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Preparation of polyaniline/TiO_2 hybrid microwires in the microchannels of a template

Shanxin Xiong [a], Qi Wang [b,*], Yinghong Chen [b]

[a] *Temasek Laboratories of Nanyang Technological University, 50 Nanyang Drive, 637553 Singapore, Singapore*
[b] *State Key Laboratory of Polymer Materials Engineering (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, China*

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Abstract

Polyaniline (PANI)/TiO_2 hybrid microwires with diameter of 160–180 nm were prepared through the sol–gel process of TiO_2 and in situ polymerization of aniline in the microchannels of anodic aluminum oxide (AAO) template. The structure, morphology and properties of the microwires were characterized with scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), fluorescence spectroscopy (FL), ultraviolet–visible spectroscopy (UV–vis) and X-ray photoelectron spectroscopy (XPS). The results show that the regular arrangement of microwires, with well-dispersed inorganic phase in the organic matrix is formed. Also, the shape of the hybrid microwires is similar to that of the template channel and the diameter of microwires is smaller than that of the template channels due to the shrinkage of volume during the sol–gel process. XPS analysis confirms that there are a lot of leftover OH groups in the hybrid system owing to the lower treatment temperature of TiO_2 gel and interactions between PANI and TiO_2, which is consistent with the results of UV–vis and FL analysis. The XRD data confirms that no obvious diffraction peak is observed in hybrid microwires at the reported treatment temperature (180 °C). FL spectra shows that the interaction and energy band match between PANI and TiO_2 cause in the blue shift of the emission peaks of hybrid microwires. It is obvious that with the applied approach, the organic/inorganic hybrid materials with slight phase separation, equable distribution, well-ordered structure and unique function can be prepared easily.

Keywords: Template synthesis; Microwires; Polyaniline; Hybrid

1. Introduction

Among conducting polymers, PANI is a promising candidate for large scale application due to its high conductivity, good environmental stability, ease of preparation, and so on [1–3]. The low efficiency of electroluminescence property of PANI can be improved effectively through the introduction of inorganic nanoparticles due to the quanta effect and energy band match. A lot of nanocomposites based on PANI such as PANI/ZrO_2, PANI/SiO_2, PANI/MnO_2 and PANI/TiO_2, have been prepared [4,5]. Among these inorganic nanoparticles, TiO_2 has received great attention because of its unique optical and electrical properties, such as acting as a charge carrier, being a photoelectric active center and optical cavity, etc. [6,7]. Liu [8] found that the efficiency of photoelectric transformation of PANI/TiO_2 nanocomposites was higher than that of TiO_2 due to the sensitizing effect of PANI, which extends the absorption range of TiO_2. The key issue for preparation of PANI/TiO_2 composites is the good dispersion of TiO_2 nanoparticles in PANI matrix, which is difficult to be obtained with conventional methods due to the agglomeration caused by high surface energy of the nanoparticles. Through the method of ultrasonic irradiation in situ polymerization, Xia and Wang [9] successfully prepared PANI/TiO_2 nanocomposites with good dispersion. Another feasible method is to prepare hybrid nanocomposites of TiO_2 and PANI. The precursors of hybrid materials can form homogeneous dispersion. Moreover, the chemical interactions between the organic phase (PANI) and inorganic phase (TiO_2) in a hybrid system can maintain a small domain size and stable dispersion. If the hybrid process is introduced into a confined environment, e.g. template channel, the resulting materials must possess especial structure and properties.

* Corresponding author. Tel.: +86 28 85405133; fax: +86 28 85402465.
E-mail address: qiwang@scu.edu.cn (Q. Wang).

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In recent years, studies on one-dimensional conducting polymers have received great attention. Nanotubes and naonrods of PANI, polypyrrole (PPy), etc., have been successfully synthesized via chemical or electrochemical methods using template synthesis or self-assembly process. Furthermore, one-dimensional organic/inorganic composite materials have also been extensively studied due to the characteristic of organic phase and inorganic phase as well as their synergetic effect. Zhang and Wan [10] prepared PANI/TiO_2 composite nanotubes using β-naphthalenesulfonic acid (β-NSA) as the dopant through the self-assembly process. However, there are few papers involving the study of PANI/TiO_2 nanohybrid microwires. In this article, the preparation of PANI/TiO_2 nanohybrid microwires using sol–gel process and in situ polymerization based on AAO template is being reported. The structure, morphology and photoluminescence properties of microwires were characterized. Also, the formation mechanism of PANI/TiO_2 nanohybrid microwires was discussed.

2. Experimental

2.1. Materials

Aniline ($C_6H_5NH_2$) was distilled under reduced pressure and stored at low temperature prior to use. Ammonium peroxydisulphate ($(NH_4)_2S_2O_8$), tetrabutyl titanate ($(C_4H_9O)_4Ti$), acetic acid (CH_3COOH) and hydrochloric acid (HCl) were used as received. AAO (Andisc13) with pore diameter of 200 nm was obtained from Whatman International Ltd.

