Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Novel fabrication of modulated carpenterworm-like zinc oxide/polyacrylonitrile composite nanofibers for photocatalytic degradation of methylene blue dye

Ying Zhou[a], Hou-Yong Yu[a,b,*], Ji-Ping Gu[a], Jia-Ying Zhu[a], Mai-Hao Zhu[a], Ying Guan[a,d], Ju-Ming Yao[a,c,*]

[a] The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China
[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China
[c] National Engineering Lab for Textile Fiber Materials & Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China
[d] Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, Zhejiang A&F University, Lin'an, Zhejiang 311300, China

ARTICLE INFO

*Article history:*
Received 27 January 2018
Revised 30 May 2018
Accepted 31 May 2018
Available online xxx

*Keywords:*
Thermal ultrasonication expansion
Composite nanofibers
Carpenterworm-like ZnO
Photocatalytic activity

ABSTRACT

Novel zinc oxide/polyacrylonitrile (ZnO/PAN) composite nanofibers with modulated carpenterworm-like and other ZnO morphologies were fabricated by simple thermal ultrasonication expansion method. The effect of different ultrasonication temperatures and immersion solutions on morphologies, microstructure and properties of the composite nanofibers were investigated by using field-emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and ultraviolet-visible spectroscopy. A possible mechanism for various morphologies of ZnO/PAN composite nanofibers at different reaction conditions was presented, and carpenterworm-like hierarchical structure with many smaller ZnO nanorods (diameter of about 201 nm) uniformly anchored onto the PAN nanofiber surface for 80-ZA composite nanofibers at thermal ultrasonication temperature of 80 °C and immersing in zinc ammonia solution. Compared to 60-W immersed in water at thermal ultrasonication temperature of 60 °C, the composite nanofibers fabricated in zinc ammonia solution (especially for 80-ZA) showed improved thermal stability and higher photocatalytic activity for methylene blue (MB). Compared to 60-W, decomposition temperature at 5% weight loss ($T_{5\%}$) was increased by 23 °C from 292 to 315 °C for 80-ZA. Meanwhile, 80-ZA showed higher photocatalytic degradation ratio of about 99.2% than 90.9–96.4% for 60-W and other samples after simulated sunlight irradiation for 7.5 h.

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## 1. Introduction

Multifunctional composites with zinc oxide (ZnO) nanoparticles show great potential photocatalysts and ultraviolet (UV)-shielding materials, due to their excellent physical and chemical stability, the photocatalytic activities and strong UV/infrared absorption of ZnO [1–5]. In general, various morphologies (nanorod, flower-like nanorod cluster) affect greatly photocatalytic and other related properties of ZnO and its composite nanofibers [6–9]. Besides, higher specific surface area and surface energy of ZnO nanoparticles make it easy to agglomerate, which further lead to the decrease of performance and restrict their application [10]. Recently, the growth of ZnO nanoparticles on nanocelluloses and polymer nanofibers as templates has been regarded as an efficient way to prepare well-dispersed ZnO with varied morphologies, which can effectively inhibit the agglomeration of nanoscale ZnO.

Recently, some novel methods including dipping [1], electrostatic adsorption [8,11] and hot–cold alternate impregnation [12] were utilized to fabricate ZnO with controllable morphologies on various templates to obtain multifunctional composites. For example, Olaru et al. used cellulose acetate butyrate (CAB) as a spin solution matrix to be impregnated into zinc salt-containing to prepare CAB/ZnO composite nanofibers by electrospinning [1], and finally larger ZnO size of 400–500 nm on the CAB nanofibers, resulting in photocatalytic degradation rate of about 47% Rhodamine B after 24 h of tungsten lamp irradiation, and 96% methylene blue (MB) dye at 20 h of visible light exposure. However, this method

* Corresponding authors at: The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China.
*E-mail addresses:* phdyu@zstu.edu.cn (H.-Y. Yu), yaoj@zstu.edu.cn (J.-M. Yao).

