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Facile synthesis of solution-disposable carbon nanotube–TiO_2 hybrids in organic media

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ABSTRACT

Oleic acid-capped TiO_2 nanoparticles (NPs) were directly grown on untreated multiwalled carbon nanotubes (MWCNTs) from a stable titanium carboxylate complex through a solvothermal aminolysis process in organic media. The shape of the TiO_2 NPs loaded on the MWCNTs can be controlled from nanodots (~3 nm in diameter) to nanorods (~5 nm in diameter, 30–40 nm in length) by changing solvent components and by Co^{2+} doping. The resulting hybrids can be well dispersed in apolar organic solvents, which may provide possibilities for manipulating them in solutions for widespread applications.

1. Introduction

Carbon nanotubes (CNTs) have drawn extensive attention owing to their promising applications in various fields. One of the most important applications is to employ CNTs as scaffolds of various oxides like TiO_2 [1–8], MnO_2 [9], SnO_2 [10], ZnO [11] and V_2O_5 [12] to construct functional carbon-based hybrids or composites. Because of the incorporation of CNTs, the photocatalytic, electrochemical, and photoelectrochemical performances of these oxides are effectively improved. Many methods have recently been developed to prepare this kind of hybrids, including self-assembly [1,2], sol–gel coating [4–6], sonochemical processing [7], and liquid/vapor phase deposition [10,11]. Most of these methods are generally employed in aqueous reactive systems [1–10], where pristine hydrophobic CNTs require to be pre-oxidized in strong acids into their hydrophilic forms containing –OH and –COOH. However, the oxidization usually causes uncontrollable damage to the structure of CNTs [4,13], undesired surface defects and shortening of CNTs, which exerts adverse effects on the conductivity and mechanical properties of pristine CNTs. So it becomes important to develop new strategies for preparing uniform hybrids with pristine CNTs as starting supports.

Herein, we reported on such a preparative strategy based on direct growth of TiO_2 nanoparticles (NPs) on pristine multiwalled CNTs (MWCNTs) from a stable titanium carboxylate complex through a solvothermal aminolysis process in apolar organic media. Because the TiO_2 NPs are capped by long-chain molecules such as oleic acid (OLA) and thus hold a hydrophobic nature, the growth of the hydrophobic NPs on the hydrophobic MWCNTs is thus facilitated by the hydrophobic interaction between the NPs and the carbon support without the need to pre-oxidize the MWCNTs. Moreover, the hybrids can be well dispersed in apolar organic solvents, which may provide possibilities for manipulating them in solutions for widespread applications. The size and shape of the TiO_2 component can also be controlled by changing the components of the organic media and by Co^{2+} doping.

2. Experimental

2.1. Materials

MWCNTs (diameter of 10–20 nm, length of ~30 μm, and purity of >99.9%) were purchased from Times Nano of China. Other chemicals were purchased from Sinopharm Chemical Reagent Shanghai Co. Ltd.

2.2. Preparation of the titanium carboxylate complex

20 mL of OLA (CP) was dried at 50 °C in a rotary evaporator for 2 h, and then heated to 70 °C in air. 5 mL of tetra-n-butyl titanate ($C_{16}H_{36}O_4Ti$, ≥98%) was added and allowed to stir for 5 min. A bright yellow complex was produced and allowed to cool to room temperature.

2.3. Preparation of the MWCNT–TiO_2 hybrids

The titanium carboxylate complex was used as the precursor of the TiO_2 NPs [14,15], OLA as both a stabilizer and an apolar solvent, and triethyl amine ($C_6H_{15}N$, ≥99.0%) as a catalyst to promote the formation

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of the TiO_2 NPs through an aminolysis process [16]. Also, an alcoholic solution of $Co(NO_3)_2$ was introduced into the reaction system to improve the dispersibility of the hybrids in apolar organic solvents [15]. MWCNTs were directly used as supports without further treatment. In order to show the ability to tune the size and shape of TiO_2 NPs, we designed three different reaction systems: (1) complex solution (3 mL), MWCNTs (20 mg) and triethyl amine (0.2 mL); (2) complex solution (3 mL), MWCNTs (20 mg), triethyl amine (0.2 mL), alcohol (2 mL), and toluene (5 mL); (3) complex solution (3 mL), MWCNTs (20 mg), triethyl amine (0.2 mL), 0.25 M $Co(NO_3)_2$ alcoholic solution (2 mL), and toluene (5 mL).

In a typical procedure, the mixtures were stirred for 2 h, then transferred into a Teflon-lined stainless steel autoclave and heated to 150 °C for 15 h. The resultant hybrids were separated from the mother solution by high-speed centrifugation (10,000 rpm), re-suspended in toluene and centrifugated until the supernatant became colorless.

2.4. Material characterization

The transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2010F electron microscope operating at 200 kV. SEM images were taken with JEOL FESEM. X-ray powder diffraction (XRD) patterns were obtained from Japan Regaku D/max-2500 using Cu Kα radiation.

