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Hollow TiO_2 containing multilayer nanofibers with enhanced photocatalytic activity

Tianzhu Zhang [a,1], Liqin Ge [b,*,1], Xing Wang [b], Zhongze Gu [b,*]

[a] Department of Inorganic Chemistry, University of ULM, 89081 ULM, Germany
[b] State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, PR China

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ABSTRACT

Hollow titania containing multilayer nanofibers was fabricated through the combination of electrospinning with layer-by-layer technique. Two different solvents, methylbenzene and THF were used to remove the template. The morphology of the obtained hollow multilayer nanofibers confirmed that THF is better than methylbenzene. The obtained hollow multilayer fiber has a diameter of about 700 nm and its shell thickness is about 140 nm. FTIR spectra show the fabrication of multilayer nanofibers. XPS measurement indicates that TiO_2 nanoparticles can be assembled successfully. The obtained multilayer hollow nanofibers have highest photocatalytic activity to degrade methylene blue solution comparing with the TiO_2 film due to their unique hollow structure.

1. Introduction

The construction of nanoparticle-loaded multilayer films has generated a great deal of interest for a number of years [1–3]. Such materials have unusual electronic and optical properties due to their large specific surface area and the quantum size effect, which are not available for the corresponding bulk materials [4–9]. Lu et al. have reported the enhanced photocatalytic properties with the presence of cavity of hollow titania spheres [10].

Among the diverse methods to prepare nanoparticles embedded within polymer films, layer-by-layer (LBL) technique provides a simple route to create nanoparticle composite films with the merit of controlling over film composition and thickness on molecular level [5–8]. There are two ways to prepare such materials: one is to adsorb the nanoparticles on an opposite charged surface and another is the in situ synthesis of nanoparticles which can be grown selectively and controlled within specific regions of multilayer films [2,3].

Nanofibers can be used in filters, sensors, biocatalysts, protective clothing, wound dressings, artificial blood vessels, controlled drug delivery, tissue growth applications and so on [11–13]. A rich variety of methods have been introduced to obtain nanofibers from all kinds of materials [14–16]. Among them, the combination of the LBL technique with electrospinning method to fabricate the hollow nanofibers is our interest because of its simple operation and easy control of its composition and shell thickness. Electrospinning is a straightforward, cost-effective method to produce novel fibers with diameters ranging from nanometers to micrometers. The obtained fibers have very high continuous surface areas comparing with other materials, for example spheres, slices and nanotubes [17–19].

Some researchers studied fibrous surface characters or fabricated hollow nanofibers through combining the LBL technique with electrospinning method [12,20–25]. In our previous publications, we have reported the fabrication of organic hollow multilayer poly(styrenesulfonate, sodium salt)/poly(allylamine hydrochloride) ($(PSS/PAH)_n$) nanofibers and investigated the effect of the template size on the hollow fibers' morphology [23]. The deposition conditions were optimized and the hollow fibers' Young modulus was also calculated [24]. It was found that the hollow nanofibers will not collapse when the ratio of the shell thickness to the template's mean radius is smaller than 0.34. We also successfully fabricated the carbon nanotube containing multilayer hollow nanofibers [25].

In this present study, we continued our work on the fabrication of hollow nanofibers. For the first time, we report here the synthesis of multilayer hollow inorganic/organic complex titania nanofibers through the combination of layer-by-layer technique with electrospinning method (Scheme 1). Their photocatalytic activity on the degradation of methylene blue was enhanced by such unique hollow structure.

* Corresponding authors. Tel./fax: +86 25 83795632.
E-mail addresses: lqge@seu.edu.cn (L. Ge), gu@seu.edu.cn (Z. Gu).
[1] Dr. Tianzhu Zhang and Dr. Liqin Ge have equal contribution to the manuscript.

