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Full Length Article

ZnO/AAO photocatalytic membranes for efficient water disinfection: Synthesis, characterization and antibacterial assay

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ABSTRACT

Novel type of ZnO/AAO photocatalytic membranes were fabricated by growing highly dense and porous network of ZnO nanosheets on nanoporous anodic aluminum oxide (AAO) using the facile hydrothermal approach. The structural properties of the membranes were investigated by field emission gun scanning electron microscopy (FEG-SEM) and X-ray diffraction spectroscopy (XRD). The ZnO nanosheet networks were found polycrystalline, showing mainly (100) and (002) ZnO reflections. The XRD results suggested that the ZnO-AAO interface promotes lattice disorder mainly along the polar-axis while the nonpolar plane remains less defective. The energy dispersive X-ray spectrometry (EDX) confirmed the formation of pure ZnO. In addition, Fourier transform infrared spectroscopy (FTIR) indicated an intense absorption band in the range of 661–780 cm^{-1} for stretching vibrations of Zn–O bond and also specified the presence of intrinsic crystal defects. The diffuse reflectance spectroscopy (DRS) revealed an optical absorption edge of 401 nm and a band gap of 3.09 eV for grown ZnO nanosheet mesh. Moreover, the DRS studies also substantiated the existence of crystal defects by recognizing a red shift in the band gap, and a trail of low energy absorptions in the reflectance spectrum in the range of 400–800 nm. Due to the corrugated surface morphology and hierarchical porosity of ZnO scaffolds on porous AAO substrates, the membranes possess a great deal of catalytic surface and demonstrated a strong antibacterial activity against waterborne bacteria Escherichia coli (E. coli) under dark and UV light conditions. Our results showed that fabricated ZnO/AAO membranes have great potency for photocatalytic disinfection of contaminated water on account of their large catalytic surface and inherent porosity which can facilitate the mass transfer and diffusion of oxygen species and Zn^{+2} ions during the disinfection process. This morphology-function relationship is highly effective for designing cost effective, efficient, environment-friendly, and self-antifouling photocatalytic disinfectants.

1. Introduction

Water pollution causes variety of health problems due to bacterial and industrial pollutants. The excellent photocatalytic properties of semiconductors such as ZnO can be employed with great confidence for solving this ever alarming environmental challenge [1]. As a result, semiconductor photocatalysis has been enjoying intensive attention in the environmental purification, and also because of its simplicity, mild reaction conditions, and low energy consumption [2,3].

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, has been used to improve carrier transport in photodetectors [4], output power in light-emitting diodes [5], and the lasing performance in optoelectronic material [6]. Moreover, upon ultraviolet (UV) excitation, it can trigger redox reactions by producing reactive oxygen species (ROS) which can decompose several bacterial contaminants [3,7]. The hierarchical ZnO nanostructures have also been studied for their promising applications in photocatalysis [3,8].

For photocatalytic performance of ZnO nanostructures, Gram negative bacterium E. coli has been extensively investigated [9]. Other than the photochemical process, the moist background can also initiate a partial decomposition reaction in ZnO that can result into the gradual release of Zn^{2+} ions which take part largely in bacterial degradation in dark conditions [10]. ZnO not only catalyzes

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by absorbing electromagnetic radiation in UV region due to its wide band gap, but also exhibits photocatalytic activity under visible irradiation in the presence of lattice defects [11]. The crystal defects in the form of oxygen vacancies are believed to play an important role in the improvement of visible light photocatalytic activity of ZnO [12,13]. Among various ZnO nanostructures, the hydrothermally grown ones normally possess intrinsic crystalline defects due to oxygen vacancies [12]. Moreover, it has been shown that high annealing temperatures can not only improve the crystallinity but also increase the density of oxygen vacancies in ZnO [13].

Different micro- and nano-hierarchical forms of ZnO have been studied for antibacterial activity in connection with their surface area [3,8]. Among nanostructures, ZnO nanoparticles are widely known for their enormous surface to volume ratio [14]. Considerable scientific investigations have been conducted on the use of ZnO nanoparticles for water disinfection. However, efficient separation of these nanoparticles cannot readily be achieved from water after completion of the disinfection process [15,16]. The toxic presence of these nanoparticles in water can pose real threats to human health. Therefore, for safe disposal of ZnO from purified water, the growth of porous ZnO structures were investigated on glass substrates [17]. For amplification of the photocatalytic surface, ZnO nanostructures were also grown on porous substrates [16].

Ceramic membranes such as nanoporous anodic aluminum oxide (AAO) are widely investigated for their promising applications in the field of photovoltaics, sensors and templating for the fabrication of one-dimensional nanostructures [18]. Moreover, the ceramic membranes have outstanding chemical and thermal stability and longer life time [19].

