

Formation of anatase TiO₂ nanoparticles on carbon nanotubes

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Anatase TiO₂ nanoparticles with a size range of 2 to 10 nm have been formed on carbon nanotubes by the controlled hydrolysis and condensation of titanium bis-ammonium lactato dihydroxide in water and electrosterically dispersed carbon nanotubes.

Environmental problems associated with the treatment of pollutants in air and water is an important subject for society, which we are faced with. Over the last decade environmental pollution remediation has arisen as a high national and global priority.¹ One of the promising techniques for the destruction of pollutants is the application of semiconductor photocatalysts.² Among these semiconductors, anatase TiO₂ has been known for its superior photocatalytic ability and most widely used for water and air purification, odor control, and sterilization.³ In order to improve photocatalytic efficiency, a great deal of effort has been devoted in recent years including synthesis of composite photocatalysts.^{4–6} For example, enhanced photocatalytic activities were observed when TiO₂ particles were embedded in a Ni film.⁵ Carbon nanotubes (CNTs) have been the focus of intensive study due to their unique structure-dependent electronic and mechanical properties^{7,8} since their discovery.⁹ A combination of unique properties of CNTs opens the potential to use CNTs for various advanced applications such as quantum wires in heterojunction devices, reinforcing materials in composites, nanoprobe in an atomic force microscopy, and catalyst support in heterogeneous catalysis.^{10–14} Metal catalysts such as Ru, Pd, Pt, Ag, Au were deposited on CNTs.^{13,14} In this Communication, we report that anatase TiO₂ nanoparticles have been coupled with CNTs successfully *via* a controlled hydrolysis and condensation of titanium bis-ammonium lactato dihydroxide (TALH, [CH₂CH(O)CO₂NH₄]₂Ti(OH)₂) in CNT-containing aqueous media.

To produce CNT-containing aqueous dispersion, 100 mg of multiwalled CNTs (MWCNTs) produced by chemical vapor deposition were dispersed in a polyethyleneimine (PEI, *M_w* = 1800, Acros organics) solution and sonicated in an ultrasonic cleaning bath (Fisher Sci. FS220). Polyethyleneimine having positively charged amino groups (NH₂⁺) adsorbed on CNTs and electrosterically dispersed CNTs in the medium. Adsorption and electrokinetic properties of polyethyleneimine are described elsewhere.¹⁵ Surface modified CNTs were then mixed with de-ionized water (Barnstead 'E-pure'). TALH (Aldrich, 50 wt.% aqueous solution) was used as a TiO₂ precursor. TALH is a water-soluble precursor, which does not require an alcohol based solution and can be slowly hydrolysed with urea at 90 °C. Urea slows down the hydrolysis of TALH.¹⁶ TALH has been used for synthesizing titania particles and titania coatings on quartz substrates.^{17,18} 125 ml of CNT solution, 1 ml of TALH and 100 mg of urea (Aldrich) were placed in a 250 ml flask and the pH of the solution adjusted from 6.5 to 4.6 employing 1 vol% acetic acid solution. The solution was magnetically stirred for 30 min at room temperature. The temperature of the solution was slowly increased. During slow heating, complexation of the negatively charged TALH with the positively charged polyethyleneimine on CNTs occurred in the solution. With further heating of the solution up to 90–100 °C, the hydrolysis and

condensation of TALH slowly occurred on the outer shell of CNTs forming anatase TiO₂ nanoparticles on the surface of CNTs. The solution was kept at the final temperature (90–100 °C) for the next 20 h. CNTs coated with TiO₂ and the extra precipitates of TiO₂ were separated by centrifugation and dried under vacuum for 10 h. The product was characterised by transmission electron microscopy (TEM, JEOL 200CX), high resolution TEM (HRTEM, JEOL 2010F), powder X-ray diffraction (XRD, Philips APD 3720), and energy dispersive X-ray spectroscopy (EDS, Oxford).

