-modified MWCNTs in the liquid reagent.

Characterization of Modified Multiwalled Carbon Nanotubes. To characterize the carboxy-modified MWCNTs, following their further modification by covalent coupling of AEPA and APTES, a detailed FT-IR study was undertaken. Shown in Figure 2 are the FT-IR spectra of carboxy-modified MWCNTs, AEPA, and AEPA-modified MWCNTs.

The FT-IR spectrum of carboxy-modified MWCNTs (Figure 2a) is in good agreement with previously reported spectra.[23] Specifically, the following bands are observed: the C=O stretch of the carboxy group at 1718 cm^{-1}; the C=C stretch of the MWCNT at 1578 cm^{-1}; the C−O stretch and out of plane deformations between 1300 and 1100 cm^{-1}; and the C−O out of plane deformation at 1097 cm^{-1}.

The FT-IR spectrum of AEPA (Figure 2b) is also in good agreement with available reference spectra.[24] There are two bands, which may be assigned to the

amine group. The first at 1638 cm^{-1} is assigned to N−H bending (scissoring) vibration; and the second at 1074 cm^{-1} is assigned (in part) to the C−N stretching vibration. There are four bands, which may be assigned to the methylene groups. The first at 2925 cm^{-1} is assigned to the asymmetric C−H stretching vibration; the second at 2853 cm^{-1} is assigned to the symmetric C−H stretching vibration; the third at 1480 cm^{-1} is assigned to the C−H bending (scissoring) vibration of the methylene group linked to the amine; and the fourth at 1416 cm^{-1} is assigned to the C−H bending (scissoring) vibration of the methylene group linked to the phosphonic acid. There are a series of bands observed between 1300 and 900 cm^{-1} in the P−O stretching region. The assignment of these bands is difficult due to the fact that the bands are relatively broad and overlap, and due to the fact that the frequencies of these bands are affected by hydrogen bonding. Despite this, it is clear that this region of the AEPA spectrum confirms the presence of a phosphonic acid group.

Following reaction of carboxy-modified MWCNTs with AEPA, the FT-IR spectrum of the resulting AEPA-modified MWCNTs was measured (Figure 2c). The observed spectral changes are consistent with previous reports and confirm that coupling has occurred.[25]

First, the bands assigned to the carboxy group on the surface of the MWCNT are absent and have been replaced by bands consistent with formation of the amide. Specifically, the band assigned to the C=O stretch of the carboxy group at 1718 cm^{-1} is replaced by a band at 1654 cm^{-1} (Amide I) assigned to the C=O stretch in the corresponding amide; the band assigned to the C=C stretch of MWCNT at 1578 cm^{-1} persists; and the bands assigned to the C−O stretch and out of plane deformations between 1300 and 1100 cm^{-1} and at 1097 cm^{-1} are no longer observed.

Second, the bands assigned to the amine group in the AEPA are absent and have been replaced by bands consistent with formation of the amide. Specifically, the band at 1638 cm^{-1}, assigned to the N−H bending (scissoring) vibration in the amine (AEPA), is no longer observed. This would typically be replaced by a band at about 1570 cm^{-1} (Amide II), assigned to the N−H bending (scissoring) vibration in the secondary amide, that is about half the intensity of the Amide I band. However, this band is not distinguishable from that assigned to the C=C stretch of MWCNT at 1578 cm^{-1}. The band at 1074 cm^{-1}, assigned to the C−N stretching vibration in the amine (AEPA), is replaced by a band at 1261 cm^{-1} (Amide III) assigned to the C−N stretching vibration in the secondary amide.

The bands assigned to the methylene groups of the covalently linked AEPA are still observed. The bands assigned to the C−H bending (scissoring) vibrations of the methylene groups linked to the amide and phos-

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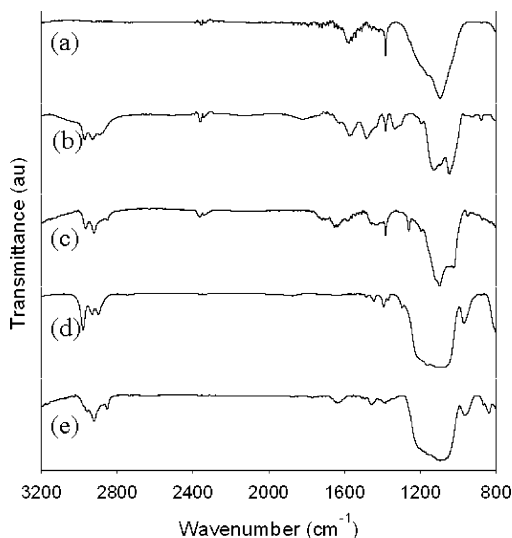
Figure 3. FT-IR spectrum of (a) carboxy-modified MWCNTs, (b) APTES, (c) APTES-modified MWCNTs, (d) SiO₂ nanoparticles, and (e) SiO₂ nanoparticles assembled at APTES-modified MWCNTs.

