



A simple route to disperse silver nanoparticles on the surfaces of silica nanofibers with excellent photocatalytic properties

Xin Wang^{*}, Huiqing Fan^{*}, Pengrong Ren, Huawa Yu, Jin Li

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

In this work, monodispersed silver nanoparticles decorated SiO₂ nanofibers were synthesized by electrospinning method, followed by thermal treatment at 600 °C. Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo-gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) were used to characterize the composite nanofibers. Accordingly, the detailed formation mechanism of SiO₂/Ag composite nanofibers was discussed. Furthermore, an excellent catalytic activity of SiO₂/Ag composite fibers was observed by a degradation reaction of methyl orange (MO) dye.

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1. Introduction

Recently, the nanoscale dispersion of metal nanoparticles [1,2] in polymeric and inorganic substrates have triggered a great interest because of not only the novel physical, chemical and biologic properties of the nanocomposite materials [3,4], but also the exciting possibilities for potential applications of the further miniaturization of electronic components, optical detectors, chemical and biochemical sensors and devices. Among these, the incorporating of silver nanoparticles (Ag NPs) into certain matrixes have received particularly more attention due to the excellent performance of the resulting nanocomposites in optics [5], electronics [6], biology [7] and catalysis [8,9]. One shape of the substrates used for Ag NPs encapsulation is nanofiber [10], whose main benefits include flexibility to form, low resistance to flow of gas and liquids, high surface area, safer operation, easy scale up and reusability [11]. As for the substrate material, the polymer is lightweight, flexible and good moldable, while inorganic material like silica is high strength, heat-stable and chemical resistance [12–15].

In the past years, as a simple and low-cost method, electrospinning technology has regained great attention to prepare large-scale ultrafine nanofibers [16,17]. Combined with it, various methods to embed Ag NPs in the fibrous matrixes have been developed and the characteristics of these nanocomposites have been studied by many researchers. Generally, the metal Ag NPs in composite nanofibers can be achieved using either electrospinning

precursor solutions containing Ag NPs [18,19] or by reducing soluble silver salts or complexes in the electrospun nanofibers by thermal [20], reducing agent [21] or UV light. However, the problem is that it is extremely difficult to disperse Ag NPs homogeneously in nanofibers by these methods for the easy agglomeration of nanoparticles, and immobilizing Ag NPs by surfactant often leads to the loss of some properties. Besides, only a few nanoparticles can be dispersed on the surface of nanofiber when the matrix is pure polymer, for the presence of a polymer layer surrounding Ag NPs can limit the interaction between reactive species and the particle surface. Therefore, convenient and effective ways to disperse ultra-fine and uniform Ag NPs in fibrous matrixes is still in strong demand.

In this study, we present a facile and economical method to prepare SiO₂/Ag composite nanofibers. The technique here relies on the electrospinning and thermal decomposition of hybrid nanofibers prepared from the solution of mainly tetraethyl orthosilicate (TEOS), polyvinylpyrrolidone (PVP), silver nitrate (AgNO₃) and hydrochloric acid (HCl). The introduction of chloridion favors the dispersion of silver particles and affects the morphology of SiO₂ fibers. The possible formation mechanism of these composite nanofibers is discussed based on the experimental results obtained. Finally, we discussed the superior catalytic activity of SiO₂/Ag nanofibers.

2. Materials and methods

2.1. Materials

Polyvinylpyrrolidone (Mw = 58000), silver nitrate (AgNO₃), TEOS, HCl, ethanol absolute and methyl orange (MO) were

^{*} Corresponding authors. Tel.: +86 29 88494463; fax: +86 29 88492642.

E-mail addresses: wangx518@163.com (X. Wang), hqfan3@163.com (H. Fan).

purchased from Shanghai Chemicals Co. (China). All chemicals are analytical grade and used without further purification. Deionized water was purified using distillation equipment.

2.2. Preparation of electrospinning solution

The SiO_2/Ag composite nanofibers were synthesized by sol-gel based on electrospinning process. In a typical synthesis, a silica gel, with the mass ratio of TEOS:ethanol absolute:deionized water:HCl = 1:4:4:1 was prepared through hydrolysis and polycondensation by stirring the above mixing solution severely for 30 min in a three-necked flask at room temperature. After that, a certain amount of PVP powder was dissolved in the silica gel directly and stirred continuously for 2 h to form a solution with the mass concentration of PVP at around 30%. Then a known quantity of AgNO_3 was added to the mixture and stirred for another 30 min to attain the homogeneity required for electrospinning. The molar ratio of AgNO_3 to a repeating unit of PVP was 1:40. With the adding of AgNO_3 , silver chloride (AgCl) was generated, and the solution underwent changes in color from clear, colorless to white.

2.3. Preparation of SiO_2/Ag nanofiber by electrospinning

We used a home-made electrospinning setup which contained basically three components: a high-voltage supply (HBGY HB-2603-1 AC), a syringe pump and an aluminum (Al) collecting plate. The syringe pump connected to a Teflon tube was used to control the flow rate. The process is that the electrospinning solution was pushed from the syringe at a constant flow rate of 2 ml/h into a 1 mm internal diameter Teflon capillary, whose needle as an anode was 12 cm distant from the grounded cathode Al plate. The Al plate was also used to collect the composite nanofibers under a high voltage of 30 kV. The collected nanofibers were then dried at 60 °C and continued to heat at a rate of 2 °C min⁻¹ to 600 °C and maintained at the temperature for 2 h in the air. Meanwhile, SiO_2 nanofibers were also synthesized using the identical procedure and parameters for comparison.

