Journal of Photochemistry and Photobiology A: Chemistry 353 (2018) 171–184

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Invited paper

Mechanistic investigation of visible light responsive Ag/ZnO micro/nanoflowers for enhanced photocatalytic performance and antibacterial activity

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ARTICLE INFO

Article history:
Received 23 August 2017
Received in revised form 24 October 2017
Accepted 13 November 2017
Available online xxx

Keywords:
ZnO
Ag
Visible light
Photocatalysis
Antibacterial

ABSTRACT

Visible light responsive Ag-doped flower-like ZnO (Ag/ZnO) micro/nanostructure photocatalysts with different loadings of Ag were successfully fabricated through surfactant-free co-precipitation and photodeposition routes. The as-prepared samples have been characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS) and photoluminescence spectroscopy (PL). The photocatalytic tests demonstrated that the Ag/ZnO micro/nanoflowers enhanced visible light responsive photoactivity towards the degradation of Fast Green dye and inactivation of Escherichia coli. Particularly, the 5 wt% Ag/ZnO samples showed excellent photoactivity in comparison with those of pure ZnO and commercial TiO_2. The PL spectra showed that the Ag incorporation could effectively stimulate the separation efficiency of photogenerated charge carrier in Ag/ZnO. The trapping experiments indicated that superoxide anion ($^{\bullet}O_2^-$) radicals and hole (h^+) were the major reactive oxygen species for the Ag/ZnO photocatalytic system. Much effort was also focused on the visible light photocatalytic antibacterial activity using Escherichia coli by observing the antibacterial response, minimum inhibitory concentration (MIC) and membrane integrity assay. The results showed that the Ag/ZnO can be used as photocatalysts and antibacterial agents for potential practical applications in the wastewater treatment.

1. Introduction

Remediation of organic, inorganic and microbial contaminants via green technologies are hot research topics in the water and wastewater decontamination areas. Advanced oxidation processes (AOPs) including photocatalysis technique have been utilized to produce the reactive oxygen species (ROS) such as hydroxyl ($^{\bullet}OH$), superoxide anion ($O_2^{\bullet-}$) radicals and hydrogen peroxide (H_2O_2) for a wide arrays of pollutants destruction [1,2]. Examples of photocatalysis application have also found in the real-world wastewater [1–3]. These highly active radicals partook in oxidation and reduction reactions, microorganisms inactivation as well as mineralization of pollutants [3–6]. A diversity of semiconductor ranging from large to small band gaps has been broadly studied for this purpose, for instance, TiO_2, ZnO, Nb_2O_5, WO_3 and CdS [7–10]. In particular, the large ZnO band gap (~3.3 eV) had high photoactivity in UV spectrum but still hindered its practicality in visible light.

Many research works have focused on ZnO morphological control by changing the synthesis techniques resulting in superior electron conductivity, large specific surface area and high adsorption of pollutants on the surface of photocatalyst [11,12]. Various ZnO nanostructures including rod-like, dumbbell-like, plates-like and cuboid-shaped have been reported [13–15]. Recently, three dimensional (3D) nanostructures with well-defined morphologies have garnered significant attention due to their unique properties and promising applications [16,17]. For instance, ZnO hierarchical microstructures displayed a superior photocatalytic performance relative to that of ZnO nanoparticles and nanorods [18]. Thus, substantial efforts have been conducted to synthesize 3D ZnO complex nanostructures with different architectures including windmill-like, wall-like, nail-shaped and flower-like by enormous physical and chemical techniques [19–22]. Nevertheless, most of ZnO complex nanostructures were synthesized from random-assembled nanorods or nanosheets

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https://doi.org/10.1016/j.jphotochem.2017.11.021
1010-6030/

under the assistance of surfactants or structure-directing reagents or via complicated rigid process.

In order to harvest the absorption of visible light and enable the efficient charge carrier shuttling, combination of 3D ZnO nanostructures with noble metals (Pt, Pd, Ag and Au) has been studied [14,23–25]. This modification has numerous merits including prevented the recombination of photogenerated electron and hole (e^-–h^+), broadened the absorption spectrum and facilitated some specific reactions on the surface of ZnO nanostructures [23–25]. The noble metals such as Pd and Au have been utilized for the ZnO–metal formation due to their high electron affinity behaviours and produced the heterojunction interface between metal and semiconductor [26,27]. Metallic levels such as Au, Ag and Pd were lower than the conduction band of ZnO, so these noble metals accumulated photogenerated e^- upon the ZnO photoexcitation and resulted in an improvement of photocatalytic efficiency [26–28].

Among the noble metals modification, Ag-containing composites are also promising for killing of bacteria in aqueous mediums [29–31]. For instance, Zhu et al. [32] used Ag/BiOI as vital composites for studying the photocatalytic inactivation of *E. coli* 8099 under visible light irradiation. Ubonchonlakate et al. [33] used Ag/TiO_2 composite films to evaluate the UV photocatalytic disinfection against P. aeruginosa. Various Ag-containing composites such as Ag/MgO [34], Ag/Ag_3PO_4 [30], Ag/TiO_2 [33,35,36], Ag/$ZnTiO_3$ [37], and Ag/CdS/ZnO [38] have been studied for the photocatalytic inactivation of bacterial. However, there is a scare report on the antibacterial activity over the visible light photocatalytic treatment using Ag/ZnO nanostructures in the literatures.