phonic acid groups are observed at 1458 cm⁻¹ and as a shoulder at approximately 1420 cm⁻¹, respectively. The fact that the band assigned to the methylene group linked to the amine is shifted to lower frequencies, while the band assigned to the phosphonic acid group is not, is consistent with amide formation.

Finally, the bands assigned to the phosphonic acid group are broadened and appear to be shifted to lower frequencies. These observations would suggest that the phosphonic acid groups are in a relatively heterogeneous environment and that they may be hydrogen-bonded to each other.

Shown in Figure 3 are the FT-IR spectra of carboxy-modified MWCNTs, APTES, and APTES-modified MWCNTs.

The FT-IR spectrum of carboxy-modified MWCNTs (Figure 3a), as discussed in detail above, is in good agreement with previously reported spectra.[23]

The FT-IR spectrum of APTES is also shown (Figure 3b) and is also in good agreement with previously reported spectra.[24] There are two bands which may be assigned to the amine group. The first at 1626 cm⁻¹ is assigned to the N–H bending (scissoring) vibration; and the second at 1051 cm⁻¹ is assigned (in part) to the C–N stretching vibration.

There are a series of bands which may be assigned to the methyl and methylene groups. The first at 2972 cm⁻¹ is assigned to the asymmetric C–H stretching vibration of the methyl groups. The second at 2930 cm⁻¹ is assigned to the asymmetric C–H stretching vibration of the methylene group. The third at 2892 cm⁻¹ is assigned to the symmetric C–H stretching mode of the methyl group. The fourth, a shoulder, at 2853 cm⁻¹ is assigned to the symmetric C–H stretching vibration of the methylene group. The fifth at 1484 cm⁻¹ is assigned to the C–H bending (scissoring) vibration of the methylene group linked directly to the amine; the sixth at about 1430 cm⁻¹ is assigned to the C–H bending (scissoring) vibration of the methylene group linked to the alkoxy-silane.

There are a series of bands observed between 1200 and 800 cm⁻¹ in the Si–O stretching region. The

assignment of these bands is difficult due to the fact that the bands are broad and overlap and due to the fact that the frequency of these bands may be affected by hydrogen bonding. Despite this, it is clear that this region of the APTES spectrum confirms the presence of an alkoxy-silane group.

Following coupling of APTES to carboxy-modified MWCNTs, the FT-IR spectrum of the resulting APTES-modified MWCNTs was measured (Figure 3c). Again, the observed spectral changes are consistent with previous reports and confirm that coupling has occurred.[25]

First, the bands assigned to the carboxy group on the surface of the MWCNT are absent and have been replaced by bands consistent with formation of the amide. Specifically, the band assigned to the C=O stretch of the carboxy group at 1718 cm⁻¹ is replaced by a band at 1655 cm⁻¹ (Amide I) assigned to the C=O stretch in the corresponding amide; the band assigned to the C=C stretch of MWCNT at 1578 cm⁻¹ persists; and finally the bands assigned to the C–O stretch and out of plane deformations between 1300 and 1100 cm⁻¹ and at 1096 cm⁻¹ are no longer observed.

Second, the bands assigned to the amine group in the APTES are absent and have been replaced by bands consistent with the formation of the amide. Specifically, the band at 1626 cm⁻¹, assigned to the N–H bending (scissoring) vibration in the amine (APTES), is no longer observed. This would typically be replaced by a band at about 1570 cm⁻¹ (Amide II), assigned to the N–H bending (scissoring) vibration in the secondary amide, that is about half the intensity of the Amide I band. However, this band is not distinguishable from that assigned to the C=C stretch of MWCNTs at 1578 cm⁻¹. The band at 1075 cm⁻¹, assigned to the C–N stretching vibration in the amine (APTES), is replaced by a band at 1261 cm⁻¹ (Amide III) assigned to the C–N stretching vibration in the secondary amide.

