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Preparation of electrospun ZnS-loaded hybrid carbon nanofiberic membranes for photocatalytic applications

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ABSTRACT

In this paper, graphene oxide/polyacrylonitrile (GO/PAN) composite nanofibrous membranes were firstly prepared by an electrospinning method. Then, the GO/PAN composite nanofibrous membranes were further transferred to graphene oxides/carbon nanofibrous membranes (GO-CNFs) by a calcination treatment. Following a solvothermal treatment, zinc sulfide (ZnS) nanopartciles were covered onto GO-CNFs to form electrospun carbon nanofibrous membranes loaded with GO/ZnS (GO/ZnS-CNFs). The composition and microstructure of GO/ZnS-CNFs were characterized by field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Raman and UV–vis diffuse reflectance spectra analysis. Due to the synergistic effect between photocatalytic activity of ZnS and excellent adsorption capacity of GO-CNFs, the resultant GO/ZnS-CNFs exhibited excellent photocatalytic activity for oxidation of p-aminotoluene and phenol under mild conditions. The resultant hybrid carbon composite membranes offer the significant advantages, such as low dosage, high catalytic activity, easy recycling and excellent stability.

1. Introduction

As known, carbon materials have been widely studied as support for catalytic applications [1,2]. Carbon nanofibers (CNFs) were a new class of flexible materials with high mechanical strength, superior electroconductibility and excellent corrosion resistance. Meanwhile, they could supply a large surface area, which is critical for nanostructure-based catalytic materials [3]. In our previous study [4], we studied activated polyacrylonitrile carbon nanofibers with BiOBr and AgBr decorating for photocatalytic degradation of rhodamine B. The photocatalytic ability was dramatically improved due to the synergistic effect between photocatalytic activity of BiOBr and AgBr, and excellent adsorption capacity of CNFs. However, these composite CNFs were easy to be broken under high-speed stirring due to their low mechanical strength. Graphene oxide (GO) comprises graphene sheets with oxygen-containing functional groups on the basal planes and the edges. It can be fabricated in large quantities at a low cost [5]. The oxygen-containing functional groups of GO increase the interlayer distance between adjacent graphene sheets and interaction strength between graphene sheets and CNFs matrix, thus, enable catalytic nanoparticles to be adsorbed on graphene sheets as well, achieving composite CNFs with higher mechanical strength [6].

As one of typical II–IV binary semiconductor materials, zinc sulfide (ZnS) has received considerable concern due to its excellent properties. According to the previous reports, ZnS exists in two main crystalline forms: the cubic sphalerite phase and the hexagonal wurtzite phase [7]. Both phases are direct and large band-gap semiconductors at room temperature (3.7 eV for the cubic sphalerite phase and 3.8 eV for the hexagonal wurtzite phase), regarded as good candidates for light-emitting materials, electroluminescent devices, photoluminescent devices, photocatalysts, solar cells, optical sensors, lasers, and optical recording materials [8–16]. Recently, researchers have focused on the synthesis of ZnS composites through combined ZnS with other nanostructured carbon materials to form the delocalized conjugated materials. These composite materials are well matched with the photocatalysts in energy level and an intensive interface hybrid effect emerges between these materials, causing rapid charge separation and slow charge recombination in the electron-transfer process [17].

p-Aminotoluene (p-toluidine) is a colorless crystal with high toxicity. Although it can be oxidated in acetonitrile by hydrogen peroxide, its rate is a very slow [18]. Using ozone as oxidizing agent to oxide p-aminotoluene, the yield of aromatic products does not exceed 15% [19]. Phenol is one of the most toxic, and is used widely in petrochemical, chemical, and pharmaceutical industries. The presence of phenol in aqueous environments presents serious problems due to its toxicity, persistence in the environment, and bioaccumulation [20]. Therefore, the removal of phenol by environmentally friendly is a major

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consideration for current research. To pursue a high efficiency method oxide p-aminotoluene and phenol is attract considerable interest in organic synthesis and environmental protection. The photo-catalytic oxidation is an environmentally 'benign' or 'green' synthesis, since it consumes low-energy photons and occurs under atmospheric pressure and at room temperature [21]. In this paper, graphene oxide/polyacrylonitrile (GO/PAN) composite nanofibrous membranes were firstly prepared by an electrospunning method. Then, the GO/PAN composite nanofibrous membranes were further transferred to graphene oxides/carbon nanofibrous membranes (GO/CNFs) by a calcination treatment. Following a solvothermal treatment, zinc sulfide (ZnS) nanoparticles were covered onto GO/CNFs to form electrospun carbon nanofibrous membranes loaded with GO/ZnS (GO/ZnS-CNFs). The catalytic activity of the resultant GO/ZnS-CNFs was investigated in oxidation of p-aminotoluene and phenol by a photochemical method. The recycling use of the catalyst was also of concern. The redox experiment was carried out without chemical additives and poisonous by-products under mild reaction conditions. The mechanism of oxidation was discussed.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, M w = 150.000) power, *N*, *N′*-dimethylformamide (DMF, AR), zinc acetate ($ZnC_2H_6O_2 \cdot 2H_2O$, AR) and sodium sulfide ($Na_2S \cdot 9H_2O$, AR) were purchased from aladdin Co. Ltd. (China).

