



A facile method to prepare bismuth doped ZnO photocatalysts and their photocatalytic property

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Manuscript received online 20 October 2020, revised and accepted 31 October 2020

ZnO and bismuth doped ZnO (Bi-ZnO) photocatalysts were synthesized by a facile solvothermal method. In this respect, three different bismuth weight percentages (0.5% 1.0% and 1.5%) of photocatalysts were prepared through an aqueous chemical growth method at low temperature and followed by precipitation. The structural and morphological properties of the photocatalysts were investigated by FTIR, SEM-EDX, XRD, and Raman spectroscopy. The photocatalytic activity of the photocatalysts were performed by degradation of Reactive Red-194 (RR-194) under UV light irradiation. SEM images of the synthesized photocatalyst were nanorod like shape. The presence of phases of ZnO and Bi₂O₃ in XRD spectroscopy confirmed a successful doping. The results revealed that 1.0-Bi-ZnO photocatalyst exhibited a better photocatalytic activity compared to ZnO.

Keywords: Bi-ZnO, photocatalysis, Reactive Red-194, solvothermal method.

Introduction

Nowadays, water pollution has become a significant matter leading to a threat for the living organisms with a growing world population and various industrial manufactural processes. Textile and dyeing industries are the major sources of water contamination causing serious health issues^{1,2}. These dyes belong to chemical classes consisting of different chromogens such as azo, acridine, azine, anthraquinone, sulfur, indigoid, nitro and phthalocyanine derivatives. Azo dyes containing an azo group (-N=N-) in their chemical structure and representing over 60% of the total dyes are used in especially textile and printing processes^{3,4}. In this respect, heterogeneous catalysis has been used as an alternative method to remove azo dyes from wastewater^{2,5}.

Doping is a useful method to enhance physical properties of ZnO. For this purpose, many dopants such as N, C, S, Cu, Co etc. have been studied to improve the photocatalytic activity of ZnO⁶. Bismuth is a good dopant candidate to reduce the rate of recombination processes between photogenerated charge carriers⁷. Recent studies of Bi-ZnO photocatalysts have focused on the degradation of organic molecules such as *o*-toluidine⁷⁻⁹. Moreover, Jayabharathi *et*

*al.*¹⁰ have demonstrated the quenching of fluorescence of phenanthrimidazole on Bi-ZnO nanoparticles. Some researchers have reported Bi-ZnO on the removal of highly toxic synthetic dyes mostly used in textile industry such as methylene blue, methyl orange^{11,12}. Thejaswini *et al.*¹³ have investigated the photocatalytic activity of α -Bi₂O₃-ZnO towards Acid Red-85.

The present study concerned with the synthesis, characterization, and photocatalytic activity of ZnO and Bi-ZnO photocatalysts. The photocatalysts were synthesized by a facile and cost-effective solvothermal method. To the best of our knowledge, the photocatalytic activity of Bi-ZnO through degradation of RR-194 has not been studied so far.

Experimental

ZnO and Bi-ZnO photocatalysts were synthesized by low temperature aqueous chemical growth method described as followed with some modifications¹⁴. 0.02 mol zinc acetate was dissolved in 200 mL distilled water and 10 mL ammonia (25%) was added dropwise under stirring. In a beaker appreciate amount of bismuth nitrate pentahydrate was dispersed in 5 mL ethanol and was stirred for 15 min. Then,

bismuth solution was added to the solution zinc acetate and ammonia. The weight percentages (wt%) of Bi/ZnO were 0.5%, 1.0%, 1.5% and samples were denoted as 0.5-Bi-ZnO, 1.0-Bi-ZnO, 1.5-Bi-ZnO, respectively. The solutions kept in a closed vessel and kept in oven at 90°C for 6 h. Afterwards, the photocatalyst was filtered, washed with distilled water, and dried at 90°C. The same procedure was repeated without the addition of bismuth nitrate pentahydrate for the synthesis of ZnO.

