

Dendrimer-Mediated Synthesis of Water-Dispersible Carbon-Nanotube-Supported Oxide Nanoparticles

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SiO₂ and TiO₂ nanoparticles of 35–45 nm size were synthesized by hydrolysis of Si and Ti precursors, respectively, in aqueous dispersions of multiwalled carbon nanotubes, which were surface-modified by covalent bonds with dendrimers. Nanoparticle-attached carbon nanotubes were water-dispersible, owing to the contribution of water-soluble dendrimers. The growth of the nanoparticles and the stability of the hybrids depended on the hydrolysis rate of the precursors.

Introduction

Nanomaterials exhibiting a variety of novel properties have been developed for many applicable purposes, such as optical or electronic devices, drug delivery systems, chemical or biological sensors, catalysts, and so on.¹ In fact, to optimize the applications of nanomaterials in these fields, it is necessary to integrate different functional nanomaterials and to create new hybrid materials with various properties and applications.² Nowadays, two of the most investigated materials in nanoscience are carbon nanotubes (CNTs) and nanoparticles (NPs). As well-known, carbon nanotubes have unique properties, such as mechanical strength, chemical stability, and electric conductivity, and are particularly suitable to assemble nanodevices.³ However, since the indispersibility of CNTs in media discourages greatly their applications in many fields, some investigations have been done to improve the dispersibility of CNTs by introducing functional groups and/or organic molecules onto CNT surfaces by a covalent or noncovalent binding method.⁴

Meanwhile, oxide NPs have many unique properties that are demanded in many applications. For instance, SiO₂ NPs are widely used as a scaffold for biosensing and catalytic purposes due to their manufacturability and compatibility with biomolecules;⁵ TiO₂ NPs possess a photocatalytic property, which is useful in both industrially and environmentally beneficial applications.⁶ As a result, complexation of CNTs with NPs, especially metal NPs, has attracted great attention,⁷ whereas successful results of the combination of CNTs with oxide NPs are very few. Lee and Sigmund⁸ have successfully deposited TiO₂ NPs on multiwalled carbon nanotubes (MWCNTs) by controllable hydrolysis and condensation, where polyethylenimine was preadsorbed on CNTs to produce water-dispersible CNTs. Recently, Bottini et al.⁹ have reported the covalent binding of MWCNTs with silica NPs, yielding hybrid composites with various morphologies. They used (aminopropyl)-triethoxysilane to functionalize CNTs and a water-in-oil microemulsion as a reaction matrix to control the sizes of the nanobeads. Silica-coated magnetic NPs were also deposited on MWCNTs by Deng et al.¹⁰ In this preparation, NPs were prefabricated before the coupling to the CNTs.

In this work, we reported a new, simple, and versatile method to produce and attach SiO₂ and TiO₂ NPs on the surface of MWCNTs through intermediation of chemically bonded dendrimers. As shown in Scheme 1, oxide NPs were directly grown onto dendrimer-functionalized MWCNTs (abbreviated as CNT/DENs) by hydrolysis of tetraethyl orthosilicate (TEOS) or titanium tetraisopropoxide (TTIP) in water. As-prepared CNT/DEN has been utilized for size-controlled *in situ* synthesis of metal nanoparticles.⁷ The content of covalently linked dendrimers in CNT/DEN was about 40 wt %. Such high coverage of dendrimers was effective for depositing a large amount of metal NPs on the surface of CNTs, yielding the water-dispersible and stable CNT/DEN/NPs.

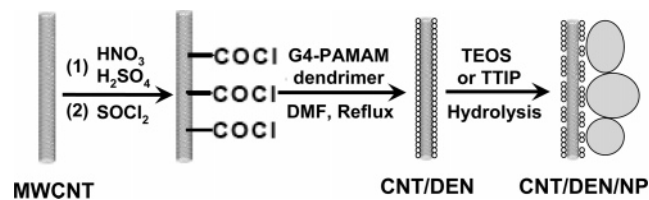
Experimental Section

MWCNTs were purchased from Wako Pure Chemical Industries, Ltd. and purified by refluxing in concentrated HNO₃ for 2 days, followed by filtering with a Millipore VC membrane (pore size 0.1 μm) and drying overnight at 60 °C. Acid-treated MWCNTs (CNT–COOH's) were obtained by refluxing purified MWCNTs in concentrated HNO₃/H₂SO₄ (3:1, v/v) for 24 h, and then they were sequentially treated with thionyl chloride to introduce chloride acid groups on the CNTs.¹¹ CNT/DENs were prepared by reacting thionyl-treated MWCNTs with NH₂-terminated fourth-generation poly(amidoamine) (G4-PAMAM) dendrimers (10 wt % in methanol, a product from Aldrich) in anhydrous dimethylformamide (DMF), followed by filtering, rinsing, drying, and redispersing in water. The covalent linkages between MWCNTs and dendrimers were proved by infrared absorption spectrometry (Bio-Rad FTS 575C instrument).

