Photocatalytic removing of methylene blue by using of Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanostructures

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Abstract

In this study, ZnO nanorods, Silver- and copper-doped ZnO nanorods and silver, copper-doped ZnO nanorods were prepared by a simple precipitation technique. The photocatalysts were characterized by various techniques such as XRD, SEM and FT-IR. The influence of dopants content on the optical properties was investigated. It has been found that the Ag or Cu doping leads to the optical band gap narrowing. Then the potential of the obtained photocatalysts were studied on degradation of methylene blue dye under UV and visible irradiation.

Keywords: Cu and Ag doped ZnO, photocatalyst, nanorods, Methylene blue.

1. Introduction

Photocatalysis is a promising technique for solving many current environmental issues [1,2]. Semiconductor absorbents offer the potential for elimination of organic pollutants [3]. Semiconductor photocatalysts such as zinc oxide and titanium oxide have been applied to degradation of contaminants in waste water and air [4,5]. For photocatalysis, ZnO has also been considered as a suitable alternative for TiO_2 due to The band-gap energy of ZnO is similar to that of TiO_2, the most used and typical photocatalytic material, so it hypothetically has the same photocatalytic ability as TiO_2 and it exhibits better performance in the degradation of organic dye molecule in both acidic and basic media [6].

The photocatalytic activity of nanostructured ZnO is expected to be enhanced because of their increased surface area [7-11]. The doping of metal ions in ZnO nanostructures can lead to effects such as enhancement in fluorescence and controlling concentration of surface defects. The

doping of Cu and Ag in ZnO is expected to modify absorption, and other physical or chemical properties of ZnO [12,13]. Recently, simultaneous doping of two kinds of atoms (co-doping) into semiconductor materials has attracted considerable interest, as it could result in a higher photocatalytic activity and special characteristics compared with single element doping into semiconductor oxides [14].

Therefore, in our study, Cu doped ZnO nanorods ,Ag doped ZnO nanorods and Cu, Ag-codoped ZnO nanostructures were synthesized through the precipitation method and their photocatalytic activities with different doping were evaluated for the degradation of methylene blue.

In our study, a simple precipitation method is developed for the synthesis of Cu doped ZnO nanorods, Ag doped ZnO nanorods and Cu,Ag-codoped ZnO nanostructures and their photocatalytic activities with different doping were evaluated for the degradation of methylene blue.

2. Experimental

2.1. Materials and Methods

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Zinc nitrate ($Zn(NO_3)_2.6H_2O$) , ammonia (25%), silver nitrate ($AgNO_3$), copper nitrat($Cu(NO_3)_2.3H_2O$) were purchased from Merck company. Deionized water was used to prepare all solutions. The samples were characterized by X-ray powder diffraction (XRD) using PAnalytical X′ per PRO X-ray diffractometer with Cu Kα radiation. The particle morphologies of the ZnO powder were observed by an AIS2100 (Seron Technology) scanning electron microscopy (SEM). The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer.

2.2. Preparation of ZnO nanorods

2.97 g of $Zn(NO_3)_2.6H_2O$ and 0.1 g $Cu(NO_3)_2.3H_2O$ was added to 250 ml distilled water to obtain a concentration of 0.04 M of zinc nitrate and 0.0016 M of cooper nitrate (4 wt% Cu relative to ZnO). The ammonia solution (25%) was added dropwise to solution to achieve pH=11, then the solution was refluxed under stirring. The white precipitation was deposited in the bottom of the flask. Finally, the mixture was centrifuged and the white solid was collected

and washed with distilled water and ethanol. The obtained solid was dried at 100 °C under oven for 3 h, followed by calcination at 450 °C for 3 h.

For Preparation of Ag-doped 2.97 g of $Zn(NO_3)_2.6H_2O$ and 0.1 g $Ag(NO_3)$ was added to 250 ml distilled water to obtain a concentration of 0.04 M of zinc nitrate and 0.0016 M of silver nitrate (4 wt% Ag relative to ZnO).

For Preparation of Cu,Ag-codoped ZnO 2.97 g of $Zn(NO_3)_2.6H_2O$ and 0.033 g $Ag(NO_3)$ and 0.05 g $Cu(NO_3)_2.3H_2O$ was added to 250 ml distilled water to obtain a concentration of 0.04 M of zinc nitrate , 0.0016 M of silver nitrate and 0.0016 M of copper nitrate.(2 wt% Ag and 2 wt% Cu relative to ZnO).

