STRUCTURE AND ELECTROCHEMICAL BEHAVIOR OF CNT - TIO$_2$ NANOCRYSTAL COMPOSITES

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Abstract

Different methods of preparation of CNT - TiO$_2$ (anatase) heterostructures have been tested in order to obtain information on the relationship between the preparation method, resulting structure of the material and its electrochemical behavior during Li$^+$ insertion. The most complete TiO$_2$ coverage of individual non-functionalized MWCNT was achieved in block co-polymer (Pluronic P123) templated TiO$_2$ thin films. This composite has the highest specific capacity of Li$^+$ insertion into TiO$_2$ lattice to form Li$_x$TiO$_2$ (688 C/g, x=0.57), however, this was accompanied by the worst reversibility (76%). On the contrary, electrodeposited TiO$_2$ on SWCNT covered only bundles of nanotubes and its Li$^+$ insertion capacity was 507 C/g (x=0.42). However, the reversibility for all electrodeposited samples was almost complete and varied around 98%. Furthermore, Li$^+$ insertion behavior studied by the cyclic voltammetry technique showed unambiguously the presence of minute amounts of monoclinic TiO$_2$(B) in addition to anatase in samples from both synthesis methods. Thirdly, non-functionalized MWCNT have been mixed by phase pure anatase nanocrystals of average size 30 nm made by hydrolysis from Ti-butoxide in ethanol dispersion of CNT. Electrochemical Li$^+$ insertion showed x = 0.54 (charge capacity of 652 C/g) with 85% reversibility.

Introduction

Carbon nanotubes (CNT) (Bethune et al., 1993，Iijima and Ichihashi, 1993) have been intensively studied due to their unique electronic and mechanical properties. Amongst other applications, CNT may be used in heterogeneous catalysis (Planeix et al., 1994) or electrochemical storage of energy (Frackowiak and Béguin, 2002). The modification of carbon nanotubes by side-wall functionalization is an important step to change their properties and the scope of their prospective applications. Besides others, carbon nanotubes were decorated by metal oxide nanoparticles such as V$_2$O$_5$ (Ajayan et al., 1995), SnO$_2$ (Han and Zettl, 2003), SiO$_2$ (Whitsitt and Barron, 2003) or TiO$_2$ (Banerjee and Wong, 2002，Gomathi et al., 2005，Kalbac et al., 2007，Lee and Sigmund, 2003，Li et al., 2003，Sun et al., 2004). The synthetic strategies for TiO$_2$ involved a precipitation on SWCNT defects via ester-like linkages to carboxylic groups (Li et al., 2003), using organic linkers to connect SWCNT and TiO$_2$ nanocrystals (Banerjee and Wong, 2002，Lee and Sigmund, 2003，Sun et al., 2004), reaction of gaseous metal chloride with the hydroxyl groups (Gomathi et al., 2005), or electrochemical deposition (Kalbac et al., 2007).

CNT-TiO$_2$ heterostructures are attractive for several reasons. There are challenges to improve the properties of TiO$_2$ as a host material for lithium insertion or to enhance the photocatalytic activity of TiO$_2$ (Yu et al., 2005). Furthermore changes of the intrinsic electronic properties of CNT caused by the inorganic semiconducting material can be studied.

In this work, three different methods for the preparation of CNT-TiO$_2$ heterostructures are investigated. Firstly, SWCNT in the form of a buckypaper have been covered electrochemically with anatase nanocrystals. Secondly, MWCNT have been mixed with TiO$_2$ made by hydrolysis of Ti-butoxide in ethanol dispersion of MWCNT. Thirdly, Pluronic P123 templated anatase-CNT thin films have been prepared by dip-coating of F-doped SnO$_2$ slides in the solution of Pluronic P123 with Ti-ethoxide (Zukalova et al., 2005) mixed with various concentration of MWCNT. Structure and morphology of materials synthesized by all three methods was characterized by X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM) and microRaman spectroscopy. Study of electrochemical Li$^+$ insertion into these materials by cyclic voltammetry revealed variations in specific charge capacity and insertion/extraction reversibility. The observed behavior is related to the structural differences between individual materials, hence to the differences in the synthesis procedure.