The bands assigned to the methyl and methylene groups are still observed. The bands assigned to the C–H bending (scissoring) vibrations of the methylene groups linked to the amide and siloxane groups are observed at 1459 cm⁻¹ and as a shoulder at approximately 1430 cm⁻¹, respectively. The fact that the band assigned to the methylene group linked to the amine is shifted to a lower frequency, while the band assigned to the methylene group linked to the alkoxy-silane group is not, is consistent with amide formation.

Further evidence for the covalent modification of carboxy-MWCNTs was provided by the EDX spectra shown in Figure 4. The EDX spectrum of AEPA-modified MWCNTs indicates the presence of phosphorus, which was not observed in the spectra of umodified purified and carboxy-modified MWCNTs. The possibility of unreacted AEPA molecules being present in the AEPA-modified MWCNTs was minimized by extensive washing using a membrane filtration apparatus. Silicon was also observed in the spectrum of the AEPA-modified MWCNTs. This was accounted for by silica impurities present following the sonication of the sample in glass. Similar impurities have been reported by Zettl et al. in the EDX spectra of SWNTs [**14m**]. It was found that repeating the washing procedure had little effect on this impurity. As a consequence, a reliable EDX analysis of
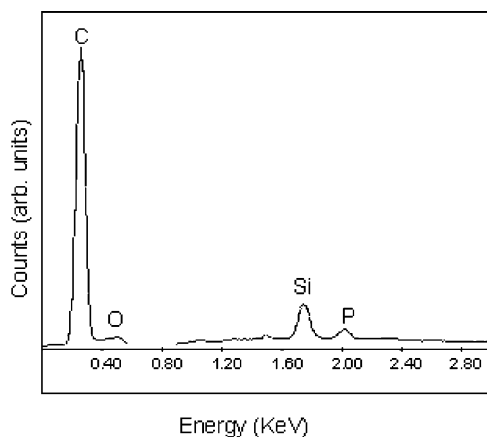
Figure 4. EDX spectrum of AEPA-modified MWCNTs.

the APTES-modified MWCNTs was precluded and no findings have been reported.

Preparation of Metal Oxide Nanoparticle Dispersions. An aqueous dispersion of titanium dioxide nanoparticles was prepared using a procedure similar to that originally described by Barbe et al.[19] As may be seen from Figure 5a, the nanoparticles are approximately spherical and possess an average diameter of 5 nm and a polydispersity of 1.31. The corresponding FT-IR spectrum is shown in Figure 2d.

A chloroformic dispersion of titanium dioxide nanoparticles was also prepared using a procedure similar to that originally described by Kotov et al.[20] Again, these nanoparticles are approximately spherical and possess an average diameter of 4 nm and a polydispersity of 1.19.

An ethanolic dispersion of silicon dioxide nanoparticles was prepared using a procedure similar to that originally described by Stöber et al. and subsequently modified by van Blaaderen and Vrij.[21,22] As may be seen from Figure 5b, the nanoparticles are approximately spherical and possess an average diameter of 7 nm and a polydispersity of 1.21. The corresponding FT-IR spectrum is shown in Figure 3d.

Templated Assembly of Titania (Semiconductor) Nanoparticles at the Surfaces of AEPA-Modified Multiwalled Carbon Nanotubes. It is known that phosphonic acids are strongly chemisorbed at the surface of a titanium dioxide nanoparticle. For example, Pechy et al.[26] reported the sensitization of nanostructured titanium dioxide films by the chemisorption of a ruthenium complex incorporating phosphonated bipyridyl ligands. Gao et al.[27] and Hahner et al.[28] have both studied the adsorption of long-chain alkane phosphonic acids at metal oxide substrates, including titanium dioxide, while Pawsey et al.[29] have studied the adsorption of similar molecules on metal oxide nanoparticles, including titanium dioxide nanoparticles.

In this context an aliquot of an aqueous dispersion of TiO_2 nanoparticles was added to a suspension of AEPA-modified MWCNTs in deionized water. Following equili-

bration of the resulting suspension for 24 h and as may be seen from the TEM in Figure 6a, a monolayer of TiO_2 nanoparticles is adsorbed at the surface of the AEPA-modified MWCNTs.