Analytical methods:

FTIR analysis was recorded using Thermo Scientific Nicolet 6700. The pellets were prepared with KBr. Raman spectroscopy was performed by a Thermo Scientific DXR Raman Microscope with Ar⁺ laser power $\lambda = 532$ nm. XRD diffractograms were recorded on a Rigaku-D/MAX-Ultima diffractometer using Cu-K α radiation with $\lambda = 1.54$ Å. SEM-EDX was acquired on a FEI-Philips XL30 instrument equipped with EDAX unit. UV-Vis spectroscopic measurements were employed on a Thermo Scientific Genesis 10S.

Photocatalytic experiments:

Photocatalytic degradation experiments were performed in a cylindrical Pyrex reaction vessel containing 50 mL of 10 mg/L RR-194 dye solution and 0.25 g/L photocatalyst. The reaction vessel was illuminated from the top with a 125 W black light fluorescent lamp. The samples were filtered through 0.45 μ m cellulose acetate Millipore HA filters.

Results and discussion

FTIR spectra of ZnO and Bi-ZnO photocatalysts are presented in Fig. 1. The wide peaks at ~ 3370 cm^{-1} and ~ 1635 cm^{-1} are attributed to the presence of hydroxyl groups on the surface of the samples^{15,16}. The strong peak at ~ 555 cm^{-1} belongs to the characteristic vibration of Zn-O bond in ZnO^{17,18}. The medium peak at ~ 900 cm^{-1} corresponds to the C-H bending of acetate group¹⁹. The peak at 1408 cm^{-1} is attributed to the symmetric C=O stretching of zinc acetate²⁰.

Fig. 2 reveals the Raman spectra of ZnO and Bi-ZnO photocatalysts. In ZnO spectrum, the main and sharp band is located at 431 cm^{-1} corresponding to E₂ (high) mode. The source of this band is the oxygen atoms in ZnO. The other bands at 325 cm^{-1} , 476 cm^{-1} , 573 cm^{-1} , 658 cm^{-1} , 1151 cm^{-1} can be attributed to 2E₂ mode, A₁ symmetry mode, A₁

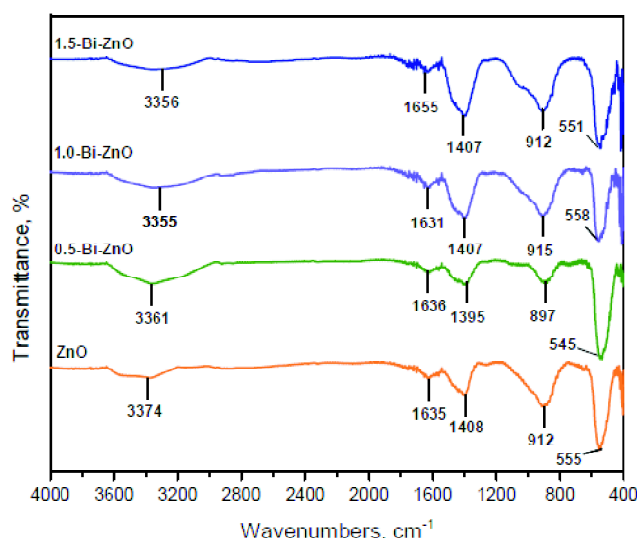


Fig. 1. FTIR spectra of ZnO and Bi-ZnO photocatalysts.

