Dispersion and Modification of Carbon Nanotubes Using a Surface Gel–Sol Technique

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The peptization process of titania gel in acidic aqueous media has been utilized for the dispersion and modification of carbon nanotubes (CNTs) in water, up to single tube level. Agglomerates and bundles of CNTs were first treated with titania precursors using a controlled adsorption process, and then the carbon nanotubes were exposed to acid moistures for forming titania gels on the surface of CNTs. Subsequently, the composite of titania and CNTs was introduced to aqueous media for the peptization of titania gel agglomerates. With the progressing of the peptization process (i.e., destruction of the titania gel agglomerates and redispersion into primary grains), these agglomerated CNTs were "drawn" apart from each other to form individual suspensions.

Tailoring the surface properties of carbon nanotubes (CNTs) is a key step for realizing the practical applications of CNTs.[1–6] In common routes for modifying CNTs, CNTs are first suspended in solvent media using severe means such as sonication or strong oxidizations to obtain individual suspensions of nanotubes for further processing.[7] However, these severe treatments are usually found cutting the carbon nanotubes short and introducing defects to the walls of carbon nanotubes, thus compromising the mechanical properties of carbon nanotubes greatly.[8] In this letter, on a complete reversely way, we modified the agglomerates and bundles of carbon nanotubes directly. Summarily, agglomerates and bundles of CNTs were first treated with precursors of titania using a controlled adsorption process, and then the carbon nanotubes were exposed to acid moistures for forming titania gels on the surface of CNTs. Subsequently, the composite of titania and CNTs was introduced to aqueous media for the peptization of titania agglomerates. With the progressing of peptization of titania in acidic aqueous media (i.e., destruction of the agglomerates and redispersion into primary grains),[9] these agglomerated CNTs were "drawn" apart from each other to form individual suspensions (Figure 1). The final individual CNTs were further stabilized by the surface-anchored and -disassociated titania nanoparticles (Figure 2b). The basis and procedures of our method are schematically shown in Figure 1. The instruments for the controlled adsorption (Figure 2a) and peptization process of titania gels on CNTs (Figure 2b) are schematically shown in Figure 2.

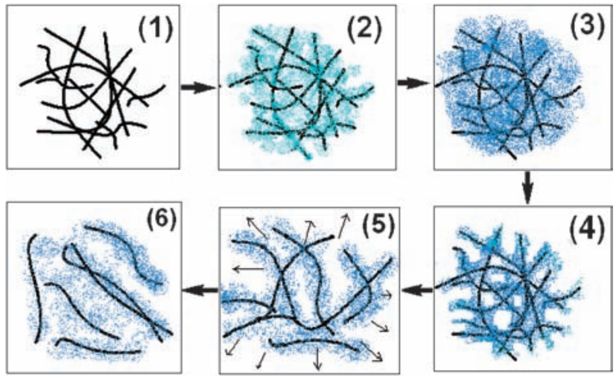

Figure 1. Dispersing and modifying CNTs using a surface gel–sol technique: (1) Agglomerates and bundles of CNTs, (2) treating the agglomerates and bundles of CNTs with titania precursors, (3) Forming titania gels on agglomerates and bundles of CNTs, (4)–(6) Dispersing CNTs in aqueous media through the peptization process of titania gels.

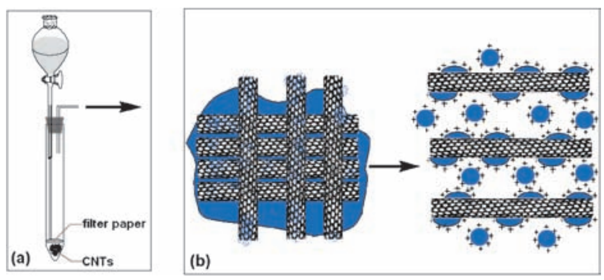

Figure 2. (a) Instruments for the controlled adsorption of TIP to CNTs and (b) Peptization process of titania gels on CNTs.

The preparation of colloidal titania nanoparticles via the hydrolysis and condensation of alkoxides is very familiar to chemists. The process of forming stable colloidal titania nanoparticles from alkoxides is also very complex and includes several steps. The results of previous research[10] show that usually there are several steps involved. During hydrolysis of the alkoxides, the first step is the nucleation and growth of primary particles which then aggregate to form large clusters and precipitates rapidly. Second step is slow peptization of the aggregates. In the end this step precipitates disappear completely, and a translucent suspension forms. Based on these principles, we utilize the peptization process of titania aggregates in aqueous media to disperse and modify carbon nanotubes.

Both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes can be modified and dispersed via this surface gel–sol technique. In a typical procedure, SWNTs (purity of SWNTs >50%) from Shenzhen Nanotech Port Co., Ltd prepared by catalytic chemical vapor deposition method (CCVD) were used directly. (1) 0.25 g of CNTs was charged to the bottom of a test tube and covered with a piece of filter paper, and then the tube was evacuated for 1 h (Figure 2a). (2) 0.25 mL of titanium tetraisopropoxide (TIP) was diluted with 2 mL of absolute ethanol, and then the TIP solution was injected to the test tube for the adsorption of TIP to CNTs. (3) The resulting CNTs was dried under vacuum to evaporate ethanol. (4) Pick away the filter paper, and then 5 mL of 0.5% nitric acid solution was introduced to the test tube. The test tube was kept in hot