Fig. 1 shows low magnification TEM micrographs of MWCNTs with TiO₂ nanoparticles formed on their outer shell. The size of TiO₂ nanoparticles is less than 10 nm, in the range of 2–10 nm. A HRTEM micrograph of the interface region between MWCNT and TiO₂ nanoparticles is presented in Fig. 2. In this micrograph, the crystal lattice of TiO₂ nanoparticles as well as the fringes of MWCNT is resolved. Furthermore, the interface between CNT and TiO₂ is clearly seen, indicating that TiO₂ nanoparticles, whose sizes are less than 3 nm, are well attached on the outermost shell of MWCNT. Fig. 3 represents EDS spectrum images taken from MWCNTs, which are coupled with TiO₂ nanoparticles. The inlay image presents a magnified section where the titanium peaks are located. EDS examination of the sample confirms the presence of atomic titanium and oxygen. XRD patterns of TiO₂ nanoparticles (extra precipitates), CNTs coated with TiO₂ nanoparticles and CNTs are presented in Fig. 4. The peaks from anatase phase of TiO₂ nanoparticles are present. The peak at 26° (2θ) from Fig. 4(b) and (c) is for CNTs.

It is shown that anatase TiO₂ nanoparticles, whose sizes are less than 10 nm, have been formed on the surface of MWCNTs by the controlled hydrolysis and condensation of a titania precursor TALH. It is also shown that CNT can be used as a

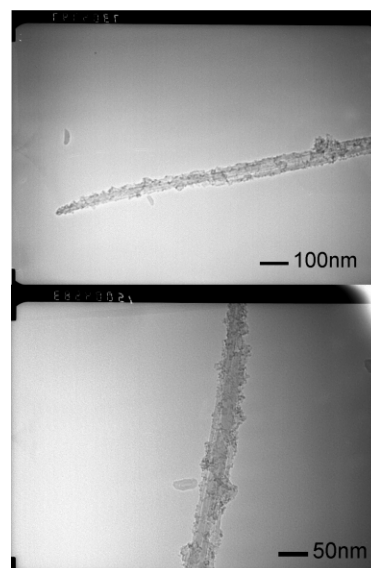


Fig. 1 Low magnification TEM micrographs of MWCNTs and anatase TiO₂ nanoparticles formed on the surface of MWCNTs.

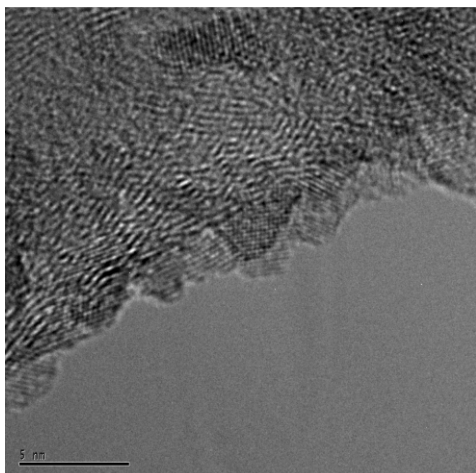


Fig. 2 HRTEM micrograph of MWCNTs coated with anatase TiO₂ nanoparticles.

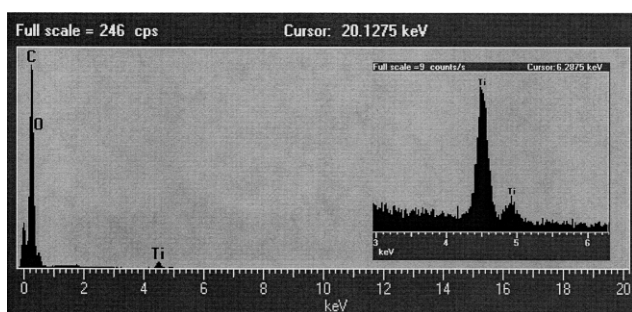


Fig. 3 EDS spectrum images of CNTs coated with TiO₂ nanoparticles. A magnified image of the titanium peak region is presented in a smaller window.

support material for anatase TiO₂ photocatalyst for environmentally beneficial applications. The photocatalytic performance as well as optical and physical properties of anatase TiO₂ nanoparticles on CNTs is currently under investigation.

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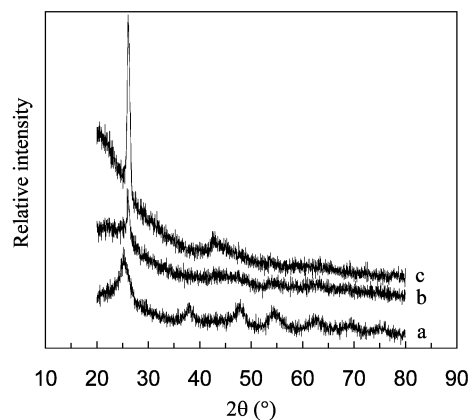


Fig. 4 XRD patterns of (a) TiO₂ nanoparticles (extra precipitate) showing the peaks from the anatase phase, (b) CNTs coupled with TiO₂, and (c) CNTs.

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