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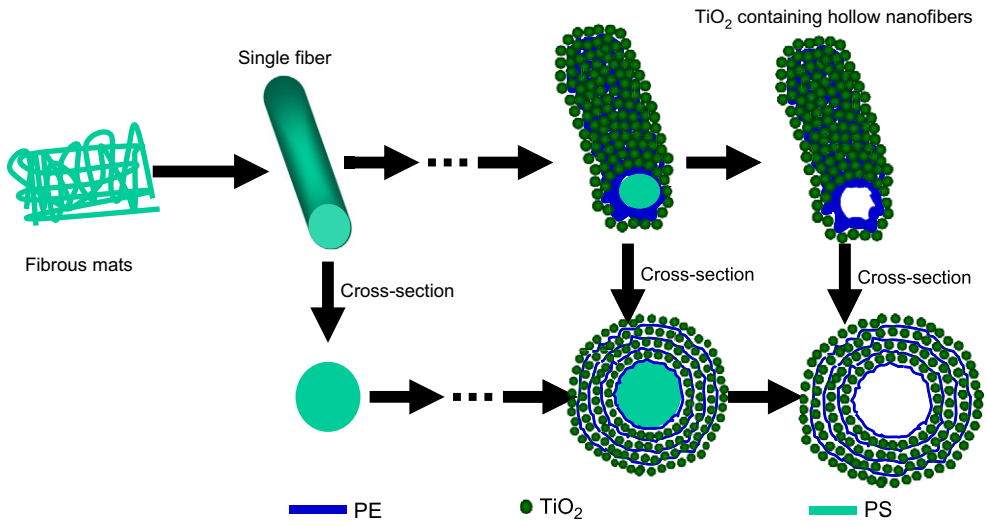


Scheme 1. The scheme for the fabrication of multilayer hollow titania nanofibers.

2. Materials and methods

2.1. Materials

Negatively charged TiO_2 (anatase) colloid aqueous suspension of 6 wt% with a pH of 10. The diameter of TiO_2 particles was 20 nm. Poly(styrenesulfonate, sodium salt) (PSS, M_w 70,000 g/mol), polyethylenimine (PEI, M_w 70,000 g/mol), polystyrene (PS, M_w 185,000 g/mol), and tetrahydrofuran (THF) were obtained from Aldrich. All these materials were used as received. NaCl was bought from Saiji company.

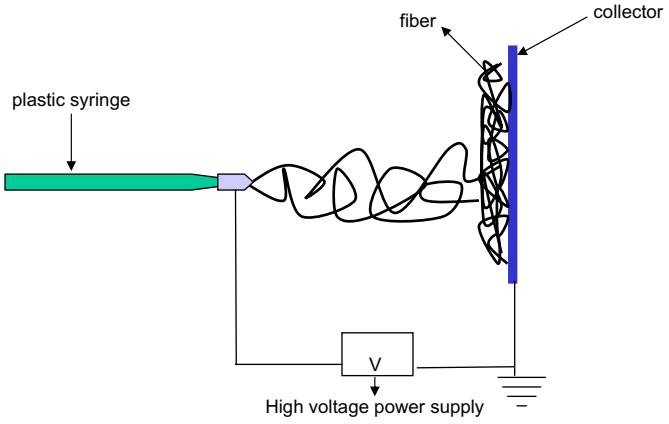
The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm^{-1}.

2.2. Fabrication of polystyrene nanofibrous mats by electrospinning

Polystyrene (PS) nanofibrous mats were prepared from the solution of polystyrene in tetrahydrofuran (THF)/*N*,*N*-dimethylformamide (DMF) (v/v 1:1). As a typical procedure, 10 ml of THF/DMF mixture solvent and 1.5 g polystyrene (PS, M_w 18,5000 g/mol) were stirred for 2 h to get a viscous gel. The obtained viscous gel was then quickly loaded into a syringe equipped with a 5 gauge stainless needle, which was connected to a high-voltage supply capable of generating voltage up to 15 kV. The feeding rate of the precursor solution was controlled using an automatic syringe pump. A plate used as the collector was placed 10 cm away from the tip of the needle for the collection of the nanofibers. The electrospinning device is shown in Scheme 2. The solution on the tip of the needle was ejected as fibers under a strong electric field towards the collector. Details on the fabrication of the fibers are given in Ref. [23].

2.3. Construction of hollow multilayer Tio_2 containing complex nanofibrous mats

PSS and PEI solutions used for adsorption were prepared in Milli-Q water with a concentration 1 mg/ml in 0.5 M NaCl. An agglomerate of PS fibrous mat was selected as template and immersed into PEI solution and PSS solution alternatively. Every circle consists of an adsorption of 30 min and the subsequent rinsing with abundant water. After the fabrication of four $(PEI/PSS)_4$ bilayers was finished, the multilayer polymer coated PS fibers were immersed into THF (2 ml) or methylbenzene and left for 5 min to remove the PS core. In order to remove the residual solution inside the fibers, the sample was centrifuged at 1000 rpm for 1 min. and then washed by solvent for three times. Finally, the products were dispersed in water for next measurement. PEI was selected as the first layer because PS fibers are negatively charged.