To confirm that the templated assembly was accompanied by bond formation, the infrared spectra of the AEPA-modified MWCNTs measured before (Figure 2c) and after (Figure 2e) adsorption of the TiO_2 nanoparticles and were compared. It is clear that there are very significant differences between these spectra.

In the first instance, the bands at 2921 and 2852 cm^{-1} assigned to the asymmetric and symmetric C−H stretches of the methylene groups in AEPA-modified MWCNTs, are reduced in intensity and shifted to lower frequencies. This is consistent with their adsorption at the surface of the nanoparticle.[29] Furthermore, the bands assigned to the methylene groups of the covalently linked AEPA are also reduced in intensity and are no longer observed. Finally, the region of the spectrum comprised of the bands assigned to the P−O stretches shows, as might have been expected, very significant changes. Specifically, these bands are broadened.

To further support the assertion that the driving force for the templated assembly of TiO_2 nanoparticles at the surface of AEPA-modified MWCNTs is the chemisorption of the phosphonic acid group at the surface of the TiO_2 nanoparticles, a number of control experiments were performed.

In the first instance, an aliquot of a chloroformic dispersion of CTAB-modified TiO_2 nanoparticles was added to a chloroformic suspension of PA-modified MWCNTs. Following equilibration for 24 h, as may be seen from the TEM in Figure 6b, there are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that, in the absence of phosphonic acid groups on the surface of the MWCNT, there is no driving force for adsorption of TiO_2 nanoparticles. It is further concluded that the presence of any unreacted carboxylic acid groups present at the surface of MWCNT do not measurably contribute under these conditions to templated assembly.

In the second instance, an aliquot of an aqueous dispersion of PPA-modified TiO_2 nanoparticles was added to an aqueous suspension of AEPA-modified MWCNTs. Following equilibration for 24 h, as may be seen from the TEM in Figure 6b, there are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that in even in the presence of phosphonic acid groups on the surface of the MWCNT, there is no driving force for adsorption of TiO_2 nanoparticles if these nanoparticles are sterically hindered from approaching the surface of MWCNTs.

In the final instance, an aliquot of an aqueous dispersion of TiO_2 nanoparticles was added to an aliquot of a chloroformic suspension of unmodified purified MWCNTs. The two-phase mixture was vigorously sonicated for 10 min. Following equilibration of the suspension for 24 h, as may be seen from the TEM in Figure 6d, there are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that in there is no intrinsic driving force for adsorption of titania nanoparticles at the surface of a MWCNT.

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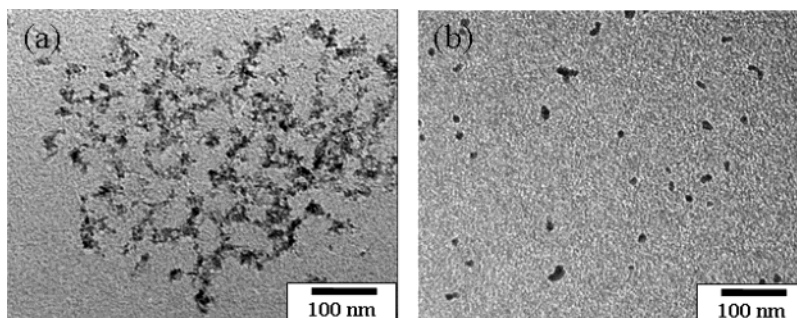(29) Pawsey, S.; Yach, K.; Reven, L. *Langmuir* **2002**, *18*, 5205.

Figure 5. (a) TEM of nanoparticles in aqueous TiO_2 dispersion. (b) TEM of nanoparticles in ethanolic SiO_2 dispersion.
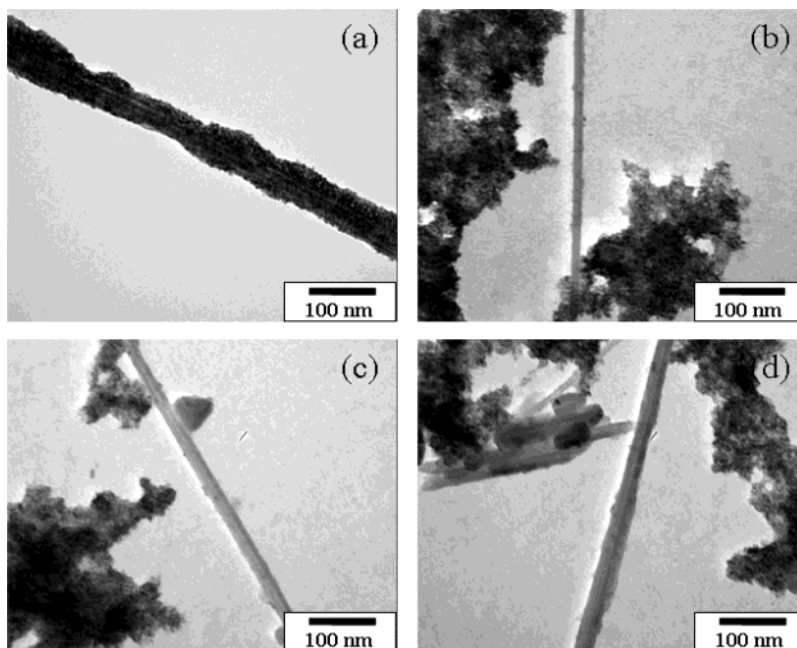

