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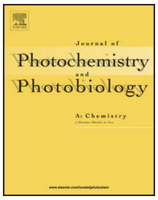

Preparation of Ag/ZnMgO nanocomposites as novel highly efficient photocatalysts by one-pot method under microwave irradiation

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ABSTRACT

A series of Ag/$Zn_{0.85}Mg_{0.15}O$ (Ag/ZnMgO) nanocomposites with different contents of metallic silver (0.85, 1.7, 3.4, and 6.7 wt%) were prepared in water using a one-pot method under microwave irradiation for 5 min. This large-scale method is fast and does not use any post preparation treatments. The X-ray diffraction (XRD) patterns have peaks corresponding to wurtzite hexagonal crystalline ZnO and cubic Ag. Purity and composition of the prepared samples were verified by energy dispersive X-ray (EDX). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that morphology of the samples changes by adding silver element. The diffuse reflectance spectroscopy (DRS) studies demonstrate that by increasing the amount of Ag, the absorption in the visible range increases. Electrochemical impedance spectroscopy (EIS) data show that in the presence of magnesium and silver elements, interfacial charge transfer resistance decreases relative to ZnO nanostructures. Activity of the nanocomposites for degradation of methylene blue was evaluated under UV irradiation. The degradation rate constant on Ag (3.4 wt%)/ZnMgO nanocomposite is about 11.2, 4.7 and 9.6-fold greater than those of ZnO, ZnMgO and Ag (3.4 wt%)/ZnO photocatalysts, respectively. In addition, influence of various operational parameters on the degradation rate constant was investigated and the results were discussed.

1. Introduction

Due to rapid increase in the world population and number of industries, the demand for clean water has exceeded the water supply in many places. In addition, various pollutants from different industries are sources of water contamination [1,2]. Hence, removal of these pollutants from wastewaters is of a great importance, because these pollutants and their degradation products (for organic pollutants) are usually toxic and carcinogenic, posing a serious hazard to aquatic living organisms [2]. Among many physical and chemical methods, photocatalytic degradation of organic pollutants using semiconductors is an effective method for water and wastewater treatment, especially in cases that the pollutants are difficult to be removed by using biological or physicochemical processes [3–5]. High stability, low-cost and non-toxicity are the main reasons for the widespread use of ZnO relative to the other photocatalysts [6,7]. In these processes, after illumination of a photocatalyst with proper irradiation, electron–hole pairs are produced as the beginning of the reactions. After that, reactive species such as hydroxyl radicals ($^\bullet OH$) and superoxide ions ($^\bullet O_2{}^-$) are produced on the surface of the catalyst to participate in the degradation reactions [8,9]. Recombination of the produced electron–hole pairs occurs on the order of nanoseconds [10]. Hence, photocatalytic activities of ZnO nanomaterials are not high enough. To address this shortcoming of ZnO, most research and development has been focused on increasing the catalytic activity [11–13]. Doping of ZnO with different metals such as Au, Pt and Ag is effective method to decrease recombination of the charge carriers [14–17]. Because of non-toxicity and low-cost, silver element is preferred for this purpose. Very recently, simultaneous loading of two kinds of elements on ZnO nanomaterials has attracted considerable interests; because, higher photocatalytic activity can be obtained relative to the single loading cases [18–21]. Subash et al. have prepared Ce-Ag co-doped ZnO photocatalyst by two-step precipitation-thermal decomposition method at 450 °C and applied them for degradation of two organic pollutants [18,19]. They showed that activity of Ce-Ag-ZnO is higher than those of Ag-ZnO, Ce-ZnO and ZnO. Zirconium-silver co-doped ZnO has been prepared by the same method and its activity for degradation of Reactive Red 120 and Acid Black 1 dyes was investigated [20,21].

Very recently, we prepared Mg-doped ZnO nanostructures in water by microwave irradiation and investigated their photocatalytic activities for degradation of methylene blue (MB) under UV irradiation [22]. The results demonstrated that the nanostructures

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with 0.15 mole fraction of Mg^{2+} ions have the highest activity among the prepared samples. In order to further enhancing the photocatalytic activity, in the present paper, a fast one-pot method was applied for preparation of Ag/$Zn_{0.85}Mg_{0.15}O$ (Ag/ZnMgO) nanocomposites in water with different contents of metallic silver under microwave irradiation for 5 min. To the best of our knowledge, these nanocomposites are reported for the first time. Degradation of MB under UV irradiation was investigated to evaluate activity of the prepared nanocomposites. Moreover, influence of various operational parameters such as content of Ag, weight of glucose, microwave irradiation time, catalyst weight, pH of solutions and scavengers of the reactive species on the degradation reaction were studied and discussed.

2. Experimental

2.1. Materials

Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), silver nitrate, sodium hydroxide, glucose, MB, 2-propanol, potassium iodide, benzoquinone and absolute ethanol were obtained from Merck and employed without further purification. Double distilled water was used for the experiments.