2.3. Photocatalysis procedure

In a typical process, the catalytic reaction was carried out in a 100 ml photoreactor (Scheme 2), which contain 10 ml of MB dye (20 mg/l) solution and 6 mg of catalyst. Before the irradiation, the solution was stirred in the dark (15 min) to allow equilibrium of the system. Irradiation was carried out using 400 W tungsten and 400 W high pressure mercury lamps as the light sources. All photocatalytic experiments were carried out at the same conditions. The distance between photoreactor and light sources was 20 cm. Samples (3 ml) were collected during the irradiation and MB solution were separated from the photocatalyst by centrifugation. The degradation was monitored by measuring the absorbance amount using a double beam UV–vis spectrophotometer (Shimadzu UV-1700) at 664 nm wavelength.

3.Results and discussion

3.1. Morphological characterizations

The morphology of the ZnO particle was examined from SEM images, as shown in Fig. 1. It was found that all synthesized ZnO nanorods were quite uniform in size. Fig. 1A,B show SEM images of the pure ZnO.

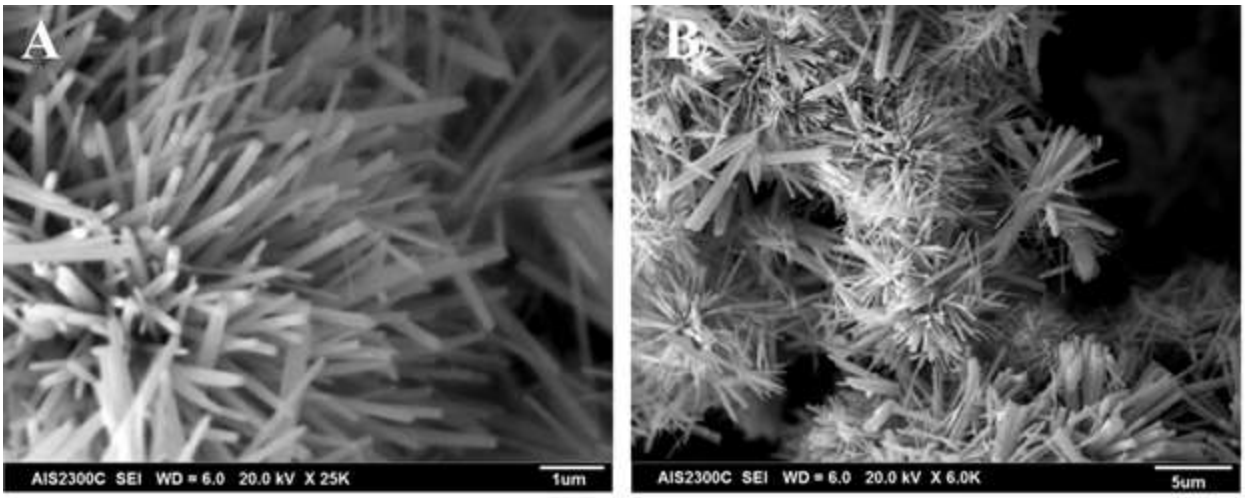

Fig. 1 The SEM images of ZnO nanorod powders

3.2. The X-ray powder diffraction

Fig. 2 shows the XRD pattern of ZnO nanorod powders. It can be seen that all these peaks are in good agreement with hexagonal (wurtzite) ZnO (JCPDS Card, No. 36-1451)

