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Function of NaOH hydrolysis in electrospinning ZnO nanofibers via using polylactide as templates

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ABSTRACT

Mixture of polylactide (8 wt%), zinc acetate (6 wt%) and hexafluoroisopropanol was first used as electrospinning solution to fabricate ZnO nanofibers. Unfortunately, after direct calcination of the precursor polylactide/zinc acetate nanofibers, only ZnO film was prepared. Surprisingly, when the precursor fibers were pre-hydrolyzed with NaOH, ZnO nanofibers with diameter of 678 nm were obtained. The mechanism analysis showed that the preserve of fiber structure was attributed to the formation of zinc polylactic acid in the process of hydrolyzation. After characterized by scanning electron microscope and transmission electron microscope, the ZnO film was found to be an aggregation of irregular nanoparticles and the ZnO nanofiber was a necklace-like arrangement of cylindrical grains. X-ray diffraction and photoluminescence measurements indicated that the crystalline quality of the ZnO nanofibers was higher than the film. Furthermore, photocatalytic performance of the ZnO samples was investigated. Comparing with ZnO film, ZnO nanofibers exhibited much higher activity.

1. Introduction

ZnO is an interesting chemically and thermally stable n-type semiconductor that has been widely used in fields such as photonic materials [1], sensors [2], field-effect transistors [3], UV and visible light detectors [4], etc. Among these applications, photocatalysis have attracted tremendous attentions [5–7]. It is well known that material properties are strongly dependant on its structure [8]. Thus, many efforts have been made to prepare one-dimensional (1D) nanostructured ZnO in this field recently. Lai et al. [9] have synthesized nanostructured flower-like ZnO materials that had a high photocatalytic activity for the degradation of Rhodamine B. Young Jang et al. [10] have prepared ZnO nanoparticles to improve the capacity of degrading methylene blue in water under the illumination of ultraviolet rays. Peng et al. [11] have fabricated nano-sized ZnO thin film to degrade wastewater with phenol. Comparing with these structures, nanofibers which have characteristics of super large surface-to-volume ratio have shown much more excellent properties [12].

ZnO fibers can be prepared through many ways such as "organic–inorganic conversion" [13], hydrothermal method [14], vapor-phase transport method [15], spray pyrolysis technique [16], thermal evaporation process [17], electrospinning [18] and so on. Among these methods, electrospinning is found to be simple, convenient and low-cost. Most of all, it can fabricate organic and inorganic nanofibers in diameter ranging from micrometers to nanometers. ZnO nanofibers could be prepared by using electrospun fibers as templates and the co-electrospinning technique. However, up to now, only a few of polymers such as poly(vinyl acetate) (PVA) [19], poly (vinyl pyrrolidone) (PVP) [20] and cellulose acetate (CA) [21] have been used as the templates to prepare ZnO fibers via electrospinning. In order to enrich the templates group, polylactide (PLA) is taken into consideration. It is a nontoxic and biodegradable aliphatic polyester derives from 100% renewable resources, such as corn and sugar beets [22]. It releases H_2O, CO_2, and humus during burning and provides excellent properties at a low price. What's more, PLA could combine its major advantage-degradability and the control of fiber shape perfectly [23]. All of the advantages make PLA as a potential candidate for

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the preparation of inorganic nanofibers through the template route. However, it has never been used as templates to prepare ZnO nanofibers. This is because that PLA could fuse with Zn(II) salt at high temperature [24] and thus cannot act as templates well. To overcome the drawbacks, NaOH has been introduced. It has been found that NaOH could modify the surfaces of PLA with many carboxyl groups [25]. This is a breakthrough to solve the problem. On one hand, NaOH reacts with Zn(II) salt and generates $Zn(OH)_2$. On the other hand, NaOH hydrolyses PLA into PLA-COOH. The two products interact with each other and regenerate PLA-$COOZn_{1/2}$. Therefore, fusion of the two components – PLA and Zn(II) salt – can be avoided. Then the original structure can be preserved after calcination. ZnO nanofibers have never been prepared through this method before.

In this work, NaOH hydrolysis has been introduced to help the formation of ZnO nanofibers for the first time. The function of NaOH was discussed and the mechanism was investigated. Photocatalytic properties of the resulting ZnO were evaluated by quantifying the degradation of methylene orange under ultraviolet light.

2. Experimental

2.1. Materials

Polylactide (PLA, M_w = 300,000 g/mol) was purchased from Shandong Institute of Medical Equipment. Hexafluoroisopropanol (HFIP, Aladdin Reagent, Shanghai, China) was used as solvent directly. Methyl orange (MO) and sodium hydroxide (NaOH) were produced by Research Institute of Guangfu Fine Chemical Engineering in Tianjin, China. $Zn(CH_3COO)_2{\cdot}2H_2O$ ($ZnAc_2$) was provided by Sinopharm Chemical Regent Co., Ltd., China.