Methods

Electrodeposition

The SWCNT-TiO$_2$ heterostructure was prepared by electrochemical oxidation of TiCl$_3$ according to the previously developed method (Kavan et al., 1993). The SWCNT buckypaper was used as a working electrode and a Pt wire as a reference and counter electrodes, respectively, in one compartment electrochemical cell. The electrochemical deposition was carried out by galvanostatic oxidation (at 1 mA/cm^2 for 3.5 hours) of 50 mM aqueous solution of TiCl$_3$ (Aldrich, 10 wt% solution in HCl). The acidity of the TiCl$_3$ solution was adjusted to pH 2.5 by slow addition of 15 wt% aqueous solution of Na$_2$CO$_3$. The resulting SWCNT-TiO$_2$ material was finally calcined for 30 min in air at 450°C. As a reference material we used the TiO$_2$ electrodeposited on F-doped SnO$_2$ (FTO) conducting glass slides under analogous conditions.

Hydrolysis from Ti-butoxide

Non-functionalized MWCNT (Nanocyl, avg. diam. 10 nm) were dispersed in ethanol (Riedel-de-Haen, absolute) and stirred at 0 °C with addition of deionized water and benzylalcohol (Aldrich, +99% purity). Then, solution of Ti-butoxide (Aldrich, 97%) in ethanol was slowly dropped into MWCNT dispersion. The resulting mixture was aged overnight, centrifuged and washed with ethanol several times,   dried and calcined in air at 400 °C for 60 minutes. The concentration of MWCNT in TiO$_2$ was 10 wt%.

Pluronic P123 templated films

Non-functionalized MWCNT (Nanocyl) were dispersed in 10% solution of Pluronic P123 (Aldrich) in 1-butanol (Aldrich, Chromasolv) and dropwise added to a solution made by a slow addition of 9.7 g of HCl (37 % Aldrich) to 12.7 g of titanium ethoxide (Aldrich). The mixture was either dip-coated (layer thickness ca. 300 nm) or doctor-bladed (thickness adjusted by a Scotch-tape) onto FTO slides or spread in a Petri dish and let evaporate. All prepared materials were finally calcined in air at 400 °C for 60 min. Two mixtures were used, with concentration of MWCNT in TiO$_2$ of 5 and 12 wt%, respectively.

Characterization methods

The Raman spectra were recorded on a T-64000 spectrometer (Instruments SA) with 2.54 eV, 2.41 eV or 1.91 eV excitations or Renishaw In-Via spectrometer with 2.41 eV or 1.58 eV excitations. Electrochemical lithium insertion was carried out in a one compartment cell with using an Autolab Pgstat-30 (Ecochemie) potentiostat. The reference and auxiliary electrodes were from Li metal. 1 M LiN(CF$_3$SO$_2$)$_2$ in ethylene carbonate(EC)/1,2-dimethoxyethane(DME) mixture (1/1 by volume) was used as electrolyte. Transmission electron microscopy (TEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB$_6$ cathode, point resolution 1.7 Å) with an EDX (Energy Dispersive X-ray) detector attached. Scanning electron microscopy (SEM) images were acquired by detecting secondary electrons only on a Hitachi 4800 FE-SEM microscope, operating at 3 kV. No special surface treatment of the samples to enhance their conductivity was performed. The BET surface areas of the prepared materials were determined from nitrogen adsorption isotherms at 77 K (ASAP 2010, Micromeritics).

Results and discussion

The morphology of SWCNT-TiO$_2$ heterostructure, where the TiO$_2$ was grown by anodic oxidative hydrolysis of TiCl$_3$ (Kavan et al., 1993) is shown on Fig. 1A. As can be seen, it retains the web-like structure of the starting nanotube material. Majority of the individual bundles is covered with anatase nanoparticles. The anatase nanoparticles seemingly grow directly on the surface of SWCNT bundles and form clusters of irregular sizes ranging from single crystalline particles (ca. 8 nm in size) up to more than 100 nm sized agglomerates (Kalbac et al., 2007). The Raman and SAED measurements suggest that anatase is the only TiO$_2$ phase present in the heterostructure, its average particle size of 8 nm was confirmed by HR-TEM observations. However, cyclic voltammogram (Fig. 2A) of the Li-insertion in the SWCNT-TiO$_2$ heterostructure exhibits not only the insertion/extraction peaks with a formal potential E$_f$= 1.8 V, common for anatase, but also additional small couples with E$_f$ of 1.5 and 1.6 V, respectively. Such peaks can be assigned to the so-called S-peaks, indicating the presence of the monoclinic phase TiO$_2$(B) (Kavan et al., 2004a).

