

Hierarchical sol–gel derived porous titania/carbon nanotube films prepared by controlled phase separation



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ABSTRACT

Titania/carbon nanotube (CNT) composite films containing hierarchical interconnected porous structure have the advantages of high surface area of mesoporous structure and micro-channels of titania as well as high conductivity and charge separation properties of CNTs. In this research, the composites were prepared with controlled phase separation of titania sol. The main parameters to control the phase separation and macroporous morphology of the films including water content, stabilizer content, polyethylene glycol content, sol concentration, and deposition speed were investigated. X-ray diffraction and Raman spectroscopy confirmed the presence of CNTs together with anatase titania phase. Transmission electron microscopy showed that a very thin layer of titania was formed on CNT surface which improved interface of TiO₂/CNT. It was found that macropores grew either with increasing water or polyethylene glycol content. However, stabilizer content and deposition speed had an inverse effect on macropores formation. Furthermore, sol concentration caused binodal decomposition and hence widened the pore size distribution. Although CNTs were ineffective in macropores formation, they strongly affected the transparency and charge separation of the composite films.

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1. Introduction

A hierarchical porous material should contain at least bimodal pore size distribution [1,2]. Titania hierarchical porous films with outstanding chemical, optical, and electrical properties have attracted tremendous attentions due to their remarkable potential applications including catalysis [3], fuel cells [4], solar cells [5], gas sensors [6], chromatography [7], smart coatings [8], and drug delivery [9]. In these materials, mesopores provide the large surface area necessary for interface reactions and macropores act as micro-channels, which permit rapid transports of reactants or redox couples to the interface [10]. These materials can be synthesized with various methods such as assembly of mesoporous particles, templating with sacrificial opals and polymeric beads, crystallization of salts, pre-patterned substrates as template, and controlled phase separation [11]. The latter method can be categorized as evaporation induced self-assembly methods, in which the preferential evaporation of solvent concentrates the initial solution in the presence of non-volatile surfactants [12].

The controlled phase separation involves the segregation of two insoluble phases through spinodal decomposition. The solubility of the initial sol decreases due the evaporation of solvent and

increase in concentration during film deposition [13,14]. This method has the advantages of one pot synthesis, low levels of organic residues, and in case of carbon nanotubes (CNT) incorporation, homogenous dispersion and suitable interfacial binding among other methods. Controlling the phase separation is very difficult and is related to various parameters including (1) water content (added water), (2) relative humidity, (3) concentration of precursor in sol, (4) choice of structure directing agent (SDA), (5) SDA content (polyethylene glycol (PEG)), (6) stabilizer content, (7) deposition rate, and (8) sol properties (boiling point, viscosity, gel time, and solubility limit for segregated components).

A large effort has been spared on the coupling of TiO₂ with CNTs due to the fact that the mobility of the carriers can be increased significantly with relatively low incorporation of CNTs in TiO₂ matrix [15–18]. Moreover, CNTs can trap electrons and promote separation of the photogenerated charge carriers in TiO₂/CNT junction due to the proper band edge positions [19]. Also, high conductivity of CNTs can possibly reduce the recombination chance of charge carriers [20]. Therefore, the TiO₂/CNT composites mostly have shown superior photocatalytic [21], sensitivity [22], electrochemical [23], and photoelectrochemical [24] properties and devices based on these composites usually showed higher overall efficiency than bare TiO₂. The in situ methods for synthesizing TiO₂/CNT composites which involve directly formation of inorganic compounds on the surface of pristine or modified CNTs,

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can be carried out with electrochemical reduction of inorganic salts, electro- or electroless deposition, sol–gel, hydrothermal, chemical vapor deposition, and physical vapor deposition [25]. Insertion of CNTs in TiO₂ matrix with appropriate interface is crucial for assurance of fine operation, which can be achieved with low temperature high homogeneity sol–gel method. Moreover, the ability to create porous thin films, proposed this method as the most suitable route for synthesizing the hierarchical interconnected porous titania/CNT composite thin films.

In this research, the hierarchical interconnected porous titania/CNT composites were synthesized by sol–gel induced controlled phase separation method. This method not only allows formation of bimodal porosity through phase separation, but also guarantees the high quality interface of TiO₂/CNT at the junction. The effect of different parameters of water content, stabilizer content, PEG content, precursor concentration, and deposition speed on the pore formation and film properties were investigated. Crystalline phases, thermal properties, interfacial morphology, and optoelectrical properties of the films were also studied.

2. Experimental

2.1. CNT functionalization and dispersion

The CNTs form bundles and ropes due the high aspect ratio of the tubes, Van der Waals forces between side walls of two adjacent tubes, and metallic catalyst residues [26]. Therefore, the functionalization of CNTs with carboxylic groups in acid medium is essential for sol–gel in situ composite preparation. 0.5 g of CNTs (multi walled CNT, 10 nm outer diameter, Shenzhen nanotech. Co., 99%) were sonicated in concentrated sulfuric acid: nitric acid = 3:1 for 10 min. The mixture was then heated at 80 °C for 1 h under refluxing, and then washed with deionized water (DIW) and centrifuged. The product was dried at 60 °C and kept dried until use.