Figure 6. TEM of TiO_2 nanoparticles assembled from solution at the surface of AEPA-modified MWCNTs. Corresponding control experiments in which (b) PPA-modified TiO_2 nanoparticles were combined with AEPA-modified MWCNTs, (c) TiO_2 nanoparticles were combined with PA-modified MWCNTs, and (d) TiO_2 nanoparticles were combined with purified-unmodified MWCNTs.

Generally, it is concluded that MWCNT templated assembly of a TiO_2 nanoparticles is observed if there are phosphonic acid groups at the surface of the MWCNTs and the approach of the TiO_2 nanoparticles to the surface of the above MWCNTs is not sterically hindered.

Templated Assembly of Titania (Semiconductor) Nanoparticles at the Surfaces of APTES-Modified Multiwalled Carbon Nanotubes. The chemisorption of alkoxy-silanes at SiO_2 substrates is well-known and is accompanied by siloxane bond formation.[30,31] Specifically the chemisorption of the triethoxysilane APTES at SiO_2 substrates has been demonstrated.

A number of workers have reported the deposition of SiO_2 on the surface of CNTs,[32–36] in some cases from solution. Other reports have described the deposition of CNTs on silica surfaces. For example, Fu et al. reported the deposition of APTES-modified SWNTs on silicon substrates [**14f**].

In this context, an aliquot of an ethanolic dispersion of SiO_2 nanoparticles was added to a freshly sonicated ethanolic suspension of APTES-modified MWCNTs. The suspension was allowed to equilibrate for 24 h. As may be seen from the TEM in Figure 7a and as was expected, the APTES-modified MWCNTs template the assembly of a monolayer of SiO_2 nanoparticles.

To confirm that the templated assembly was accompanied by siloxane bond formation, the infrared spectra of the APTES-modified MWCNTs were measured before (Figure 3a) and after (Figure 3e) adsorption of the SiO_2 nanoparticles and were compared. It is clear that there are very significant differences between these spectra.

In the first instance, the C−H stretching region of the spectrum is simplified. The bands assigned to the asymmetric and symmetric C−H stretches of the methyl group are no longer observed. This is consistent with the elimination of the ethoxy groups from APTES-modified MWCNTs in the course of siloxane bond

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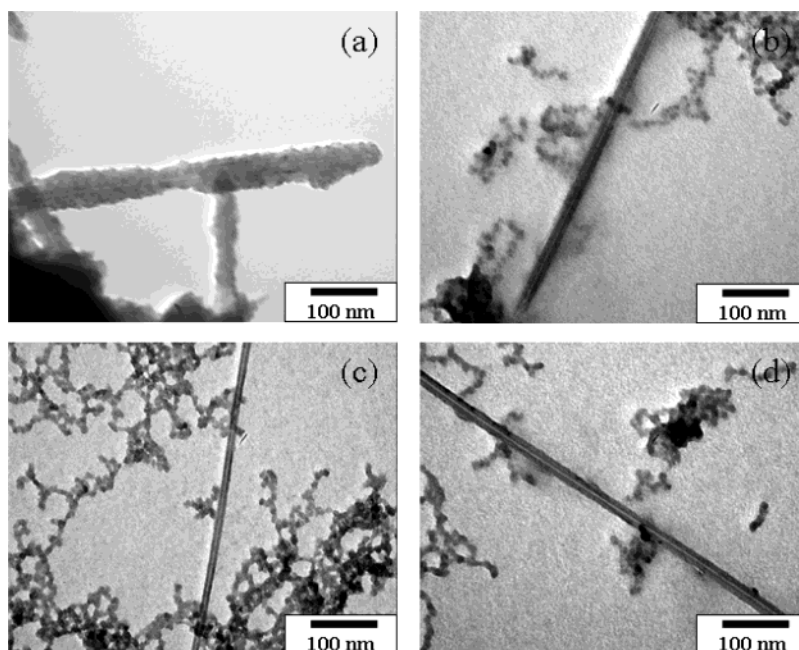
Figure 7. TEM of SiO$_2$ nanoparticles assembled from solution at the surface of APTES-modified MWCNTs. Corresponding control experiments in which (b) APTES-modified SiO$_2$ nanoparticles were combined with APTES-modified MWCNTs, (c) SiO$_2$ nanoparticles were combined with PA-modified MWCNTs, and (d) SiO$_2$ nanoparticles were combined with purified-unmodified MWCNTs.