2.2. Preparation of PANI/TiO_2 hybrid composites

TiO_2 sol was prepared using the method similar to that described by Hamasaki et al. [11]. The mixture solution of 5 ml tetrabutyl titanate and 25 ml ethanol was stirred in an ice-water bath. Then 0.5 ml water and 1.5 ml acetic acid were added to another 25 ml ethanol. The ethanol–water–acetic acid solution was slowly added to tetrabutyl titanate–ethanol solution. After the color of system became milky white (formation of sol), 2.5 ml aniline was added to 50 ml TiO_2 sol with magnetic stirring. The mixture solution was kept for 1 week at room temperature. When the mixture solution became yellow, ointment-like material, a mixing solution of 1.0 mol l^{-1} ammonium peroxydisulphate and hydrochloric acid (1.1 mol l^{-1}) were introduced. The sample was kept for 24 h at room temperature, then washed with distilled water and finally treated at 180 °C for 2 h in air.

2.3. Preparation of PANI/TiO_2 hybrid microwires

AAO membrane was treated with 0.5% (w/w) HCl solution to remove impurities on the surface of template, then washed three times with distilled water, and dried at 110 °C for 1 h. The mixture solution of TiO_2 sol and aniline was filled into the channels of template under negative pressure using vacuum filtration. The reaction system was kept for 2 days at room temperature to form TiO_2 gel. Then, the template was immersed into a solution of ammonium peroxydisulphate (1.0 mol l^{-1}) and hydrochloric acid (1.1 mol l^{-1}). The polymerization reaction was carried out for 4 h with magnetic stirring in an ice-water bath, and then the reaction was conducted for 24 h at room temperature. After being carefully washed with distilled water, the sample obtained was heat treated at 180 °C for 2 h in air.

2.4. Preparation of bare PANI and TiO_2

The pure sample of PANI and TiO_2 were prepared for contradistinction study. For PANI, 1.0 ml aniline was dissolved in 1.1 mol l^{-1} hydrochloric acid with magnetic stirring in an ice-water bath for 1 h. 10 ml 1.0 mol l^{-1} ammonium peroxydisulphate was added drop by drop into the solution for polymerization to occur. The whole reaction lasted for 24 h. The PANI synthesized was washed several times with distilled water and dried at 50 °C in a vacuum oven. For TiO_2, the previously prepared TiO_2 sol was subjected to gelation at room temperature for 1 week and then calcination at 450 °C for 2 h. The resulting powder was washed several times with distilled water and dried at 50 °C in a vacuum oven.

2.5. Characterization

The morphology of hybrid microwires was observed with JEOL JSM-5900LV scanning electron microscope. The samples were prepared as follows: AAO template with PANI/TiO_2 hybrid microwires in its pores was glued on a piece of glass using epoxy resin as an adhesion agent. The surface of the template was carefully polished with fine grit sandpaper to remove the PANI or TiO_2 on the surface of the membrane. Then the sample was treated with 10% (w/w) NaOH solution to partly dissolve the template for exposure of hybrid microwires. The surface of the sample was sputtered with ~10 nm of Au prior to SEM imaging. TEM images of PANI/TiO_2 microwires were recorded with JEM-100CX transmission electron microscope. The samples of TEM testing were obtained by the following process: Firstly, the AAO template was fully removed with 10% (w/w) NaOH solution. Then, the solution was dialyzed to pH value 7. In the final step, the microwires were dispersed with ultrasound to form a suspension of microwires. Before observation, the suspension was dropped onto a copper grid. X-ray diffraction patterns of hybrid system were taken on X'pert Pro MPD X-ray diffractometer, Cu Kα, wavelength 1.5418 Å. X-ray photoelectron spectroscopy (XPS) was performed on a XSAM 800 X-photoelectron spectrometer with a Mg Kα X-ray source. In the data analysis, the binding energy of the core level C 1s was set at 285 eV to compensate the surface-charging effects. Elemental stoichiometries were calculated from peak area ratios corrected with the sensitivity factors. The fluorescent spectra of samples were taken on Hitachi-850 fluorescent spectrometer. UV–vis spectrum was recorded with SHIMADZU UV-240 UV–vis spectrograph. The microwires suspension was used for FL and UV–vis analysis.

3. Results and discussion

3.1. Preparation of PANI/TiO_2 hybrid microwires

Fig. 1 shows the SEM images of the PANI/TiO_2 hybrid microwires prepared. It can be seen that the PANI/TiO_2 hybrid microwires have a uniform arrangement; the shape of hybrid microwires is similar to that of template channels in Fig. 1a. As can be seen in Fig. 1b, the template channel is not fully filled by hybrid microwires and there are some space between the microwires and template channels. It is caused from the volume shrinkage of hybrid microwires during the formation process of TiO_2. Another phenomenon observed is that the surface of microwires is not very smooth. All of above findings are different from the results of our previous works [12]. In our previous work, we successfully synthesized PANI microtubes using the same template. The diameter of the acquired PANI microtubes is bigger than that of the template channels owing to the expansion of PANI microtubes after the template is removed and the surface of PANI microtubes are very smooth. The probable reason is that the two phases of PANI and TiO_2 are micro-separated in hybrid system during sol–gel process and polymerization. These results were further proven by TEM analysis.

Fig. 2 shows the TEM images of PANI/TiO_2 hybrid microwires with different magnification. As can be seen, the structure of PANI/TiO_2 hybrid microwires is solid, the diameter of hybrid microwires is in the range of 160 nm to 180 nm, and the surface of microwires is rough. In addition, many black dots