Nano-Structures & Nano-Objects 13 (2018) 21–29

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

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

Surface adsorption of lead ions and degradation of an organic dye with a nano photocatalyst synthesized via a simple hydrothermal method

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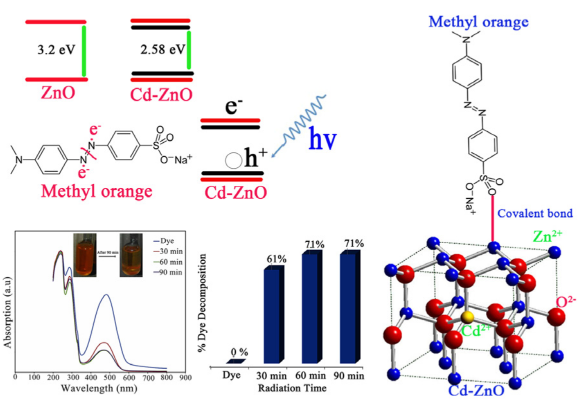
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 May 2017
Received in revised form 7 August 2017
Accepted 4 November 2017

Keywords:
Cd-ZnO
Nanostructure
Methyl orange
Hydrothermal
Photocatalyst
Optical properties

ABSTRACT

In this work, Cd^{2+} was doped into ZnO crystal lattice via a hydrothermal method. The effect of different parameters on the product size and morphologies were studied such as reaction time and temperature, surfactant and cadmium source value. The results showed each parameter has a significant effect on the product size and morphology. The optical properties of the products were studied and the results showed different factors such as particle size and cadmium source value can change the ZnO band gap. The photocatalytic activity of the product was studied by decomposition of methyl orange as dye and the results showed the product decomposed dye molecules structure stronger than bare ZnO nanostructures. Also, the surface activity of the synthesized nanostructures was examined by removing Pb^{2+} from the water and the results showed that the product can remove Pb^{2+} more than 44% from the water. The products were characterized by X-ray diffraction pattern (XRD), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM) and ultra violet–visible (UV–Vis) spectra.

1. Introduction

Environmental pollution is one of the serious concerns for the scientific community as it is directly associated with the human health and living organism [1]. The toxic organic compounds such as chemicals, dyes, pesticides, etc. are important pollutants that release in the water, spread aesthetic pollution and disturbed the environment [1–3]. The photocatalytic degradation method is extremely developed to remove organic pollutants from the water [4–14]. Also, in recent years many scientists focused on the synthesis of nanophotocatalyst due to their high surface activities [15–33]. For this purpose, metal oxide semiconductors have been used due to their band gap energies which are suitable to adsorb light under visible or UV regions. Among various metal oxide semiconductors, ZnO attracts much attention due to its

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https://doi.org/10.1016/j.nanoso.2017.11.003
2352-507X/

Table 1

Sample No	$Zn(NO_3)_2 \cdot 6H_2O$	$Cd(NO_3)_2 \cdot 9H_2O$	Surfactant	$Zn(acac)_2$	Temperature (°C)	Reaction time (h)
S1	0.3 g	0.03 g	SDS	–	180	24 h
S2	0.3 g	0.03 g	CTAB	–	180	24 h
S3	0.3 g	0.03 g	PEG	–	180	24 h
S4	0.3 g	0.03 g	–	–	100	24 h
S5	0.3 g	0.03 g	–	–	140	24 h
S6	0.3 g	0.03 g	–	–	180	18 h
S7	0.3 g	0.03 g	–	–	180	30 h
S8	–	0.03 g	–	0.3 g	180	24 h
S9	0.3 g	0.03 g	–	–	180	24 h
S10	0.3 g	0.02 g	–	–	180	24 h
S11	0.3 g	0.05 g	–	–	180	24 h

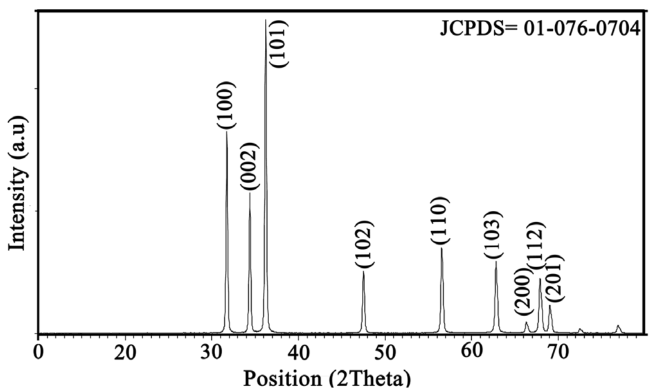

Fig. 1. XRD pattern of S9.