3. Results and discussion

The SEM and TEM images of the pristine MWCNTs (Fig. 1a) and the MWCNT–TiO_2 hybrid (hybrid-1, Fig. 1 b–d) prepared in the first system are shown. Compared with the pristine MWCNTs, the MWCNT–TiO_2 hybrid became "fatter" (Fig. 1a and b). The TEM image of a typical hybridized MWCNT (Fig. 1c) shows that long TiO_2 nanorods with uniform length and diameter (30–40 nm × 5 nm) densely self-assemble onto the MWCNTs and form uniform nanorod coatings. The high revolution TEM image of the hybrid shows clear lattice fringes of the anatase-type TiO_2. TiO_2 NPs [7] and flowers [4] have been assembled onto CNTs, but such CNT-based 1D–1D type hybrids have not been reported yet. Our successful preparation of the 1D–1D hybrid indicates that our method is effective. This novel hybrid may have important applications related to the 1D–1D hybrid architecture.

For the second reaction system, much shorter TiO_2 nanorods (<10 nm in length) were produced and formed Hybrid-2 (Fig. 1e).

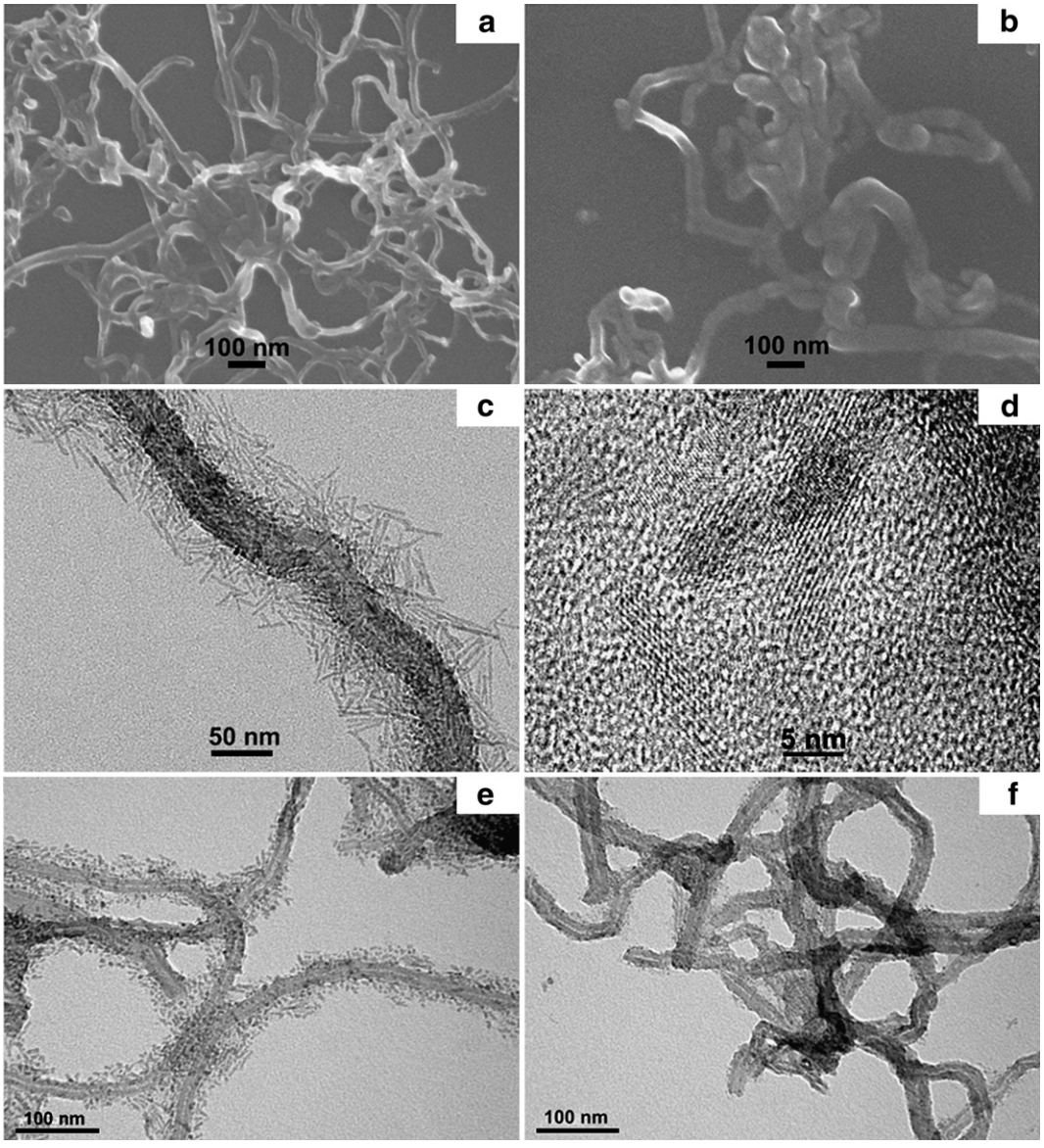

Fig. 1. (a) SEM image of the pristine MWCNTs; (b) SEM, (c) typical TEM and (d) HRTEM images of hybrid-1; (e) TEM image of hybrid-2 and (f) TEM image of hybrid-3.