Scheme 2. The scheme for the electrospun devices.

In order to fabricate the multilayer TiO_2 coated PS fibers, TiO_2 (pH 10) was used instead of PSS as described previously. PEI/TiO_2 multilayer film coated PS fibers were treated with THF to obtain the hollow multilayer titania containing nanofibers.

2.4. Measurements of scanning electron microscopy (SEM)

The samples were prepared for the scanning electron microscopic (SEM) observation S-3000N (HITACHI, Japan).

2.5. Photocatalytic activity measurements

The photocatalytic activities of the hollow TiO_2/PEI hybrid hollow fibers were evaluated by measuring the decrease in concentration of methylene blue dye in the reaction solution. Deionized water was used as a blank. The solution was irradiated by a 300 mW/cm^2 UV light under ambient condition (295 K, RH 80%, in air) with stirring. The change of absorption at 665 nm was

represents the change of the concentration of methylene blue using an UV–vis spectrophotometer (U-4100, Hitachi).

2.6. Measurement of X-ray photoelectron spectroscopy (XPS) spectra

XPS (ESCALB MK-II) analysis was carried out using a monochromatized Mg Kα X-ray source (1253.6 eV). The base pressure in the analytical chamber was in the order of 10^{-9} Pa. Narrow XPS spectra were recorded in order to obtain the chemical state information about titanium. After baseline subtraction, the curves were fitted by using a combination of Lorentzian and Gaussian line shapes. To correct the energy shift due to sample charging, the data were calibrated to the adventitious C1s peak at 284.6 eV.

3. Results and discussion

3.1. Effect of the solvent on the hollow polyelectrolyte fibers' morphology

The typically electrospun nanofibrous mats which compose of polymer nanofibers possess three-dimensional (3D) structures with pores in micro- and sub-microsize. In this research, electrospinning technique was employed to construct PS nanofibrous mats [20]; the obtained mats will be used as the templates and their microscopic structures are shown in Fig. 1. It was observed that the electrospun fibers were weaved to form porous membranes. The distribution of fiber's diameters was in the range from 920 to 1320 nm. Generally, the surface-area-to-volume ratio of the porous mat is one to two orders of magnitude higher than that of the flat thin films [23].

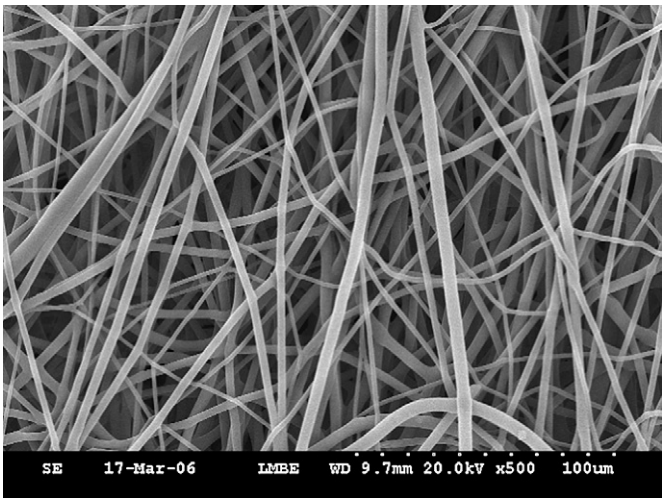


Fig. 1. SEM images of PS nanofibers.

In our previous study, we have optimized the deposition conditions and estimated Young modulus [23, 24]. Removing the template is one of the key steps in preparing multilayer hollow nanofibers. The solvent employed to remove the template should satisfy the following rules: it can dissolve the template but cannot dissolve the shell. In this research, polystyrenes are used as templates. THF and methylbenzene are effective solvents for PS and the results are shown in Fig. 2. Both THF and methylbenzene can be used as removing solvent to obtain hollow nanofibers. The morphologies of the hollow nanofibers obtained from THF are better than the ones from methylbenzene. The possible reason may be because the polarity of PS is similar to that of methylbenzene. According to the compatibility and similitude principle, PS is more easily dissolved in methylbenzene than in THF which may produce instantaneous high pressure in the fiber, which will lead to numerous broken short fibers as shown in Fig. 2a. Comparing with methylbenzene, PS can dissolve in THF slowly, which results in longer hollow multilayer nanofibers with better morphology.