2.4. Characterization and photocatalytic activity measurements

X-ray diffraction (XRD) data of the nanofibers were obtained on an X'Pert MPD Philips diffractometer with $\text{Cu K}\alpha$ radiation at room temperature. The morphologies of the nanofibers were examined using a Zeiss Supra 55 field emission scanning electron microscopy (FE-SEM) operated at 20 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray (EDS) spectra were performed on a Tecnai F30 G² apparatus with an acceleration voltage of 300 kV. Thermo-gravimetric analysis (TGA) was performed on a Q600-SDT analyzer with a heating rate of 10 °C min⁻¹ under a flow of air gas. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5400 spectrometer using $\text{Al K}\alpha$ ($E = 1486.6$ eV) radiation. The ultraviolet-visible (UV-vis) spectra were recorded using a Shimadzu UV-3150 spectrophotometer.

The photocatalytic reaction suspension was prepared by adding the sample (40 mg) to 40 ml of MO solution with a concentration of 10 mg/L. The suspension was sonicated for 1 h and then stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium prior to UV irradiation. The suspension was then irradiated by UV light under continuous stirring. Decolorized solution for various time intervals was subjected to spectra measurement after centrifugation.

3. Results and discussion

XRD measurements of the composite nanofibers before and after heat treatment were carried out in order to trace the

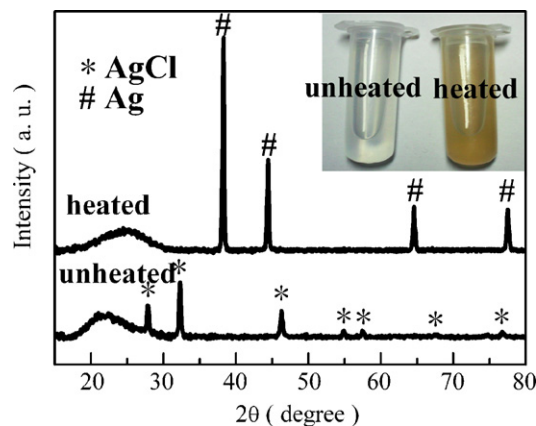


Fig. 1. XRD patterns of composite nanofibers before and after heated. The inset is the photograph of composite nanofibers dissolved in ethanol before and after heated.

formation of silver in the nanofibers. From Fig. 1 we can see that before heated (lower curve), all the diffraction peaks could be readily indexed to silver chloride with a calculated lattice constant $a = 5.55$ Å, which is in good agreement with the reported data of 5.5491 Å (space group Fm-3m [225]; JCPDS No. 31-1238). For the nanofibers heated at 600 °C for 2 h (upper curve), the diffraction peaks with 2θ values of 38.2°, 44.4°, 64.5° and 77.5° correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal faces of the face-centered cubic (fcc) silver respectively [22]. And the calculated lattice constant is 4.08 Å, very close to the reported literature value of 4.0861 Å (space group Fm-3m [225]; JCPDS No. 65-2871). Additionally, the broad diffused reflection peaks at 2θ value between 20° and 25° observed in both the samples are indicative of the characteristics of amorphous silica sol and silica [23]. No other reflections are observed, indicating that silver chloride had pyrolyzed entirely into silver with no impurity existed after annealing at 600 °C for 2 h. Thermodynamic studies have suggested that silver is more stable than Ag_2O at temperatures of >189.8 °C in air [24]. Therefore, any Ag_2O that is present decomposes to metallic silver during the calcination heating-up stage. In the cooling stage from the calcination temperature, the amount of Ag_2O that is formed is very low since the formation of Ag_2O is a very slow process at low temperature [25]. So no Ag_2O is observed in the XRD spectrum. Besides, another evidence for the formation of Ag NPs is the color of the fibers, which changed from white to pale yellow after heating for 2 h, as seen in the inset of Fig. 1, owing to the surface plasma resonance (SPR) of the Ag NPs produced in the composite fibers. However, the SPR is not very obvious in the UV-vis absorption spectrum, which may be attributed to extremely low content of Ag NPs in our nanofibers.

Typical SEM images of composite nanofibers with adding AgNO_3 in the precursor solution before and after heated are shown in Fig. 2(a) and (b), which clearly illustrate the copiousness in quantity and the uniformity in shape that could be routinely accomplished in this synthesis. The fibers are randomly oriented and large interconnected voids are present. Unlike pure polymer fibers, which show major shrinkage and degradation at high temperatures [26], the rigid network of inorganic silica enables the composite fibers to retain their shape, prevent major shrinkage after heating at 600 °C while the average diameter of the fibers is reduced from roughly 400 (± 50 nm) to 300 nm (± 50 nm).

Besides, compared with SiO_2 fibers (inset in Fig. 2(b)), the morphologies of composite fibers become more irregular and much thicker. We deduce that, with the adding of silver nitrate to the spinning solution, neutral silver chloride is formed, leaving excessive chloridion, which decreases the charge density in the spinning solution, weakens the localized charge effects on the

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