For the synthesis of CNT/DEN-supported SiO₂ NPs, excess TEOS in ethanol was added dropwise into the aqueous dispersion of CNT/DEN under vigorous stirring, and the reaction mixture was aged for 10 days. The mixture was filtered with a Millipore VC membrane (pore size 0.22 μm) and rinsed at least 10 times with water to eliminate completely free oxide NPs. Then the hybrids were dispersed in water for further characterization. The control experiment was carried out by preparing oxide NPs (CNT/NPs) from CNT–COOH's (without dendrimers) according to the same procedure as described above. The products were filtered and rinsed.

Transmission electron microscopic (TEM) images were obtained on a Hitachi H-7000 equipped with a CCD camera,

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SCHEME 1: Schematic Illustration of the Dendrimer-Mediated Synthesis of CNT-Supported Oxide NPs

operating at an accelerating voltage of 100 kV. The specimens for TEM were prepared by dropping the dispersion of a product onto the carbon-coated copper grid, followed by air-drying. Ultraviolet–visible (UV–vis) absorption spectroscopic measurements were performed on a Shimadzu UV 2200 spectrometer with a 1 cm quartz cell.

Results and Discussion

It is known that dendrimers with well-defined structures and definite compositions are especially useful to synthesize metal NPs. Many kinds of metal NPs with different sizes and shapes have been produced by using dendrimers,¹² but the cases of using dendrimers to synthesize oxide NPs are rare. Very recently, Juttukonda et al.¹³ found that dendrimers were good protectors (or stabilizers) for SnO₂ NPs. A successful example before them was reported by Nakanishi and Imae,¹⁴ by whom TiO₂ NPs were manufactured by hydrolysis of TiCl₄ or TTIP in aqueous solutions of dendrimers or dendrons, respectively. The dendritic polymer-protected TiO₂ NPs showed a remarkably enhanced photocatalytic activity. However, to the best of our

knowledge, there is no report of the use of dendritic polymers to synthesize and anchor oxide NPs on the surface of CNTs.

In the present work, the successful production and hybridization of SiO₂ and TiO₂ NPs on CNT/DEN were confirmed by TEM. TEM images of purified MWCNTs and CNT/DENs and the hybrids of CNT/DEN with oxide NPs, abbreviated as CNT/DEN/SiO₂ and CNT/DEN/TiO₂, are shown in Figure 1. Differently from MWCNTs (Figure 1a), a thin layer of 4–5 nm thickness was found on the surface of CNT/DENs (Figure 1b). It was assumed to consist of covalently bonded dendrimers, because the diameter of the G4-PAMAM dendrimer is in the range of 4–5 nm.¹⁵ Such thin shells were uniformly observed on the whole surface of the CNTs. From Figure 1c,d, it is evident that oxide NPs were attached to the whole surface of CNT/DENs and no free NPs existed out of the CNT region, indicating that oxide NPs were coordinated with dendrimers on the CNTs. As a result, the hybrid materials were very stable: after sonication for 5 h in water, very few exfoliated oxide NPs were detected by TEM.

In addition, SiO₂ NPs were in the range of 35–45 nm in size and coated the CNT surface with an islandlike distribution. TiO₂ NPs had sizes similar to those of SiO₂ NPs but covered almost the whole surface of CNT/DENs as with a pearl necklace. The difference between the morphologies of CNT/DEN/SiO₂ and CNT/DEN/TiO₂ may originate from the different hydrolysis rates of TEOS and TTIP in water. When SiO₂ NPs were synthesized, the mixture of TEOS and CNT/DENs was aged for 10 days to ensure the complete hydrolysis of TEOS. As for TiO₂ NPs, no aging was needed: when TTIP was dropped into the aqueous dispersion of CNT/DENs, an opalescent dispersion