2.2. Preparation of GO/ZnS-CNFs

Typically, the GO solution was firstly fabricated on the basis of a modified Hummer's method [22]. Then, 1.0 g PAN, 0.1 g GO and 0.5 g zinc acetate were dissolved in 10 mL DMF by rapid stirring for 12 h to obtain a homogeneous solution. About 8 mL of the solution was placed in a 10 mL syringe. The syringe was placed in a syringe pump that maintained a solution feeding rate of 0.08 mm/min. The distance between the needle tip and collector was 12 cm, and the voltage was set at 15 kV. Subsequently, the sample was annealed at 550 °C for 3 h in pure nitrogen with a heating rate of 2 $°C\ min^{-1}$ to obtain intermediate products. The intermediate products were put into 6 mM NaS solution and transferred to a 80 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 6 h. Finally, the product was dried at 60 °C for 6 h to obtain GO/ZnS-CNFs membranes. The mass fraction of ZnS on GO/ZnS-CNFs membranes is about 13.24% that calculated by EDS analysis.

2.3. Photocatalytic conversion of 4-aminotoluene to 4-nitrotoluene

The photocatalytic activity of GO/ZnS-CNFs membranes were detected through the photocatalytic oxidation of 4-aminotoluene in the mixed solution which the volume rate of water to acetonitrile is 3:2. The photocatalytic oxidation of 4-aminotoluene experiment was conducted in a photochemical reaction equipment with a 500 W metal halide lamp as the light source. In every experiment, 2 × 5 cm of GO/ZnS-CNFs membrane was added into 10 mL of 4-aminotoluene solution ($0.002\ mol \cdot L^{-1}$). The concentrations of 4-aminotoluene after an appropriate irradiation time were measured by HPLC technique. The mobile phase for HPLC was a mixture of water and acetonitrile in a ratio of 3:2 (v/v).

2.4. Characterization

The structures and crystal phase of the as-prepared samples were analyzed with a SIEMENS Diffractometer D5000 X-ray diffractometer (XRD) with Cu Kα radiation source at 35 kV, with a scan rate of $4°\ s^{-1}$ in the 2θ range of 5–80°. X-ray photoelectron spectroscopy (XPS) data were obtained with an obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The ULTRA-55 field emission scanning electronmicroscopy (FE-SEM) at an accelerating voltage of 10 kV and JSM-2100 transmission electron microscopy (TEM) was used to characterize the morphology of the as-prepared samples. Raman spectra were recorded using a micro-Raman spectroscopy (TriVista TR557 Princeton Instruments). The Agilent high performance liquid chromatography (HPLC) 1100 was used to confirm the products in the reaction. The concentration of organics was measured by UV1901PC UV–vis spectrophotometer (Shanghai Aucy Technology Instrument CO.,LTD, China).

3. Results and discussion

The schematic representation for preparation of GO/ZnS-CNFs membranes is shown in Scheme 1. The GO/PAN composite nanofibrous membranes are firstly prepared by a electrospunning method. Then, the GO/PAN composite nanofibrous membranes are further transferred to GO-CNFs by a calcination treatment. Fig. 1A shows the electrospun nanofibers after calcination treatment are the homogeneous nanofibrous mats with reveal bulge structure. Apparently, a large number of pores are observed on the surface of as-prepared samples, as shown in Fig. 1B. These pores are formed due to the release of gases pyrolysis of polymer matrix during the calcination process [23,24], which are beneficial for absorbing the organic molecules onto the catalytic active sites on the surface of composite nanofibers. Following a solvothermal treatment, zinc sulfide (ZnS) nanoparticles are covered onto GO-CNFs to form electrospun carbon nanofibrous membranes loaded with GO/ZnS (GO/ZnS-CNFs). Fig. 1C and D are the SEM images of GO/ZnS-CNFs membrane at different magnifications. The microcosmic structure of the membrane is maintained after solvothermal reaction and the ZnS nanoparticles with a diameter at about 10 nm exhibit a good dispersity on the surface of nanofibers. The energy dispersive X-ray spectroscopy (EDS) verify the existence of C, O, Zn and S elements in GO/ZnS-CNFs membrane samples (Fig. 1E), and atom ratio of S/Zn closed to 1: 1 (inset in Fig. 1E) suggests that nanoparticles distributed in composite membrane are ZnS. The S, Zn, C, and O edge mappings are shown in Fig. 1F-I, respectively. It can be seen that the orange color (assign to S), red color (assign to Zn), white color (assign to C) and green color (assign to O) are uniformly distributed in the sample of GO/ZnS-CNFs membranes.

The resultant GO/ZnS-CNFs membranes are expected to present outstanding mechanical flexibility, enabling them to maintain the original dimensions after folding and crushing (Fig. 2). Apparently, the strategy has shown excellent versatility and scalability for potentially large-scale fabricating lightweight graphene-based carbon nanofibrous products by employing specific textured matrices. The high mechanical flexibility may be contributed to the including of GO nanosheets, which have numerous oxygen-containing functional groups and presents the high specific surface area and crumpled surface nanofibers with curling edges, could play a beneficial role in enhancing interfacial interaction with the GO and the carbon nanofibrous matrix [25].

To further obtain the microscopic morphology and structure information, the transmission electron microscopy (TEM) analysis of GO/ZnS-CNFs has been performed. As shown in Fig. 3A, a light-colored layer on the surface of nanofibers can be observed. Further magnification of surface structure of nanofibers, the light-colored layer is consisted of many nanosheets, indicating that the GO is successfully incorporated onto the nanofibers, as shown in Fig. 3B. Furthermore, no clear interface between the GO nanosheets and the CNFs can be founded, indicating that the junction at the edges of GO and CNFs might be linked by strong interaction [26]. Besides, many nanoparticles also can be observed in the nanofibers. The crystalline nature of these nanoparticles is further investigated by high resolution TEM (HR-TEM) (Fig. 3C). The lattice fringes with a d-spacing of 0.313 nm, 0.192 nm, 0.164 nm are contributed to the (111), (220), (311) crystal planes of ZnS [27]. Three distinct diffraction rings are seen from the