https://doi.org/10.1016/j.jtice.2018.05.050
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Please cite this article as: Y. Zhou et al., Novel fabrication of modulated carpenterworm-like zinc oxide/polyacrylonitrile composite nanofibers for photocatalytic degradation of methylene blue dye, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.05.050

has laborious dipping process and CAB as the matrix or template is easy to degrade under acidic conditions. Yu et al. used carboxylated nanocelluloses (NC) to electrostatically adsorb zinc nitrate solution to produce $Zn(OH)_2$ nanoparticles by simple precipitation, and finally the NC/ZnO composites with ZnO nanoparticles in diameter of 20–140 nm were obtained [11]. Sample NC/ZnO-0.5 can decompose 93% of MB dyes after UV light irradiation for 100 min, suggesting high photocatalytic activity of the NC/ZnO composite due to smaller ZnO size. But preparation methods of nanocellulose and its composite were complicated and needed multiple-step processes, and recycling of NC/ZnO composites with nanoscale size was difficult after dye treatment. Zhou et al. used polyacrylonitrile (PAN) as a matrix and zinc chloride as a zinc source to prepare spinning solution for obtaining PAN/$ZnCl_2$ composite nanofiber via electrospinning, and then various ZnO nanorods with diameter of 100–300 nm and length of 400–857 nm were anchored on the PAN nanofibers through repeatedly hot–cold alternate impregnation method [12]. PAN/ZnO composites showed high degradation rate of 65–100% MB dyes after 8–14 h irradiation under the mercury lamp. Nevertheless, the repeatedly hot-cold alternate impregnation method was too complicated, and relatively long degradation time was still required for PAN/ZnO composites, possibly due to larger ZnO nanoparticles with only rod-like shape. From above, polymers, graphene, or nanocellulose as templates have shown many shortcomings to restrict applications of ZnO composites. Hence, there is a big challenge to search an efficient template for growth of ZnO nanoparticles with modulated morphologies by simple method.

In this work, novel simple thermal ultrasonication expansion method was presented to fabricate ZnO nanoparticles with various morphologies (sheet-like, thornball-like, carpenterworm-like, irregularly granular) on PAN nanofibers as template/carrier, in which mechanically stable PAN nanofibers were treated with zinc ammonia solution at different thermal ultrasonication temperatures and then immersed into zinc ammonia solution or water for further growth of ZnO nanoparticles on nanofibers. Moreover, the effect of different thermal ultrasonication temperatures and immersion solutions on morphologies, microstructure, thermal stability and photocatalytic performance of the ZnO/PAN composite nanofibers were investigated.

## 2. Materials and methods

### 2.1. Materials

Polyacrylonitrile (PAN, Mw = 90,000) was purchased from Spectrum China Ltd. Ammonium hydroxide ($NH_3 \cdot H_2O$), zinc chloride ($ZnCl_2$) and N,N-dimethylformamide (DMF) were purchased from Hangzhou Gaojing Fine Chemical Industry, Co. Ltd. Methylene blue (MB) were supplied by Tianjin Yongda Chemical Reagent Company. Zinc ammonia solution (chemical formula of $[Zn(NH_3)_4]^{2+}$) was prepared by adding zinc chloride into deionized water with magnetic stirring, and then dropping the ammonia into the mixed solution until the solution was clear and its pH value was about 10.1. All other chemicals in reagent grade were used without further purification.