2.2. Preparation of ZnO nanofibers

Transparent spinning solution containing 6 wt% $ZnAc_2$ was prepared by adding $ZnAc_2$ to 8 wt% PLA in HFIP solvent, followed by magnetic stirring at ambient temperature for 6 h. Then the polymer solution was loaded into a glass dropper which was connected to a high-voltage supply (DW-P303-5AC High Voltage (0–30 kV), Dongwen High-voltage Power-supply Company, China). A grounded counter electrode was connected to a collector aluminum foil, which was placed 20 cm away from the orifice. The electric field was maintained at 15 kV. All electrospinning processes were carried out at room temperature. The fibers were exposed to the air overnight to facilitate further evaporation of the solvent.

Afterwards, the PLA/$ZnAc_2$ composite nanofibrous membrane was divided into two parts. One part was directly calcined at 600 °C in air for 4 h to obtain ZnO film. The other part was pre-hydrolyzed in a 0.2 N NaOH aqueous solution for 15 min at ambient temperature, and washed with distilled water sufficiently; then it was dried in vacuum at 30 °C for 12 h and followed by calcination in the same way as the original PLA/$ZnAc_2$ composite nanofibrous membrane. Then ZnO nanofibers can be obtained.

2.3. Characterization

Scanning electron microscope (SEM, SHIMDZU SSX-550, Japan) equipped with an energy-dispersive X-ray spectrometer (EDX) was used to study the morphology and composition of the samples. Based on the SEM images, the mean diameters of the composite nanofibers were analyzed using image visualization software ImageJ (about 100 measurements per field). TEM images were obtained using a JEM-2000EX (Japan) transmission electron microscope for samples deposited on carbon coated copper grids. Thermal gravimetric analysis (TGA) was carried out by using PerkinElmer Pyris 1 TGA (United States) from 50 to 700 °C at a heating rate of 10 °C/min under a flowing air atmosphere. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument (Switzerland) at a heating rate of 20 °C/min from 50 to 400 °C under nitrogen. In order to evaporate the solvent, the samples were kept in a constant temperature of 50 °C for 20 min before testing. Fourier transform-Infrared radiation (FT-IR) spectrometer (SHIMDZU, 1.50SU1, Japan) was used to identify the vibration in functional groups present in the fibers. The structure of the ZnO nanofiber was characterized by an X-ray diffractometer (Siemens D5005XRD) with CuKa radiation. The photoluminescence (PL) spectrum was recorded at room temperature using a Xe lamp with an excitation wavelength of 325 nm by a PerkinElmer LS 55 (United States) fluorescence spectrometer.

2.4. Photocatalytic activity measurements

Firstly, 36 mg of the ZnO film and fibers were respectively suspended in 90 ml of methyl orange (MO) aqueous solution (10.4 mg/L). Then, the mixture was added to a quartz tube and irradiated by the UV-radiation lamp (λ = 365 nm) with continuously magnetic stirring at room temperature. At different intervals, the catalysts were separated from the suspensions by filtration through cellulose membranes. Afterwards, a few milliliters of solution were withdrawn and loaded in a UV–vis spectrophotometer (SHIMDZU UV-3600, Japan). The relative concentration of MO was monitored by comparing its characteristic absorption intensity of the 464 nm peak with that of the original MO solution [23].

3. Results and discussion

3.1. Morphology

Fig. 1 showed SEM images of the PLA/$ZnAc_2$ composite nanofibers treated in different ways. Original nanofibers (Fig. 1(a)) were generally smooth and round, with mean fiber diameter of 468 nm. However, after calcination at 600 °C, a plat film (Fig. 1(c)) was generated instead of fiber. It was supposed that the PLA component of PLA/$ZnAc_2$ composite nanofibers melted upon heating, leading to the transformation of fiber to molten PLA. With the temperature further increased, $ZnAc_2$ melted as well. They mixed together and formed a film. After PLA and $ZnAc_2$ decomposed, ZnO film was left behind.

After hydrolyzation with NaOH (Fig. 1(b)), apparently, the original fibers became coarse, irregular, distorted, and intertwined at many loci. This was caused by the partial degradation of the polymer chain [25]. In addition, some fibers stick together to form larger fibers. It was due to the $Zn(OH)_2$ precipitates produced by the reaction between $ZnAc_2$ and NaOH. The precipitates had merged and filled in the pores among the adjacent nanofibers [21]. As a result, the mean diameter increased to 711 nm. It was believed that in the hydrolytic process of PLA/$ZnAc_2$ (as shown in Fig. 2), the carbonyl group polymerized in the PLA polymer was readily liberated [25], and then reacted with part of the $Zn(OH)_2$ precipitates to regenerate PLA-$COOZn_{1/2}$. Subsequently, when they were suffered from roasting, on one hand, the PLA-$COOZn_{1/2}$ and residual $Zn(OH)_2$ decomposed into ZnO; on the other hand, the network structure still retained in an excellent fashion. The two respects resulting in the formation of ZnO nanofibers (Fig. 1(d)). After statistics, mean diameter of the fibers was 678 nm. Its shrinkage was ascribed to the decomposition of the polymer.

Fig. 3 showed TEM images of the calcined PLA/$ZnAc_2$ composite nanofibers dealt with and without hydrolyzation. It can be seen that after direct calcination of the original fibers (Fig. 3(a)), ZnO film was obtained. It seemed to be an aggregation of irregular nanoparticles.