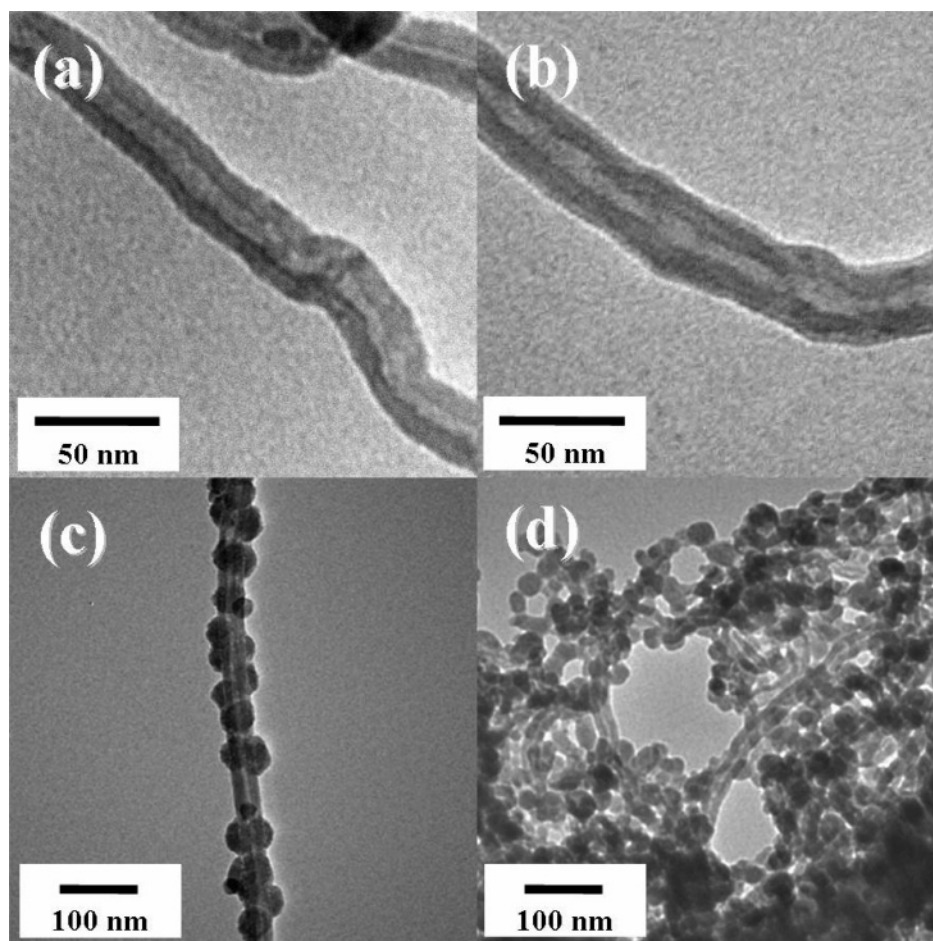


Figure 1. TEM pictures of (a) MWCNTs, (b) CNT/DENs, (c) CNT/DEN/SiO₂, and (d) CNT/DEN/TiO₂.

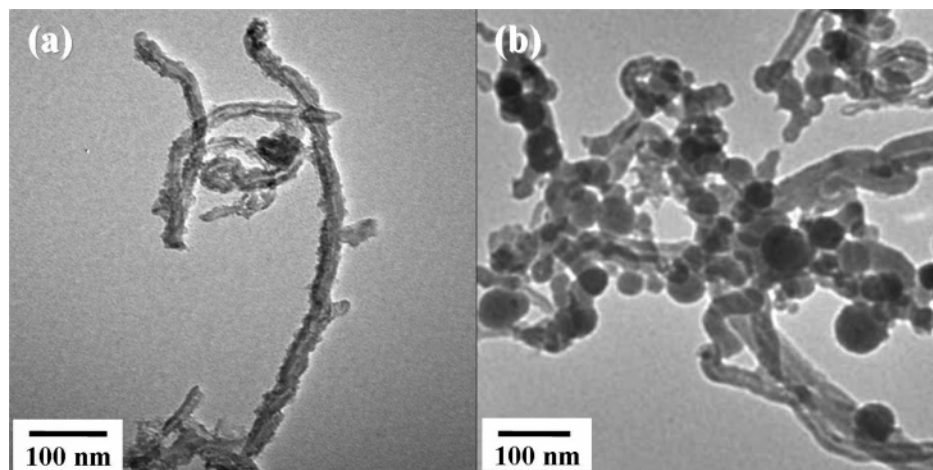


Figure 2. TEM pictures of (a) CNT/SiO₂ and (b) CNT/TiO₂ synthesized in the presence of CNT-COOH's without dendrimers.

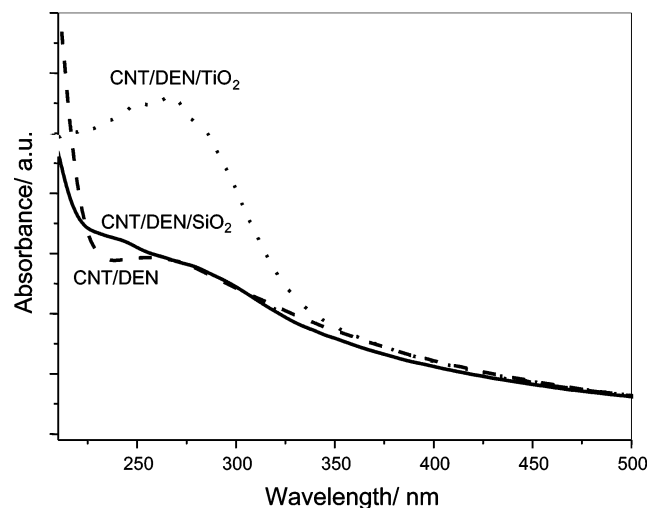


Figure 3. UV-vis absorption spectra of aqueous dispersions of CNT/DENs, CNT/DEN/SiO₂, and CNT/DEN/TiO₂ just after preparation.

was immediately visualized, supporting the formation of TiO₂ NPs. These results indicate that the hydrolysis rate of TTIP is much faster than that of TEOS, so that TiO₂ NPs grow more quickly than SiO₂ NPs and thus a large number of TiO₂ NPs are coordinated with dendrimers and grow on the CNTs.