formation. Furthermore, the bands at 2921 and 2852 cm^{-1} assigned to the asymmetric and symmetric C−H stretches of the methylene groups in APTES-modified MWCNTs are shifted to lower frequencies. This is consistent with siloxane bond formation.[30]

In the second instance, the ethoxy groups from APTES in the course of siloxane bond formation would be expected to simplify the C−H bending region of the spectrum and clearly this is the case. The band at 1459 cm^{-1} is assigned to a superposition of the methylene groups alpha and beta to the amide group, while the band at 1385 cm^{-1} is assigned to the methylene group alpha to the siloxane.

In the final instance, the region of the spectrum comprised on the bands assigned to the Si−O stretches shows, as might have been expected, very significant changes. Specifically, the spectrum is now dominated by the absorption of the SiO$_2$ nanoparticles.

To further support the assertion that the driving force for the templated assembly of SiO$_2$ nanoparticles at the surface of APTES-modified MWCNTs is the chemisorption of the triethoxysilane group at the surface of the SiO$_2$ nanoparticles, a number of control experiments were performed.

In the first instance, an aliquot of an ethanolic dispersion of SiO$_2$ nanoparticles was added to an aliquot of a chloroformic suspension of PA-modified MWCNTs. Following equilibration of the suspension for 24 h, as may be seen from the TEM in Figure 7b, there are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that, in the absence of triethoxysilane groups on the surface of the MWCNT, there is no driving force for adsorption of SiO$_2$ nanoparticles.

In the second instance, an aliquot of an ethanolic dispersion of APTES-modified SiO$_2$ nanoparticles was added to an ethanolic suspension of APTES-modified MWCNTs. Following equilibration of the suspension for 24 h, as may be seen from the TEM in Figure 7c, there

are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that even in the presence of triethoxysilane groups on the surface of the MWCNT, there is no driving force for adsorption of SiO$_2$ nanoparticles if these nanoparticles are sterically hindered from approaching the surface of the MWCNTs.

In the final instance, an aliquot of an ethanolic dispersion of SiO$_2$ nanoparticles was added to an aliquot of a chloroformic suspension of purified but otherwise unmodified MWCNTs. Following equilibration of the suspension for 24 h, as may be seen from the TEM in Figure 7d, there are no nanoparticles adsorbed at the surface of the MWCNT. It is concluded that there is no intrinsic driving force for adsorption of silica nanoparticles at the surface of a MWCNT.

Generally, it is concluded that MWCNT templated assembly of SiO$_2$ nanoparticles is observed if there are triethoxysilane groups at the surface of the MWCNTs and the approach of the SiO$_2$ nanoparticles to the surface of the above MWCNTs is not sterically hindered.

Conclusions

We have reported on the preparation and characterization of phosphonic acid-modified and alkoxy-silane-modified MWCNTs. We have also reported on the use of these MWCNTs to template the assembly of titanium dioxide and silica nanoparticles, respectively.

This represents an extension of our recent work in which modified MWCNTs were used to template the assembly of metal nanoparticles to include the use of modified MWCNTs to template the assembly of semiconductor and insulator nanoparticles.

This extension of our work widens the range of possible applications for these nanowires, in the case of metal nanoparticles, and nanowire-like forms, in the case of semiconductor and insulator nanoparticles.

In the case of these nanowire-like forms, they can certainly be viewed as potential building blocks for nanoscale switches. They may also be viewed as potential building blocks for sensors and other devices.

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