3.2. Fabrication of hollow multilayer PEI/TiO_2 complex nanofibers

In order to obtain four bilayer PEI/TiO_2 fibers, PS nanofibers were immersed into PEI and TiO_2 suspensions, alternatively. SEM images of PS/$(PEI/TiO_2)_4$ are shown in Fig. 3. Different from the PS bare nanofibers, multilayer PEI/TiO_2 coating PS fibers possess rougher surface. After coating, the distribution of fibrous diameters was in the range from 1100 to 2000 nm. The diameter of the TiO_2 nanoparticles is about 20 nm. Fig. 3 shows that TiO_2 nanoparticles were coated on the PS fibrous surface, but the particle's size is much larger than 20 nm because of the nanoparticle aggregation during multilayer fabrication. According to our previous results [23], the thickness for single layer polyelectrolyte is about 15 nm, the total thickness for four bilayer PEI/TiO_2 is about 140 nm, which is consistent with our experimental results.

Hollow multilayer PEI/TiO_2 can be obtained by selectively removing the PS template with THF as shown in Fig. 4. The hollow structure (inset picture) has the inner diameter of about 700 nm and the shell thickness of about 140 nm. The obtained hollow fiber has smaller diameter than that of the template. The possible reason is that TiO_2 nanoparticles do not have flexible curl structure. After the template is removed and dried, the obtained hollow fiber will shrank during SEM sample preparation.

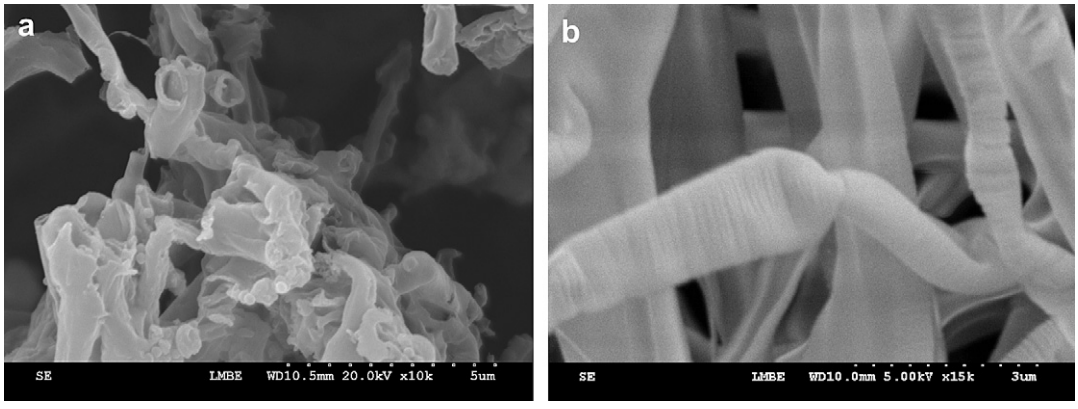


Fig. 2. SEM images of (a) hollow multilayer $(PEI/PSS)_4$ nanofibers (methylbenzene as solvent); (b) hollow multilayer $(PEI/PSS)_4$ nanofibers (THF as solvent).

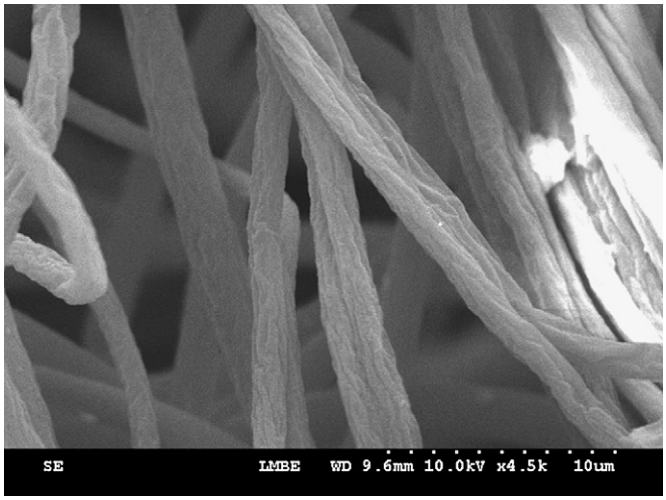


Fig. 3. SEM images of PS/(PEI/TiO_2)$_4$.