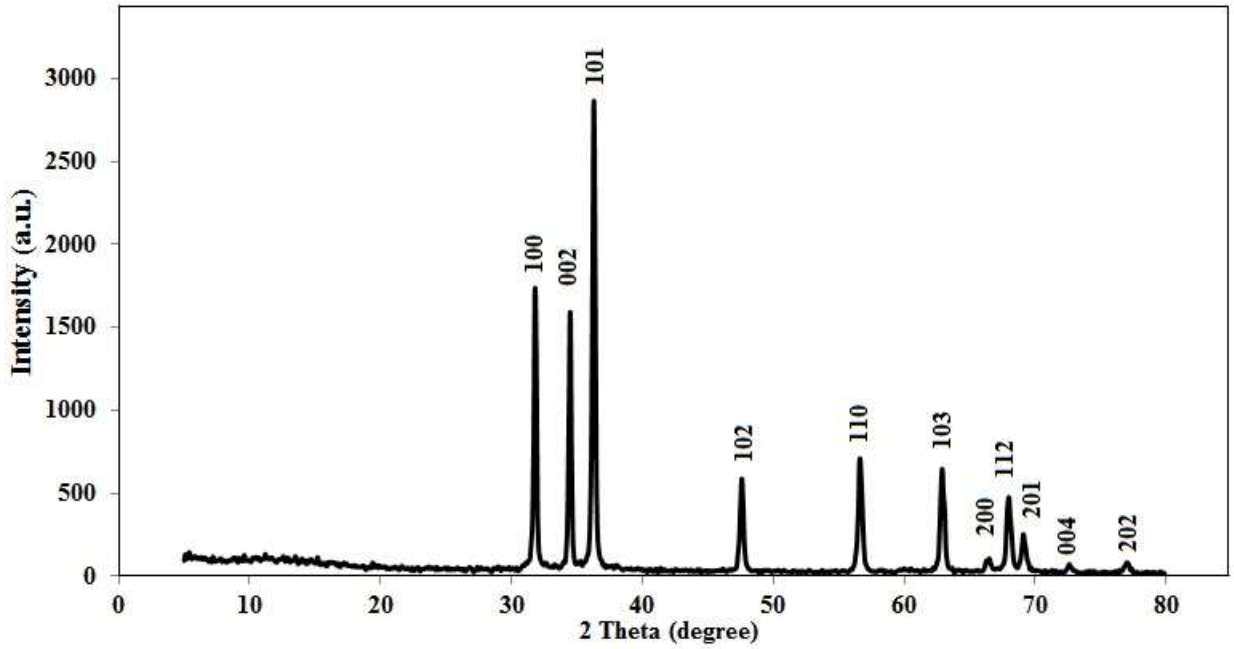

Fig. 2. The XRD pattern of ZnO nanorod powders

3.3. Optical properties

The UV–vis diffuse reflectance spectra (DRS) of the synthesized ZnO nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanorods are shown in Fig. 3A. The spectrum reveals a characteristic absorption peak of ZnO at wavelength of 368, which can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band (O2p → Zn3d) [15].

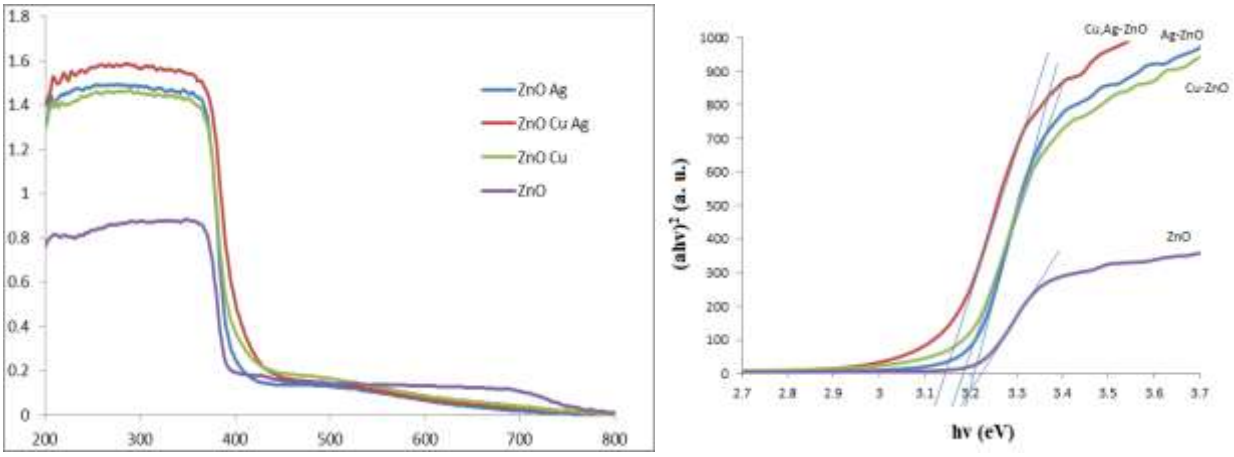

Fig. 3 (A) The diffuse reflectance spectra (DRS) of the synthesized ZnO nanorods and nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanorods and (B) the plot for band-gap energy (E_{bg}) of ZnO and nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO

3.4. Fourier transforms infrared spectroscopy

Fig. 4 shows the FT-IR spectra of the ZnO nanorods. The appearance of a sharp band at 401 and 501 cm−1 in the FT-IR spectra confirms the synthesis of ZnO because it is the characteristic absorption band for the Zn–O stretching vibration [16].