Figure 1B shows a SEM image of the MWCNT-TiO$_2$ (anatase) mixture from hydrolysis of Ti-butoxide. Anatase crystals aggregate to 100-200 nm oval particles, which partly cover clots of MWCNTs. Covered individual tubes are rarely observed by TEM. As can be seen, there is only negligible interaction between MWCNTs and anatase. This is probably due to the defect-less nature of the used nanotubes and also due to the absence of a surfactant in the preparation process. XRD confirms the presence of pure anatase, with average coherent domain size 30 nm. The cyclic voltammogram (Fig. 2B) shows the exclusive presence of anatase, no TiO$_2$(B) is present in this material.
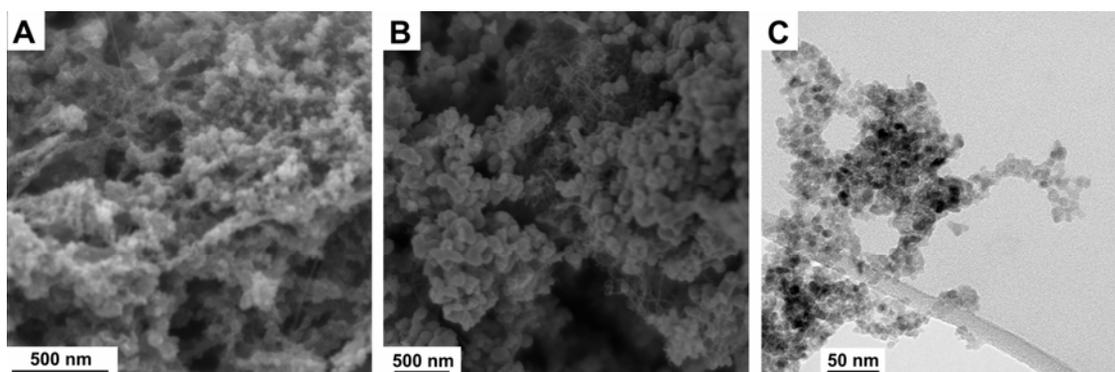
Figure 1. Electron microscopy images of A) SWCNT-TiO₂ electrodeposited (SEM), B) MWCNT-TiO₂ from Ti-butoxide (SEM) and C) MWCNT-TiO₂ from Pluronic templated thin film (TEM).

Figure 1C shows a TEM image of MWCNTs fully covered by anatase nanocrystals from the Pluronic P123 templated sample. The average anatase particle size is 10 nm, as determined by XRD measurements. Although the nanotubes are non-functionalized, the SEM observations also indicate the full coverage of nanotubes by TiO_2. The Pluronic P123 block co-polymer acts probably not only as a template for the TiO_2 itself but also as a dispersant for the nanotubes (Moore et al., 2003). The cyclic voltammogram (Fig. 2C) shows the presence of TiO_2(B) in trace amount.

Raman spectroscopy measurements show blueshifts (Δ = 1-3 cm^{-1}) of all anatase peaks in the heterostructure compared to pure anatase. The RBM and TG modes of SWCNT in the heterostructure with electrodeposited TiO_2 are blueshifted too (Kalbac et al., 2007). However, the exact values of the blueshifts differ with excitation wavelength, with the largest being observed for 2.41 and 2.54 eV (Δ = 4-5 cm^{-1}). Mostly semiconducting tubes are in resonance at these wavelengths. On the contrary, the spectra excited by 1.91 eV, where mostly metallic tubes are in resonance in our sample, show smaller blueshifts (Δ = 2 cm^{-1}). This points to a smaller interaction between metallic tubes and anatase compared to semiconducting ones. In addition to that, higher intensity of the D band in the heterostructure shows that the electrodeposition induced defects on the SWCNTs. The heating of SWCNT at the same conditions without deposited TiO_2 does not cause any significant change of the D mode. Hence, the enhancement of the D-mode is induced solely by the interaction of SWCNT with TiO_2, but not by creating defects during calcination in air.
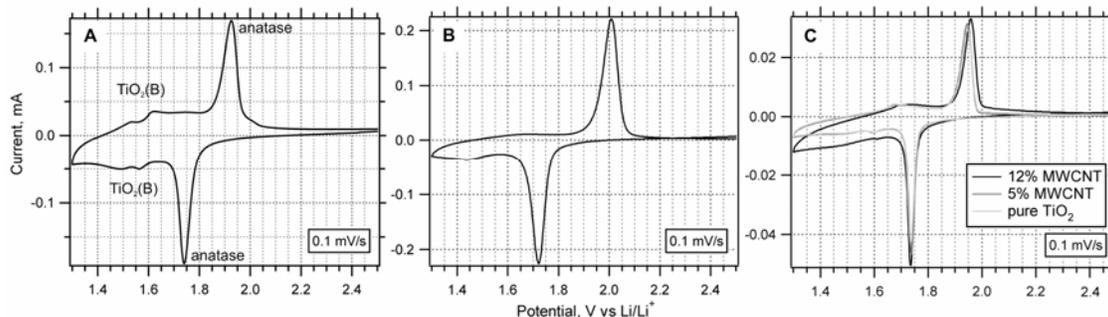