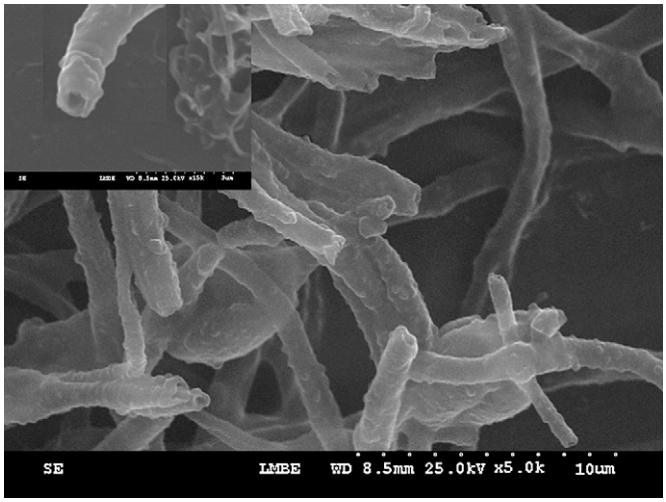


Fig. 4. SEM images of hollow multilayer (PEI/TiO_2)$_4$ nanofibers (inset picture is the head part of the fiber).

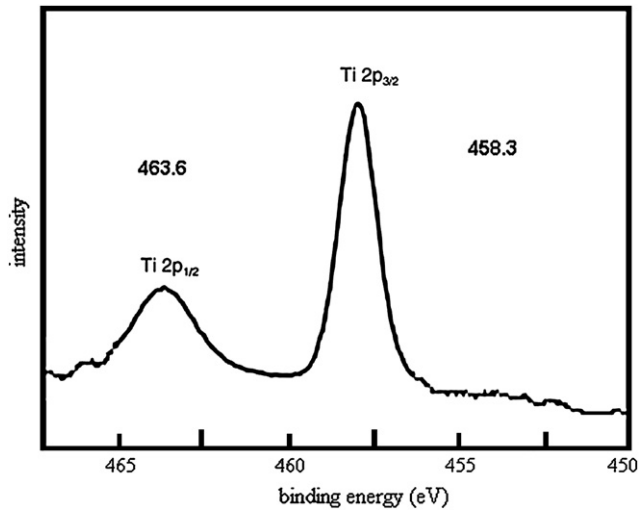


Fig. 5. XPS results of hollow multilayer (PEI/TiO_2)$_4$ nanofibers.

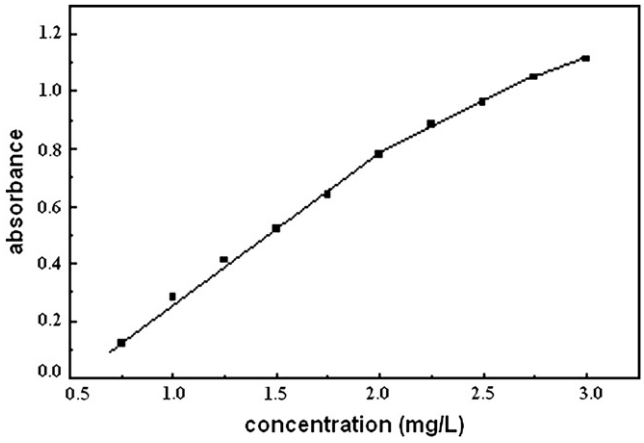


Fig. 6. The relationship between absorbance and concentration.

XPS measurement confirmed that the TiO_2 nanoparticles are adsorbed on the obtained hollow fibrous surface because of their limited escape depth of photoelectrons and the surface sensitivity (Fig. 5). It is clear that the fibers containing Ti elements. The binding energies of the Ti 2p3/2 and Ti 2p1/2 peaks are at ca. 459.1 and 453 ± 0.2 eV, respectively, which are consistent with TiO_2 formation [26]. These results prove that the crystalline phase of TiO_2 nanoparticles was kept during the coating process and adhered on the fibrous surface.