For efficient separation of disinfectants from purified water, highly adherent ZnO nanostructured films with inherent porosity can be effectively employed. Such characteristic porosity can not only conserve a large photocatalytic surface but can also promote the transfer of reactive species. For growth of these structures, the porous surface morphology of AAO substrates can positively be considered. Herein, we report the synthesis of highly porous networks of ZnO nanosheets on nanoporous AAO substrates by using the simple hydrothermal route. The grown ZnO nanosheet scaffolds were found well adherent to AAO substrates. The water-borne bacterium, E. coli was selected as a target bacterium to evaluate the antibacterial performance of as-synthesized ZnO/AAO composite membranes. The large catalytic surface and hierarchical porosity of ZnO mesh on porous AAO substrate are the promising structural features that contribute to the mass production and transfer of chemical species during photochemical disinfection process and also render them an intrinsic antifouling ability. In summary, the prepared ZnO/AAO photocatalytic membranes can perform multifunctional activities, including inactivation of pathogens and self-antifouling.

2. Experimental

2.1. Materials

A 99.999% pure aluminum sheet of 1 mm thickness was used for the synthesis of AAO substrate by following the two-step mild anodization method, reported elsewhere [18]. All chemical reagents used in the fabrication process of the ZnO/AAO membranes were of analytical grade and used without further purification.

2.2. Synthesis of ZnO/AAO membranes

The AAO substrates were immersed in 1% 1-dodecanethiol for few minutes to facilitate the subsequent seeding of ZnO nuclei. For preparation of the sol–gel solution, 0.11 g of zinc acetate dihydrate ($Zn(CH_3COO)_2).2H_2O$) was mixed in 50 ml of methanol at 60 °C and 0.03 g of sodium hydroxide (NaOH) was dissolved in 25 ml of methanol at 60 °C. Finally, the sol–gel solution was obtained by mixing these two solutions slowly for 2 h at 60 °C while stirring vigorously. For deposition of the seed layer, the dried AAO substrates were treated with as-prepared solution for three times by employing dip coating scheme to acquire an appreciable homogeneity and uniformity for the layer. Every coating step was followed by annealing the substrates at 100 °C for 10 min.

ZnO nanosheets were grown hydrothermally on the seeded AAO substrates in an equimolar (0.02 M) growth solution of hexamethylenetetramine (HMTA: $C_6H_{12}N_4$), and zinc nitrate ($Zn(NO_3)_2.6H_2O$) in deionized water using a homemade hydrothermal reactor. The growth solution was obtained after continuously stirring this equimolar solution at 80 °C for 2 h. The seeded AAO substrates were made to float right on the top of the growth solution by fastening one side of the substrate to a buoyant substance while the other side was facing the solution. The reaction temperature was kept 90 °C in the reactor. After 3 h of hydrothermal growth, the membrane samples were washed in DI water and annealed at 350 °C for 1 h. To get a free standing membrane, Al support was chemically etched using methods described elsewhere [18]. Fig. 1 represents a schematic illustration of different steps of the fabrication process of ZnO/AAO membranes.

2.3. Characterizations

The surface morphology of the fabricated AAO substrate and ZnO nanosheet scaffold on AAO substrate was studied by field emission gun scanning electron microscope (FEG-SEM) using the model MIRA-3 Tescan at an accelerating voltage of 20–30 kV. The compositional studies of the ZnO/AAO membranes were carried out by energy dispersive X-ray spectrometer (EDX) attached to the FEG-SEM. The crystal structure of the membranes was determined by using a X'Pert PRO 3040/60 Philips X-ray diffractometer (XRD) at accelerating voltage of 40 kV using CuKα line (λ = 0.1542 nm). The functional group analysis of the membranes was performed in the transmittance mode on a Thermo Scientific (model Nicolet 6700) Fourier transform infrared spectrophotometer (FTIR), in a spectral range of 400–4000 cm^{-1}. For optical characteristics, the diffuse reflectance spectra (DRS) of the membranes were investigated in the wavelength range of 200–850 nm on a Perkin Elmer UV-vs diffuse spectrophotometer provided with an integrating sphere attachment and Spectralon diffuse reflectance standards.

2.4. Antibacterial assay

Agar diffusion assay was performed using Mueller Hinton agar (Merck Germany) in order to determine the antibacterial activity of the ZnO/AAO membrane against water-borne bacterium E. coli. To eliminate the surface contamination, the membranes along with plates and materials were sterilized under UV radiation for 1 h before start of the experiments. An amount of 0.1 ml of fresh bacterial culture of E. coli containing 10^8 –10^9 CFU/ml was blended with semi-solid agar and poured on the plates containing membranes. After incubation at 37 °C for 8, 16 and 24 h, the zones of bacterial inhibition around the membrane samples were measured in millimeters. 30 μg doxycycline disks were used as positive control in these experiments. For photocatalytic activity, a low pressure UV source centered at 365 nm was used. All experiment was performed in triplicate in aseptic conditions to ensure the reproducibility.