According to the above discussion, Ag-doped flower-like ZnO (Ag/ZnO) micro/nanostructures may enhance the photocatalytic and antibacterial activities. In this regard, the Ag/ZnO micro/nanostructures were fabricated by a facile surfactant-free co-precipitation and photodeposition techniques. The photoactivity of as-prepared micro/nanostructures was evaluated in the degradation of Fast Green (FG) dye under visible light irradiation. The formation and the roles of ROS in the photocatalytic degradation of FG were then studied with the use of appropriate scavengers and PL measurement. Moreover, the antibacterial activity of the micro/nanostructures was tested using Escherichia coli (*E. coli*) under visible light irradiation. To further understand the bacterial inactivation action, the leakage of membrane integrities during the photocatalytic inactivation was examined. The possible mechanism for the enhanced photocatalytic and antibacterial activities of the Ag/ZnO micro/nanostructures was finally discussed.

2. Experimental

2.1. Materials

In this study, all chemicals were analytical reagent grade and used without additional purification or treatment. Deionized water (DI) was utilized throughout the experiment.

2.2. Synthesis of Ag/ZnO micro/nanostructures

The flower-like ZnO micro/nanostructures were prepared by a co-precipitation process. In a typical experiment, 0.1 M of Zn $(NO_3)_2{\cdot}6H_2O$ was dispersed in 100 mL of DI and stirred for 20 min, followed by addition of 0.1 M of NaOH (100 mL) into above mixture and continuously stirred for 30 min. The final pH of the solution after the addition of NaOH solution was found to be 12. The resulting mixture was refluxed at 65 °C for 8 h. After cooling to room temperature naturally, the white precipitates obtained were filtered and washed with DI and ethanol for several times. The white products were dried in an oven at 90 °C for 2 h for further use.

0.20 g of as-prepared ZnO powders were dissolved into 100 mL DI and sonicated for 20 min, then $AgNO_3$ with different weight percentages (0, 2.5, 5 and 10 wt%) were dissolved into above solution under constant stirring. Ag nanoparticles were loaded on the ZnO samples through a photoreduction method under sunlight irradiation (between 11:00 and 14:00 during the months of September and November) with light intensity of 5.7×10^5 lux for 2 h. The black precipitates solution was filtered and washed with DI for several times. The obtained black products were subsequently dried in an oven at 90 °C for 3 h and finally calcined at 550 °C for 2 h.

2.3. Characterization

The as-prepared samples were analyzed using X-ray diffraction (XRD) pattern tested on a Philips PW1820 diffractometer with Cu Kα radiation in the range of 20°–80°. The morphology of the photocatalyst was observed on a Quanta FEG 450 field emission-scanning electron microscope (FESEM) with an energy dispersive X-ray spectroscopy (EDX) analysis. Transmission electron microscopy (TEM) image was taken using a Philips CM-12 operated at 120 keV. X-ray photoelectron spectroscopy (XPS) spectra were obtained via an Omicron els 5000 spectrophotometer using Al Kα at 1480 kV as a radiation source. UV–vis diffuse reflectance spectrum (DRS) was measured using a Perkin Elmer Lambda 35 UV–vis spectrophotometer with $BaSO_4$ as a reference. The photoluminescence (PL) measurement was recorded using a Perkin Elmer Lambda S55 spectrofluorometer with a Xe lamp excitation wavelength of 325 nm at room temperature. The Ag content of samples was detected using a Shimadzu AA-6650 atomic absorption spectrophotometer (AAS).

2.4. Measurement of photocatalytic test

The photoactivity of the as-prepared Ag/ZnO samples was tested by the degradation of FG dye in aqueous solution. The experiments were performed as follows: 0.1 g of photocatalyst was placed into 100 mL of 5 mg/L FG aqueous solution with the natural solution pH of 6.65 in a beaker. Throughout all of the experiments, air was bubbled into the solution at a constant flow rate of 3 mL/min. The suspension was continuously stirred with a magnetic stirrer at a constant rotational speed of 700 rpm. The heterogeneous mixture was equilibrated for 60 min in the dark. Subsequently, the solution was exposed to a 45 W compact fluorescent lamp at a fixed distance of 12 cm between itself and surface of the dye. The average light intensity striking the surface of the reaction solution was about 1.02×10^4 lux as measured by a digital luxmeter. A total UV leakage of the compact fluorescent lamp was 0.81 mW cm^{-2} as determined by UVA and UVC radiometers (Series 9811, Cole Parmer, USA). Since the intensity of UV light was very low, it can be assumed that the photodegradation was mainly due to the action of visible light. It is also worth noting that the contribution of UV light was much lower than in case of solar light, which typically contains UV flux in the range of 2–3 mW cm^{-2} [3]. After certain time intervals, 5 mL of aliquot was taken out from the solution, centrifuged and the FG concentration was analyzed using a Hach DR6000 UV–vis spectrophotometer at 624 nm wavelength. At the same time, the comparison studies with commercial TiO_2 (Merck, 100% anatase, purity ≥99%) were also carried out. For mineralization test, 2 mL of filtered supernatant was added into HR COD vial and placed inside the Hach DRB 200 COD reactor at 150 °C for 2 h. The COD vial was then measured using an UV–vis spectrophotometer to determine the mineralization efficiency of FG dye.