Synthetic Metals 220 (2016) 533–537

Contents lists available at ScienceDirect

Synthetic Metals

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

Short communication

Ag-ZnO photocatalyst anchored on carbon nanofibers: Synthesis, characterization, and photocatalytic activities

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ARTICLE INFO

Article history:
Received 27 June 2016
Received in revised form 18 July 2016
Accepted 21 July 2016
Available online 29 July 2016

Keywords:
Carbon fiber
Ag-ZnO
Semiconductor
Photocatalysis
Antibacterial

ABSTRACT

In this study, a novel photocatalytic and antibacterial Ag-ZnO decorated carbon fiber composite was synthesized by a simple electrospinning method followed by the hydrothermal treatment. Aqueous suspension containing Ag and ZnO precursors with the carbon nanofibers was kept in the hydrothermal process at 140 °C for 2 h to obtain a homogenous distribution of Ag-ZnO NPs throughout the surface of carbon fibers. The studies of the photocatalytic degradation of methylene blue (MB) and antibacterial performance against Escherichia coli *(E. coli)* indicated that the as-synthesized composites show enhanced adsorption, visible-light-driven photocatalytic, and antibacterial properties than that of pristine ZnO particles. Therefore, this work provides a facile method of the preparation of carbon fiber based composites which may have potential applications in the environmental fields.

1. Introduction

In recent years, semiconductor photocatlysis has drawn considerable attention as a green technique with potential for complete elimination of toxic organic pollutants and pathogens in the environment [1]. Among various oxide semiconductor photocatalyst, ZnO, a direct wide band gap (3.37 eV) semiconductor has been extensively studied due to its high photosensitivity, non-toxicity, high luminescence properties, and low cost [2]. However, there still exist some drawbacks of ZnO photocatalyst such as low utilization of visible light and rapid recombination of photo-generated electron-hole pairs, which limit its wide applications in wastewater treatment [3]. Therefore, it is important to extend the optical absorption of ZnO from UV to visible light region and hinder the recombination of the photogenerated electron-hole pairs for improving photocatalytic efficiency of ZnO. Addition of metallic nanocrystals, such as Au, Pt, Ag has turned out to be a feasible method to achieve enhanced photocatalytic activity of ZnO nanostrucutes [2,4,5]. In particular, among the metallic species, silver (Ag) has shown an enhanced electron hole separation and interfacial charge transfer ability along with visible light excitation of ZnO [5]. Beside this, Ag NPs show excellent antibacterial activity which is helpful for the removal of pathogens from the water [6].

Although the decreasing of particle size is one effective way to increase the surface area of photocatalyst, they may create a serious issue due to the difficulty of separating the utilized nanostructured photocatalyst from the treated water. Moreover, agglomeration of extremely nano-sized particles is another problem limiting their widespread application in wastewater treatment. It may bring about a breakthrough when these semiconductor NPs can be assembled into the fiber, which will solve the problem of agglomeration and possess the easiness of separation and recovery for practical photocatalytic application. Carbon nanostructures such as carbon nanofibers (CNFs) and nanotubes (CNTs) have attracted great interest due to their unique anisotropic properties and wide range of potential applications [3]. The carbon fiber can be considered as a potential support to deposit different semiconductor NPs on its surface. Owing to significant advantages in terms of extremely high surface area, porosity, adsorption capacity, and high conductivity, the carbon nanofibers can be applied in photocatalysis along with semiconductor materials for the wastewater treatment. It has already been reported that the CNFs efficiently capture and transport photo-generated electrons through highly conductive long CNFs which is helpful in the hindering the recombination of electrons and holes and improving the photocatalytic efficiency [7]. Our previous works [3,8] showed that incorporation of semiconductor NPs into the electrospun carbon nanofibers can prevent the loss of catalyst and can be repeatedly used. Further, the as synthesized

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http://dx.doi.org/10.1016/j.synthmet.2016.07.027
0379-6779/

nanocomposite fiber exhibited a strong adsorption capacity, resulting fast removal of organic pollutants. In light of this, here, we investigated the synthesis of Ag-ZnO NPs decorated carbon nanofibers with simultaneous adsorption and degradation capacity for the effective removal of organic pollutants from water. We further investigated the antibacterial property of the produced photocatalyst.

2. Experimental

2.1. Preparation of Ag-ZnO/carbon fiber composite

Carbon nanofibers were prepared from electrospun PAN nanofibers as accordance with our previous report [3]. The Ag-ZnO NPs were incorporated on carbon nanofiber by applying hydrothermal method. Briefly, 25 mg of carbon nanofiber was added into the mixture of 0.5 g of bis-hexamethylene triamine and 0.75 g of zinc nitrate hexahydrate in 50 g of water. Then, 20 mg of $AgNO_3$ was added and stirred for 3 h. The mixture was placed in a Teflon crucible and kept inside the autoclave at 140 °C for 2 h. The product obtained after cooling was filtered off, washed with distilled water and ethanol, and dried at 60 °C for 12 h. For comparison, pristine ZnO particles were also prepared by the same method without using carbon fibers.