To reveal the essential role of dendrimers in the formation of NPs and the process of hybridization on CNTs, control experiments were carried out by hydrolyzing the precursors in aqueous dispersions of acid-treated MWCNTs (CNT-COOH's) without dendrimers. The products were characterized by TEM, and the pictures are shown in Figure 2. In the absence of dendrimers, no SiO₂ NPs were remarkably detected even after aging of the reaction mixture for 15 days (Figure 2a). It was confirmed from this result that a large amount of SiO₂ NPs could not be formed without dendrimers on the CNTs. As for TiO₂ NPs, a few particles were seen on the CNT-COOH surface, and some CNT-COOH's were free from NPs (Figure 2b). The sizes of TiO₂ NPs ranged from 50 to 150 nm and were large in comparison with the dendrimer-mediated case. The results unambiguously prove that dendrimers are very important as scaffolds for the formation, attachment, and growth of oxide NPs on CNTs.

It should be noticed that the as-obtained hybrid materials were well dispersed in water, since water-soluble dendrimers were bonded to CNTs. UV-vis absorption spectra of CNT/DENs, CNT/DEN/SiO₂, and CNT/DEN/TiO₂ are displayed in

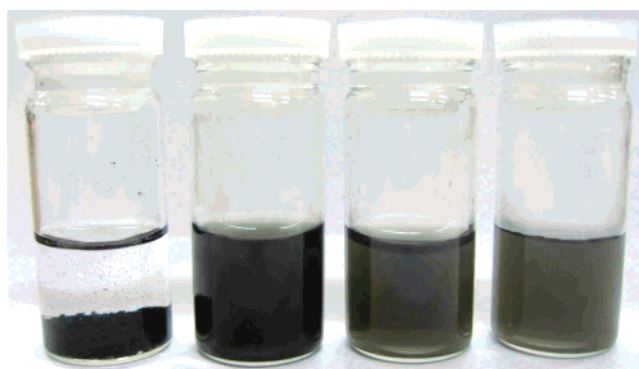


Figure 4. Comparison of the stability of MWCNTs, CNT/DENs, CNT/DEN/SiO₂, and CNT/DEN/TiO₂ (from left to right) in water.

Figure 3. In the range of 220–500 nm, CNT/DEN/SiO₂ showed increasing absorbance toward shorter wavelengths, similar to the spectrum of CNT/DENs, and no distinct absorption band was observed. However, the spectrum of CNT/DEN/TiO₂ showed a dramatically intensified absorption band at 270 nm, which was in agreement with the absorption band of dendrimer-protected TiO₂ NPs.¹⁴ The electronic absorption results confirmed the successful synthesis and the attachment of TiO₂ NPs to CNT/DENs.

It should also be noted that the stabilities of CNT/DEN/SiO₂ and CNT/DEN/TiO₂ in water were slightly different from each other (see Figure 4). The dispersion of CNT/DEN/SiO₂ was stable for at least 2 months, just like the dispersion of CNT/DENs but unlike the dispersion of MWCNTs. However, the dispersion of CNT/DEN/TiO₂ gave rise to some precipitates after two weeks, which may be due to the high loading of TiO₂ NPs in the hybrid of CNT/DEN/TiO₂.

Conclusions

SiO₂ and TiO₂ NPs have been successfully grown on dendrimer-modified MWCNTs. Control experiments proved that the covalently bonded dendrimers played an essential role in the formation, fixation, and growth of oxide NPs on CNT surfaces. TiO₂ NPs were more abundantly attached on CNT/DENs than SiO₂ NPs, owing to the different hydrolysis rates, although the hybrid CNT/DEN/TiO₂ was unstable in comparison with CNT/DEN/SiO₂. Obviously the method in the present work can be generalized to synthesize other oxide NPs supported by CNTs, such as ZnO, SnO₂, and Fe₃O₄. Moreover, since water-

soluble dendrimers were attached by covalent bonds, the dispersibility and stability of the as-obtained products in media were promoted. These aspects of the present procedure will open the way for many applications such as biocompatible delivery systems, biosensors, electronic devices, photonic devices, and heterogeneous catalysts.

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