### 2.2. Preparation of ZnO/PAN composite nanofibers

As our previous work reported [12], the PAN nanofibers were fabricated from 12 wt% PAN in DMF solutions by electrospinning at voltage potential of 18 kV, tip-to-collector distance of about 15 cm and flow rate of 0.7 mL/h. ZnO/PAN composite nanofibers were prepared by the thermal ultrasonication expansion method at different temperatures and then various immersion solutions (Fig. 1). Briefly, the electrospun PAN nanofibers were immersed in 100 mL of zinc ammonia solution (zinc ammonia solution is a coordination compound formed by zinc ions and ammonia molecules) at 60 °C, 70 °C and 80 °C for 30 min of thermal ultrasonication (the pH value of zinc ammonia solution did not change after thermal ultrasonication, the pH value still kept at about 10.1). Then, the treated composite nanofibers were further immersed into the 100 mL of deionized water or zinc ammonia solution at room temperature for 30 min, and finally washed three times to be dried at 120 °C for 1 h. The resulting ZnO/PAN composite nanofibers were denoted as 60-W, 60-ZA, 70-ZA and 80-ZA, where the 60, 70 and 80 were the temperature, while W and ZA represented the immersion solutions of water and zinc ammonia, respectively. The preparation process is shown in Fig. 1.

### 2.3. Characterization of ZnO/PAN composite nanofibers

The morphological structures of ZnO/PAN composite nanofibers were observed on field emission scanning electron microscopy (FE-SEM, JCM-6000) at acceleration voltage of 15 kV at room temperature. Chemical structures was tested by KBr disk method with FT-IR spectrometer (Nicolet 5700, Thermo Electron Corp, USA) in the wavelength range from 4000 to 400 $cm^{-1}$. The crystalline structure were investigated by using Thermo Electron Corp ARL X'TRA Xray diffraction (XRD) system with monochromated high-intensity Cu$K\alpha$ irradiation ($\lambda = 1.54056$ Å) in the $2\theta$ range of 5–80° The thermal stability of 8–12 mg samples were evaluated by using a thermogravimetric analyzer (Pyris Diamond I, Perkin Elmer Corp) under dynamic nitrogen atmosphere with gas flow rate of 30 mL/min, where TGA curves were recorded in temperature range from 30 to 800 °C at rate of 20 °C/min. UV–visible diffuse reflectance spectra (UV–vis DRS) were characterized on a UH4150 spectrophotometer with integrating sphere and $BaSO_4$ as a reference material.

### 2.4. Photocatalytic tests of ZnO/PAN composite nanofibers

According to other literatures and our reported methods [10–12], photocatalytic activity of ZnO/PAN composite nanofibers were measured by photocatalytic degradation of methylene blue (MB, a model dye) under simulated sunlight (500 W Hg-arc lamp with UV cut off filter ($\lambda > 420$ nm)). The 50 mg of composite nanofibers were dispersed into 10 mL of MB aqueous solution (10 mg/L), and then put in the dark under magnetic stirring to reach adsorption–desorption equilibrium between photocatalyst and MB dyes. Photodegradation efficiency was determined by using U-3900 spectroscopy to record absorbance value (absorption wavelength of 665 nm) of the solution at given irradiation time intervals. The photocatalytic degradation ratio (PDR) was calculated as follows: PDR (%) $= \frac{A_0 - A_T}{A_0} \times 100\%$, $A_0$ and $A_T$ indicated initial MB absorption and MB absorption at time $T$, respectively. In addition, determination of ZnO release in 80-ZA (as a model sample) was performed by using an ICP-MS model 7500a Agilent (Santa Clara, CA, USA).

## 3. Results and discussion

Fig. 2a shows that PAN nanofibers have good distribution and smooth shape without beads with a diameter of 249 nm. Fig. 2b–e exhibited various ZnO morphologies of ZnO/PAN composite nanofibers in zinc ammonia solution at different thermal ultrasonication temperatures. Fig. 2f shows various sizes and morphologies of ZnO/PAN composite nanofibers. It can be seen that after sonicating at 60 °C, 60-ZA composite nanofibers showed sheet-like ZnO with diameter of about 2.94 μm and thickness of about 150 nm on PAN nanofibers (Fig. 2b). A thorn ball-like ZnO with a diameter of around 2.32 μm consisting of nanorods (about 588 nm in length and 220 nm in diameter) was obtained at the thermal ultrasonication temperature of 70 °C (70-ZA) (Fig. 2c). When the thermal

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