2.2. Characterization

The surface morphology of nanofibers was studied by using a field-emission scanning electron microscope (FE-SEM, Hitachi S-7400, Japan) and JEOL JEM 2010 transmission electron microscope (TEM) operating at 200 kV(JEOL Ltd, Japan). The phase and crystallinity were characterized by using a Rigaku X-ray diffractometer (Rigaku Co., Japan) with Cu Kα (λ = 1.54056 Å) radiation. Room temperature photoluminescence (PL) spectrum was measured by Perkin Elmer Instrument (LS-55). The UV–visible spectra were obtained with a UV–vis spectrometer (Lambda 600, Perkin Elmer, USA) over the range of 200–800 nm.

2.3. Photocatalytic activities

The photocatalytic activities were studied by degradation of MB under both UV (λ = 365 nm) and visible light (Mercury lamp (2000 W); wavelength: 400–800 nm) irradiations. In each case, before irradiation, 50 ml of dye solution (10 ppm concentration) and 25 mg of catalyst were mixed and magnetically stirred in the dark for 30 min to ensure an adsorption-desorption equilibrium. After centrifugal separation, the concentration of the dye in the supernatant was analyzed by a spectrophotometer. Next, the photocatalytic dye degradation test was carried out under UV and visible light irradiations, separately. At specific time intervals, 1 ml of the sample was withdrawn from the system and centrifuged to separate the residual catalyst, and then the observance intensity was measured at the corresponding wavelength.

2.4. Antibacterial performance

The antibacterial performance of as synthesized photocatalysts was investigated by a zone inhibition method using *Escherichia coli* (*E. coli*) as a model microorganism. Using a spread plate method, nutrient agar plates were incubated with 1 ml of the bacterial suspension containing approximately 106 colony-forming units (CFU)/ml. The photocatalysts were gently placed on the inoculated plates and were then incubated at 37 °C for 24 h. Zones of inhibition were determined by measuring the clear area formed around each photocatalyst.

3. Results and discussion

Fig. 1 shows the morphology of the pristine carbon nanofibers and the as-obtained Ag-ZnO/carbon composite samples. The pristine carbon fiber showed smooth surface morphology with uniform diameter approximately 270 ± 10 nm. The homogeneous distribution of Ag-ZnO particles throughout the surface of carbon fiber was obtained after the hydrothermal treatment (Fig. 1B). The strategy of loading of a small amount of zinc NPs prior to electrospinning process produces zinc NPs distributed fibers which was advantageous for providing the nucleation sites for the growth of Ag-ZnO particles during hydrothermal synthesis and holding the Ag-ZnO particles on the surface of the fibers. Fig. 1C shows the TEM-EDX along the randomly chosen line. As shown in Fig. 1C, all the used materials (C, O, Zn, Ag) could be detected confirming that the Ag-ZnO/carbon heteroarchitectures were successfully prepared.

The crystalline structures of the as obtained sample and pristine ZnO were determined by the XRD patterns as shown in Fig. 2. The pristine ZnO revealed the distinct peaks at 2θ values of 31.85, 34.5, 36.4, 47.65, 56.6, 62.8, 66.3, 68.1, 69, and 76.8° with their corresponding crystalline planes (1 1 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), and (2 0 2), respectively [3]. Other than ZnO, the extra peaks at 2θ values of 37.8, 44, and 64° corresponding to the crystal planes (111), (200), and (220), respectively, indicated the presence of Ag metal in the composite photocatalyst [6]. A peak centered at 2θ values of 25.2° attributed to the (002) planes of the carbon structure [3,7]. From the obtained results, it can be confirmed that the Ag is well-doped on the surface of ZnO with carbon fiber as a base.

The light absorption behavior of the pure ZnO and Ag-ZnO/carbon fiber was analyzed by UV–vis absorption spectroscopy and shown in Fig. 3A. As compared to pristine ZnO particles, a red shift of the optical absorption edge was noticed in Ag-ZnO/carbon composite fiber which might be due to the strong interfacial electronic coupling between the ZnO and Ag NPs which causes the intense photon scattering and increased photocatalytic activity in direct light [9]. Further, we calculated the band gap energy for the as-synthesized photocatalyst according to our previous report [6,8]. Briefly, for a semiconductor material, the absorbance in the vicinity of the onset due to the electronic transition is given by the following equation [8,10].

$$\alpha = \frac{K(h\nu - E_g)^n}{h\nu} \quad (1)$$

where, 'α' represents the absorption coefficient, 'K' represents a constant, 'Eg' represetns the band gap, and 'n' represets a value that depends on the nature of the transition (1/2 for a direct allowed transition or 2 for an indirect allowed transition). The calculated bandgap energy value for the composite photocatalyst was found to be ~3.0 eV which is lower than that of the pristine ZnO (3.37 eV) [11]. This finding shows that the photocatalytic efficiency of the composite fiber has been enhanced and it can utilize both UV and visible light. Further, we studied the photo generated electron-hole recombination process by the photoluminescence (PL) spectra at room temperature and the results are shown in Fig. 3B. The pristine ZnO particles showed three emission bands. The first band is the UV near-band-edge (NBE) emission with a wavelength of ~415 nm [12]. The band at ~482 nm is probably caused by radiative transition of electron from shallow donor levels, created by the oxygen vacancy to the valence band. The third band appeared at ~531 nm which can be likely attributed to the interstitial oxygen [13]. These intensities were found to be suppressed in the case of Ag-ZnO/carbon nanofiber composite suggesting that the rate of e-h recombination has been reduced,