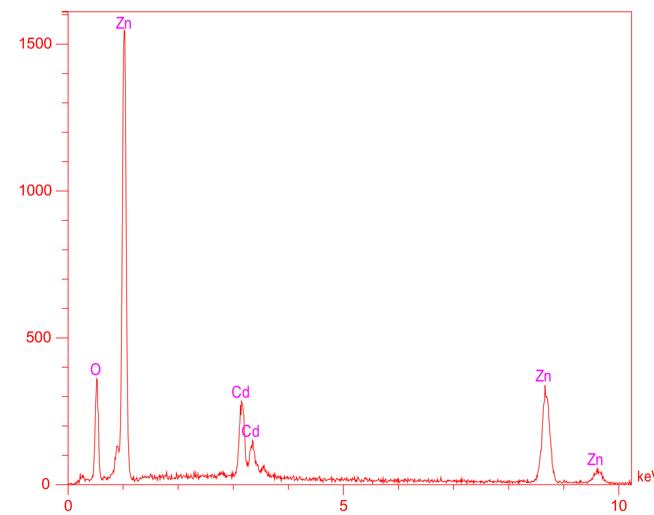

Fig. 2. EDS spectra of S9.

biocompatibility, easy to fabrication and so on. Zinc oxide is related to wide band gap semiconductors groups with large excitonic binding energy (59 meV) [34]. Due to the large band gap of ZnO, it can only absorb an ultra violet range of electromagnetic radiation and hence its optical applications and photocatalytic activity is restricted. To solve this problem many efforts were done to engineering the ZnO band gap. For example, by substitution of different elements in the ZnO crystals, we can reduce the ZnO band gap and consequently increase light absorption range [35–38]. ZnO and doped ZnO have important applications in high-level techniques such as catalytic, electrical, optoelectronic, [39,40] and quantum devices [41,42]. Until now different methods were served to the synthesis of ZnO nanostructures such as sol–gel [43], electrodeposition techniques [44], aqueous thermal deposition [45,46] and vapor–liquid–solid (VLS) methods [47,48]. In this work, we synthesized Cd doped ZnO nanostructures via a simple hydrothermal method. By doping Cd in ZnO crystal lattice, we can decrease the band gap of ZnO and improve the photocatalytic degradation of methyl orange as an organic compound. In this experimental procedure, we synthesized Cd2+ doped ZnO nanostructures via a simple hydrothermal method. Also, we studied the effects of different parameters such as the reaction time and temperature, cadmium source value on the product size and morphology. In addition, to decreasing the particles size of the products, three kinds of surfactants were used. Besides using surfactant, we used a zinc complex for increasing the steric effect and subsequently decreasing the particles size. After preparation the products, they were used as photocatalyst for degradation of methyl orange and as surface adsorber to removing methyl orange and some heavy metal ions from the water.

2. Experimental

All the chemicals reagents used in the experiments such as $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2$, NaOH, CTAB, SDS, and PEG were of analytical grade and used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. UV–Vis spectra were recorded using a UV–Vis spectrophotometer (PerkinElmer). In a typical experimental procedure, 0.3 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in a certain amount of the water. Another solution was prepared by dissolving a certain amount of $Cd(NO_3)_2$ (based on Table 1) in the water under vigorous stirring. After that. Two solutions were mixed together under stirring and pH of the final solution was adjusted to 12 with a NaOH solution. Then the reaction vessel was transferred to the autoclave and exposed heated at different temperatures at different times. The obtained precipitates were collected and washed several times with water and absolute ethanol and dried at 80 °C for 12 h. The experimental conditions are listed in Table 1. A proposed mechanism for the synthesis of Cd-ZnO is shown below.

$$Zn(NO_3)_2 \cdot 6H_2O + H_2O \rightarrow Zn(OH)_2.$$

$$Zn(OH)_2 + Cd(NO_3)_2 \rightarrow \text{Cd-}Zn(OH)_2$$

$$\text{Cd-}Zn(OH)_2 \xrightarrow{\Delta} \text{Cd-ZnO}$$

3. Results and discussion

Fig. 1 shows XRD pattern of the product. All the peaks in the pattern belong to ZnO crystal with hexagonal phase and JCPDS number 01-076-0704. The peaks placed at 31.9°, 34.5°, 36.7°, 47.5°, 56.5°, 63°, 66.5°, 68°and 69°are belonged to (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively. The