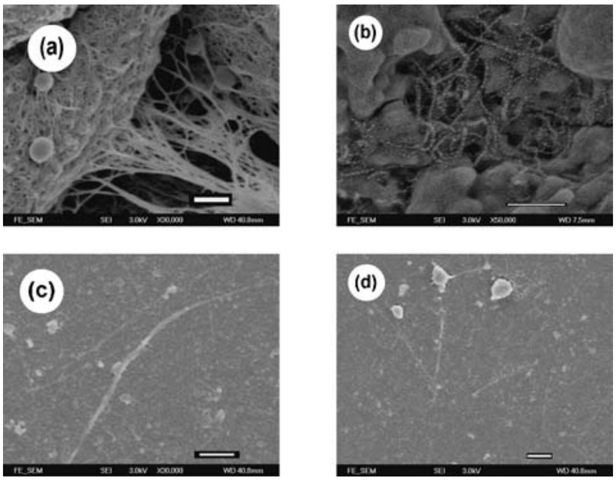

Figure 3. SEM images of: (a) Agglomerates and bundles of pristine SWNTs, (b) agglomerates and bundles of SWNTs having been modified with titania precursors, (c) bundles of SWNTs modified by titania, and (d) individuals of SWNTs modified and dispersed by titania nanoparticles (bar = 500 nm).

water bath (80–100 °C) for 1 h for the formation of titania gels on CNTs. The composite of CNTs and titania were introduced to 100 mL of 0.5% nitric acid solution, stirring at 80 °C for 1–6 h for the peptization of titania gels. With the progressing of peptization of the surface-anchored titania gels, CNTs were dispelled to individuals and were further stabilized by positively charged titania nanoparticles (Figure 2b). The process was monitored using scanning electron microscopy imaging method (FE-SEM, JEOL JSM-6335F).

Figure 3a presents a representative SEM image of pristine SWNTs, indicating that most of the SWNTs were typically held together as bundles and entangled agglomerates. Figure 3b shows a SEM image of the SWNT agglomerates having been modified with titania precursors, indicating that titania gel matrices have been formed between and on the agglomerates of CNTs. Figures 3c and 3d exhibit the SEM images of SWNT bundles and individuals having been modified and dispersed by titania nanoparticles. As shown in Figure 2b, the final SWNTs were not only modified by titania nanoparticles but also stabilized by the positively charged titania nanoparticles. Both the surface-anchored titania nanoparticles and the disassociated titania nanoparticles are used as solid dispersant to stabilize carbon nanotubes in aqueous media. Compared with previous work using highly charged nanoparticles as solid dispersants to prepare individual suspensions of carbon nanotubes,[11] the method developed in paper not only gives a new route for the dispersing of CNTs with surface-anchored solid particle dispersant but also provides a simple way for the modification of CNTs with titania nanoparticles.

This method can be reasonably extended to disperse and modify multiwalled carbon nanotubes (MWNTs). Figure 4a shows a typical TEM (transmission electron microscopy, JEOL JEM-2010) image of pristine MWNTs dispersed in water by ultrasonic treatment, indicating that MWNTs are presenting as entangled agglomerates. Figures 4b and 4c present the TEM images of MWNTs modified and suspended by titania nanoparticles, indicating that individual MWNTs have been obtained and that the surface-anchored titania nanoparticles can also be

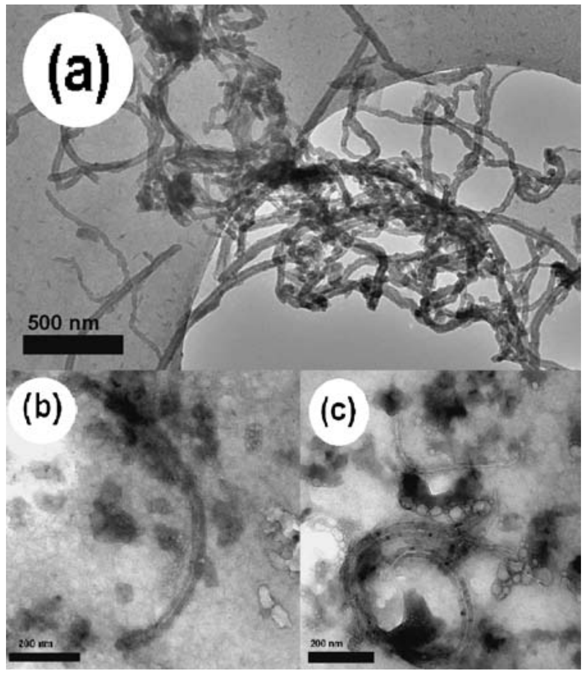

Figure 4. TEM images of: (a) Agglomerates and bundles of pristine MWNTs suspended in water by ultrasonic treatment, bar = 500 nm; (b) and (c) individual MWNTs suspended by titania nanoparticles (bar = 200 nm).

observed clearly.

In summary, a direct route, based on the peptization process of titania aggregates in aqueous media, for the modification and dispersion of CNTs was described. Agglomerates and bundles of SWNTs and MWNTs were modified with titania precursors directly without using any additional predispersing procedures. Aqueous suspensions of CNTs containing both individuals and bundles of carbon nanotubes are obtained, thus providing a new method for the dispersing of carbon nanotubes with solid particle dispersants. Compared with previous work for the functionalization of CNTs with titania,[12] our method is simpler and maneuverable and can be extended to other oxide precursors to prepare new functional CNTs-based materials. This titania–CNT product may find potential applications in ceramics, catalysis, biological sensing, and nanotube electronics.

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Published on the web (Advance View) October 7, 2006; doi:10.1246/cl.2006.1258