Figure 2. Cyclic voltammograms of A) SWCNT-TiO₂ electrodeposited, B) MWCNT-TiO₂ from Ti-butoxide, and C) MWCNT-TiO₂ from Pluronic templated thin film, in 1M LiN(CF₃SO₂)₂ + EC/DME (w/w 1:1) electrolyte solutions for scan rate of 0.1 mV/s.

The results of Li$^+$ insertion are summarized in Figure 2 and Table 1. As can be seen from Table 1, the MWCNT-TiO₂ heterostructures prepared by Ti-butoxide hydrolysis and Pluronic templated process exhibit higher Li$^+$ insertion capacity than pure anatase (with x~0.5) (Kavan et al., 1995, Kavan et al., 1996). However, this is accompanied by a considerably lower reversibility of the insertion/extraction process. The irreversible capacity may be ascribed to the formation of a solid electrolyte interface (SEI) in the central canal of the nanotubes and/or mesopores formed by nanotubes entanglement (Frackowiak and Béguin, 2002). In the case of SWCNT-electrodeposited TiO₂ heterostructure, the insertion capacity is 507 C/g (x = 0.42). In comparative experiments, it was not possible to achieve such results with TiO₂ electrodeposited on FTO, where the highest achieved charge capacity was 460 C/g (x = 0.38). Earlier studies of pure electrodeposited TiO₂ indicated x being between 0.15 to 0.39 (Kavan et al., 1996, Kavan et al., 2004b). The small insertion capacity was ascribed to dense

packing of the electrodeposited layers (Kavan et al., 1996). It increased to x = 0.57 if the porosity of the electrodeposited TiO$_2$ was increased via templating to inverse opal structure (Kavan et al., 2004b). Obviously, the interspersed carbon nanotubes have similar beneficial effect on the Li-storage capacity (Kalbac et al., 2007).

Table 1. Structure and electrochemical Li$^+$ insertion behaviour of differently prepared CNT-TiO$_2$ heterostructures.

Sample origin	CNT content, wt%	BET surface area, m^2/g	Anatase particle size, nm	Coverage	Li insertion capacity, C/g	Li insertion coeficient, x	Reversibi-lity, %
Electrode-position	---	---	8	bundles, partial	507	0.42	98
Ti-butox. hydrolysis	10	95	30	clots, partial	652	0.54	85
Pluronic templated	12	160	10	tubes, majority	688	0.57	76
	5	145	10	tubes, majority	630	0.52	82
	0	140	10	---	585	0.49	85

Conclusions

The electrodeposition of TiO$_2$ represents a simple and convenient way for the preparation of SWCNT-TiO$_2$ heterostructure where the SWCNT bundles are covered with TiO$_2$ anatase nanocrystals mixed with small amount of monoclinic TiO$_2$(B). The frequency shifts of the Raman modes of SWCNT evidence interaction of SWCNT with TiO$_2$ in the heterostructure. Although the electrodeposited TiO$_2$ decorates preferentially defect sites in SWCNT, our electrodeposition method works also on pristine, non-oxidized SWCNT. The Li$^+$ insertion capacity of our SWCNT-supported electrodeposited TiO$_2$ is substantially improved in comparison to the carbon-free electrodeposited TiO$_2$. The lithium storage capacity was found to be 507 C/g with 98% reversibility.

The hydrolysis of TiO$_2$ from Ti-butoxide in ethanol dispersion of non-functionalized MWCNTs gave phase pure anatase nanocrystals of average size 30 nm. These nanocrystals are not attached to the MWCNTs, which is caused by absence of defects on the nanotubes and a surfactant. Electrochemical Li$^+$ insertion capacity was 652 C/g with 85% reversibility.

The Pluronic P123 templated MWCNT-TiO$_2$ heterostructures exhibit a full coverage of nanotubes by anatase nanocrystals of average size of 10 nm. Electrochemical Li$^+$ insertion capacity was found to be 688 C/g with 76% reversibility. The low reversibility is probably due to the formation of solid electrolyte interface in the nanotubes' interior.

Acknowledgements

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