3.3. Photocatalytic activity of the obtained hollow multilayer PEI/TiO_2 complex nanofibers

The photocatalytic activity of TiO_2 primarily depends on its physicochemical properties, such as morphology, particle size, surface area and porosity [27]. In order to study the photocatalytic activity of the obtained hollow multilayer PEI/TiO_2 hybrid nanofibers, the degradation of methylene blue catalyzed by the multilayer PEI/TiO_2 hybrid nanofibers was carried out under irradiation of UV light at room temperature. The UV–vis absorbance spectrum of the reaction mixture was recorded to measure the concentration of the methylene blue. Fig. 6 shows the standard work curve of the relationship between absorbance and concentration, one can find that if the concentration is lower than 2 mg/ml, the absorbance increases linearly with the concentration. Fig. 7 shows the degradation rate of methylene blue under the irradiation of UV light with different catalysis conditions: without catalyst of any TiO_2 material added (curve a), with the prepared TiO_2 films composed of anatase TiO_2 (curve b) and multilayer hollow TiO_2 complex nanofibers (curve c).

In the case of no TiO_2 nanoparticles as control experiment, we hope to investigate the effect of the morphology on the photocatalytic activity. The use of TiO_2 films as another control experiment is due to its well-known high photocatalytic activity. Table 1 shows the absorbance with the time. After three samples were irradiated for 60 min, respectively, the degradation of methylene blue without catalyst was found to be only 3% (curve a), the one with TiO_2 film was 50% (curve b), while the highest degradation (70%) was obtained with the hollow multilayer PEI/TiO_2 hybrid nanofibers (curve c) as catalyst. Complete degradation of methylene blue was not obtained with the obtained hollow multilayer PEI/TiO_2 nanofibers in 1 h irradiation. From the above results, the photodegradation rate of methylene blue with catalysis of the hollow PEI/TiO_2 hybrid nanofibers was faster than that of two control experiments (a and b). Such enhanced photocatalytic property may be contributed to a main reason: the obtained hollow multilayer nanofibers have very high continuous surface areas to

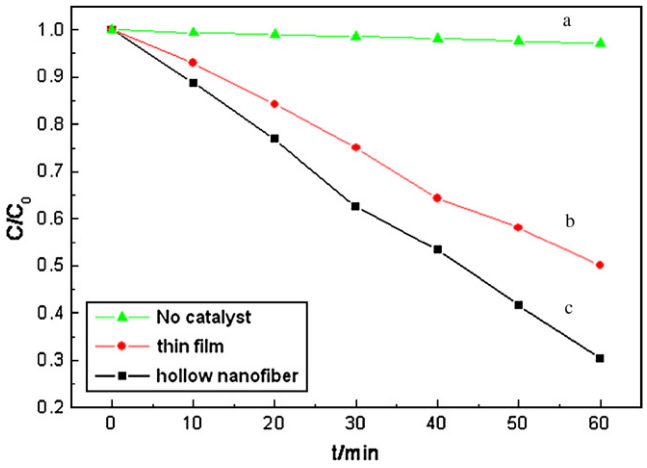


Fig. 7. The photocatalytic curve for methylene blue.

Table 1
The absorbance with the time for different materials

Degradation time (min)	0	10	20	30	40	50	60
Hollow nanofiber	0.781	0.693	0.600	0.488	0.417	0.325	0.234
TiO_2 film	0.785	0.730	0.661	0.589	0.505	0.456	0.393
No catalyst	0.778	0.773	0.770	0.767	0.763	0.759	0.756

absorb methylene blue dye uniformly, therefore this results in the increased photocatalytic degradation of methylene blue dye [23].

4. Conclusions

Hollow titania containing multilayer nanofibers was fabricated by the combination of electrospinning and layer-by-layer technique. The two different solvents, methylbenzene and THF used to remove the template and the result confirmed that THF is better than methylbenzene. The obtained hollow multilayer fibers have diameters of about 700 nm and their shell thickness of 140 nm. FTIR spectra show some structure characters of multilayer nanofibers. XPS measurement shows that TiO_2 nanoparticles were assembled successfully. The obtained multilayer hollow nanofibers have highest photocatalytic activity to the degradation of methylene blue solution compared with the TiO_2 film because of their unique hollow structure. Such novel structure materials with high surface area potentially can be used as photocatalyst in the future.

Acknowledgements

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