2.2. Porous film preparation

Sol preparation method for film deposition was discussed elsewhere [27]. Typically, tetrabutyl orthotitanate (TBT, Ti(OC₄H₉)₄, 99%, Merck) was dissolved in ethanol (EtOH, C₂H₅OH, analytical grade, Merck). The solution was stirred for 30 min and diethanol amine (DEA, NH(CH₂CH₂OH)₂, reagent grade, Merck) was added to the solution as stabilizer and stirred for 1.5 h in order to complete the ligand exchange reactions. Then, the hydrolyzing solution containing ethanol and water was added drop wisely to the former solution and stirred for 1 h. The stable dispersion of functionalized CNT in ethanol was added to the initial sol. Afterward, various amounts of PEG (average molecular weight 1000, H(OCH₂CH₂)_nOH, Merck) were also added. The resultant sol was stirred for another 1 h and maintained for 2 h in order to complete the hydrolysis and condensation reactions. The final composition of the sol in molar ratio was TBT:DEA:DIW = 1:1:1 with 0.75 mol/L concentration and 0.6 wt.% CNT. Higher amounts of CNTs deteriorate the optical transparency of the films.

The films were deposited on soda lime glass substrates (ultrasonically washed with ethanol, acetone, and DIW) with dip coating method under controlled relative humidity of 30%. After that, the films were dried at 300 °C for 10 min. The process of dip coating and drying was repeated 10 times and finally the films were calcined at 550 °C for 1 h in air. The $w = \text{DIW:TBT}$ molar ratios of 0.5, 1, and 1.5 were considered for investigating the effect of water content on pore formation. Besides, the $s = \text{DEA:TBT}$ molar ratios of 0.5, 1, and 2 were considered for studying the effect of stabilizer content on pore formation. The PEG amounts of $p = 0.5, 1, 1.5,$ and 2 g/L, TBT concentration of $c = 0.5, 0.75,$ and 1 mol/L, and

deposition speed of $d = 30, 60,$ and 120 mm/min were also considered. In all specimens, while one parameter was changed, the other parameters were held constant.

2.3. Characterization

The phase structure of the films was studied by X-ray diffraction method (XRD) with Philips X-pert pro PW1730, 40 kV, 30 mA with radiation of Cu- $\kappa\alpha$, $\lambda = 1.54056 \text{ \AA}$ in the range of 20–80°. Raman spectra were recorded using BRUKER (SETERRA, spectral resolution $< 3 \text{ cm}^{-1}$) micro Raman spectrometer equipped with the confocal microscope. The samples were excited with the 785 nm line of argon laser operating at the power of 25 mW. The morphologies of the resultant films were observed by field emission scanning electron microscope (FESEM) with Hitachi S4160. High resolution transmission electron microscope (HRTEM) Philips CM30 was utilized to study the CNT sidewalls coverage with titania. The thermal analyses of the samples were performed on DTC/TG (SII Nanotechnology, A6300) in the range of 25–900 °C at 10 °C/min under air atmosphere. The optical transmittance spectra were recorded in the wavelength range of 200–1000 nm (UV–Vis spectroscopy, PG instrument T80+ spectrophotometer). The surface roughness and morphology of the films were investigated with atomic force microscopy (AFM), Dual Scope DS 95–200/50 in contact mode. Photoluminescence spectra were recorded by photoluminescence spectroscopy (PL), Avantes Avaspec2048 in wavelength range of 200–1100 nm and excitation wavelength of 380 nm.

3. Results and discussion

3.1. Phase structure analysis

The XRD pattern of the film with $w = 1, s = 1, c = 0.75 \text{ mol/L}, p = 1 \text{ g/L}, d = 60 \text{ mm/min}$, and 0.6 wt.% CNT after calcination at 550 °C is shown in Fig. 1. The XRD pattern indicates that the film is mainly comprised of anatase phase (JCPDS 21-1272). The XRD pattern of CNT powders is also compared with titania pattern in this figure. This pattern matched with graphite pattern with a slightly shift to lower diffraction angle due to the curvature of side walls, which causes higher distance between two adjacent (002) planes [28]. CNTs in composite film cannot be detected by XRD due to the overlapping (002) peak of CNT with (101) peak of anatase and existence of CNT in trace amount in composite film.

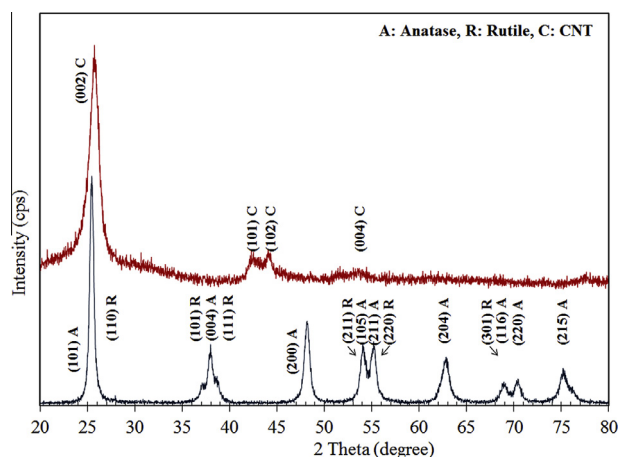


Fig. 1. XRD patterns of the film with $w = 1, s = 1, c = 0.75 \text{ mol/L}, p = 1 \text{ g/L}, d = 60 \text{ mm/min}$, and 0.6 wt.% CNT after calcination at 550 °C and functionalized multi-walled CNTs after acid treatment.

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