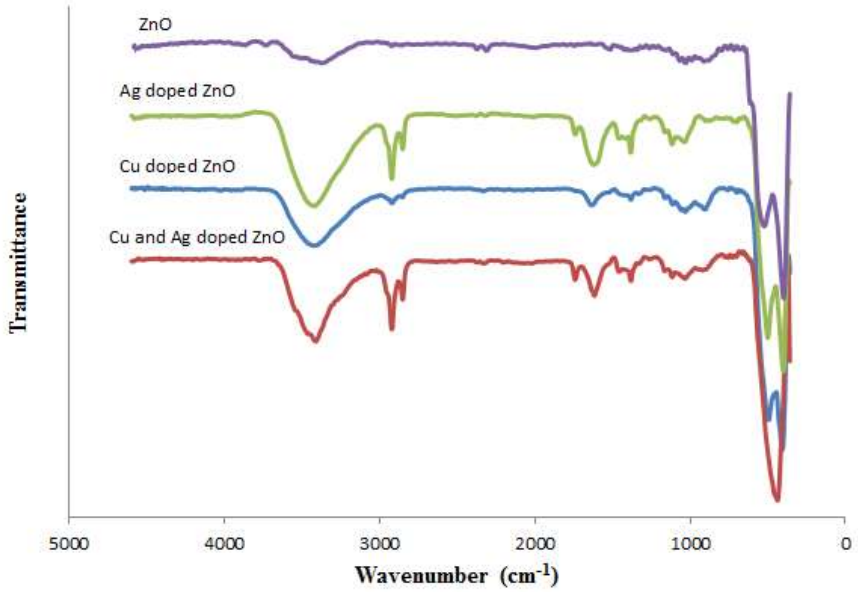

Fig. 4 The FT-IR spectrum of the synthesized ZnO nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanorods .

3.5. Photocatalytic degradation of methylene blue

The photocatalytic activities of as-synthesized four kinds of catalysts were evaluated by the degradation of organic dyes methylene blue in aqueous solution under light irradiation. The ZnO nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanorods with a high specific surface area, were used as photocatalysts for the decomposition of methylene blue by the superoxides and/or hydroxyl radicals formed at their interface. The characteristic absorption of MB at 664 nm was chosen to monitor the photocatalytic degradation process. Fig. 5 shows a typical photocatalytic degradation process of MB (initial concentration: 5 mg/l, 20 ml) using ZnO nanorods and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nanorods . (0.005 g) under visible light irradiation.

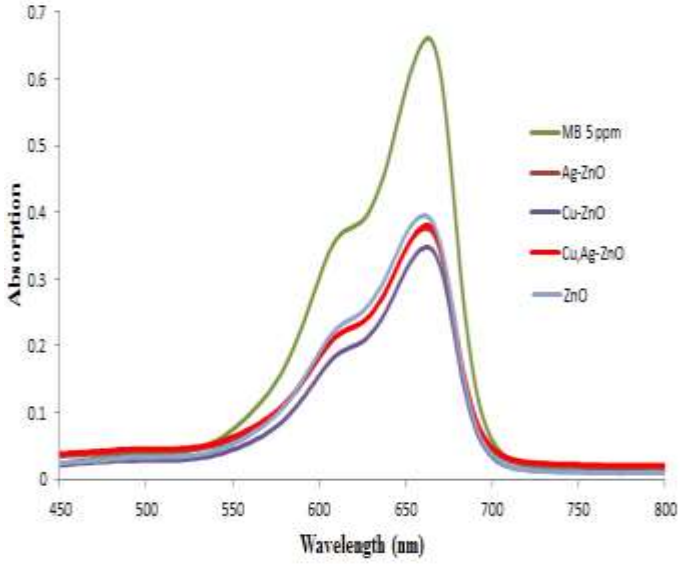

Fig. 5. The absorption spectra of the MB solution (initial concentration:5mg/l, 20 ml) with ZnO doped (0.005 g) under visible light irradiation

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