2.2. Instruments

The X-ray diffraction (XRD) patterns were recorded by a Philips Xpert X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm), employing scanning rate of 0.04 °/s in the 2θ range from 20° to 80°. Surface morphology and distribution of particles were studied *via* LEO 1430VP scanning electron microscopy (SEM), using an accelerating voltage of 15 kV. The purity and elemental analysis of the products were obtained by energy dispersive analysis of X-rays (EDX) on the same SEM instrument. For SEM and EDX experiments, samples mounted on an aluminum support using a double adhesive tape coated with a thin layer of gold. Transmission electron microscopy (TEM) investigations were performed by a Philips CM 120 instrument with an acceleration voltage of 100 kV. Diffuse reflectance spectra (DRS) were recorded by a Scinco 4100 apparatus. In order to obtain electrochemical impedance spectroscopy (EIS) data, a μautolab3 instrument was used at the frequency range of 10 mHz–10 kHz with a signal amplitude of 10 mV.

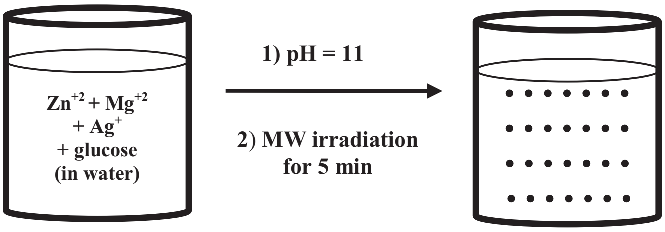
The pH of solutions was measured by Metrohm digital pH meter of model 691.

2.3. Preparation of the nanocomposites

In a typical procedure for preparation of Ag (3.4 wt%)/ZnMgO nanocomposite, 3.731 g zinc acetate, 0.769 g magnesium nitrate, and 0.0836 g silver nitrate along with 0.3 g of glucose (as a reducing agent [23]) were dissolved in 100 ml of distilled water under stirring at room temperature. Then, aqueous solution of NaOH (5 M) was dropwise added into the solution under stirring at room temperature until pH of the solution reached to 11. The brown suspension was irradiated in air for 5 min with 55% of output. The formed precipitate was centrifuged and washed two times with double distilled water and ethanol to remove the unreacted reagents and dried in an oven at 60 °C for 24 h. The schematic diagram for preparation of the nanocomposites is illustrated in Scheme 1.

2.4. Photocatalysis experiments

Photocatalysis experiments were performed in a cylindrical Pyrex reactor with about 400 ml capacity. The reactor was provided with water circulation arrangement to maintain the temperature at 25 °C. The solution was magnetically stirred and continuously aerated by a pump to provide oxygen and complete mixing of the reaction solution. A UV Osram lamp with 125 W was used as UV source. The lamp was fitted on the top of the reactor. Prior to illumination, a suspension containing 0.1 g of the photocatalyst and 250 ml of MB (2.75×10^{-5} M) was continuously stirred in the dark for 30 min, to attain adsorption equilibrium. Samples were taken from the reactor at regular intervals and centrifuged to remove the photocatalyst before analysis by spectrophotometer at 664 nm corresponding to maximum absorption wavelength of MB.



Scheme 1. The schematic diagram for preparation of Ag/ZnMgO nanocomposites under microwave irradiation for 5 min.

3. Results and discussion

3.1. Characterization of the photocatalysts

Fig. 1 demonstrates the XRD patterns for the as-prepared ZnO, $Zn_{0.85}Mg_{0.15}O$ (ZnMgO), Ag (3.4 wt%)/ZnO and Ag/$Zn_{0.85}Mg_{0.15}O$ (Ag/ZnMgO) photocatalysts. For ZnO nanostructures, the diffraction peaks correspond to (1 0 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), (0 0 4) and (2 0 2) planes in agreement with a wurtzite hexagonal crystalline phase (JCPDS file number of 36-1451) [24]. The prepared ZnMgO nanostructures have an XRD

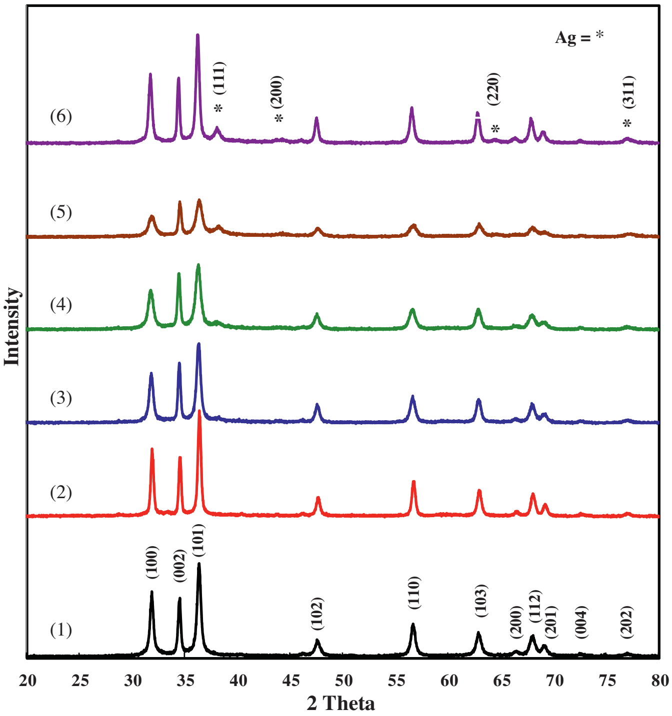


Fig. 1. The powder XRD patterns for: (1) ZnO, (2) ZnMgO, (3) Ag (0.85 wt%)/ZnMgO, (4) Ag (1.7 wt%)/ZnMgO, (5) Ag (3.4 wt%)/ZnMgO and (6) Ag (3.4 wt%)/ZnO.