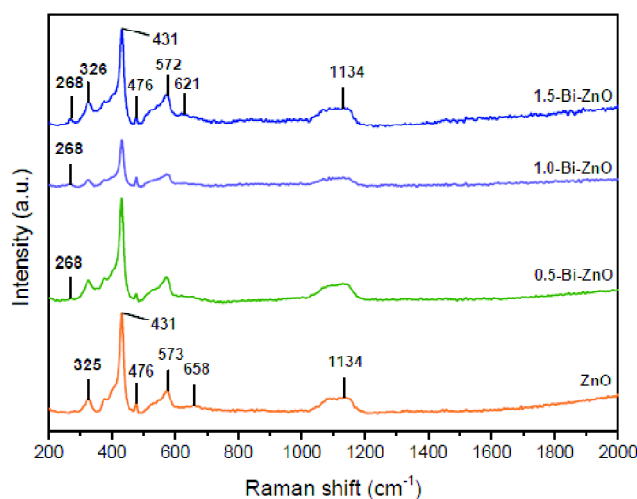


Fig. 2. Raman spectra of ZnO and Bi-ZnO photocatalysts.

(LO) modes, TA+LO, contributions of 2A₁ (LO) and 2E₁ (LO) modes, respectively^{21,22}. The spectra of Bi-ZnO photocatalysts exhibit a great similarity of ZnO. The difference between the Raman spectra of ZnO and Bi-ZnO is the presence of a new peak positioned at 268 cm^{-1} indicating the characteristic of the Bi-O bond in α -Bi₂O₃²³.

The XRD diffractograms of ZnO and Bi-ZnO photocatalysts are shown in Fig. 3. In the diffractogram of 1.5-Bi-ZnO, the peaks at $2\theta = 31.78^\circ$, 34.42° , 36.26° , 47.56° , 56.60° , 62.86° , 66.36° , 67.94° and 69.06° 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)

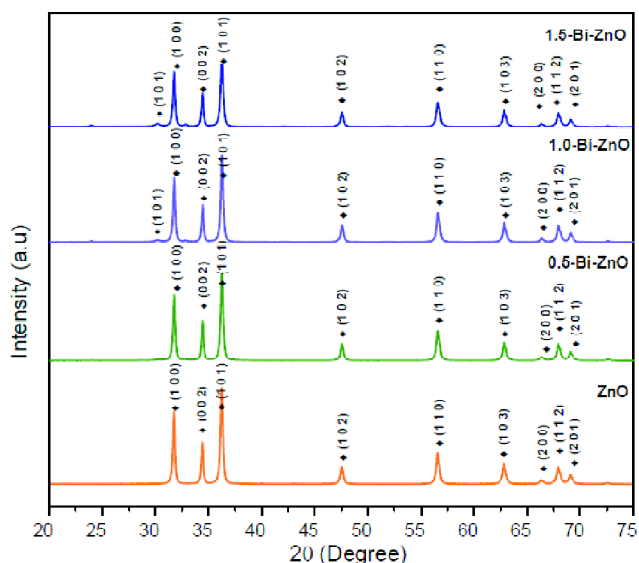


Fig. 3. XRD diffractograms ZnO and Bi-ZnO photocatalysts (• Bi₂O₃, ♦ ZnO).

crystal planes of ZnO, respectively (JCPDF 80-0075) while the peak at $2\theta = 30.18^\circ$ corresponds to (1 1 0) crystal plane of Bi₂O₃ (JCPDF 51-1161). The peaks of Bi-ZnO are slightly shifted to a higher wavenumber compared to ZnO because of the difference between the ionic radius of Zn and Bi²⁴. Hence, the presence of Bi³⁺ in ZnO lattice reveals a successful impregnation of doping procedure²⁵. The reason of the absence of Bi₂O₃ peak in the XRD of 0.5-Bi-ZnO can be explained by suppressing of Bi₂O₃ due to a low amount of Bi₂O₃ concentration or a high-level dispersion of Bi³⁺ ion in the lattice of ZnO¹¹. The crystallite particle size values calculated by Scherrer equation are in a range between 29 to 31 nm for both ZnO and Bi-ZnO photocatalysts.

As can be seen from Fig. 4, ZnO and Bi-ZnO doped photocatalysts exhibit nanorod like shape with a length in the range of 1.5–8 microns. Bismuth doping has been al-

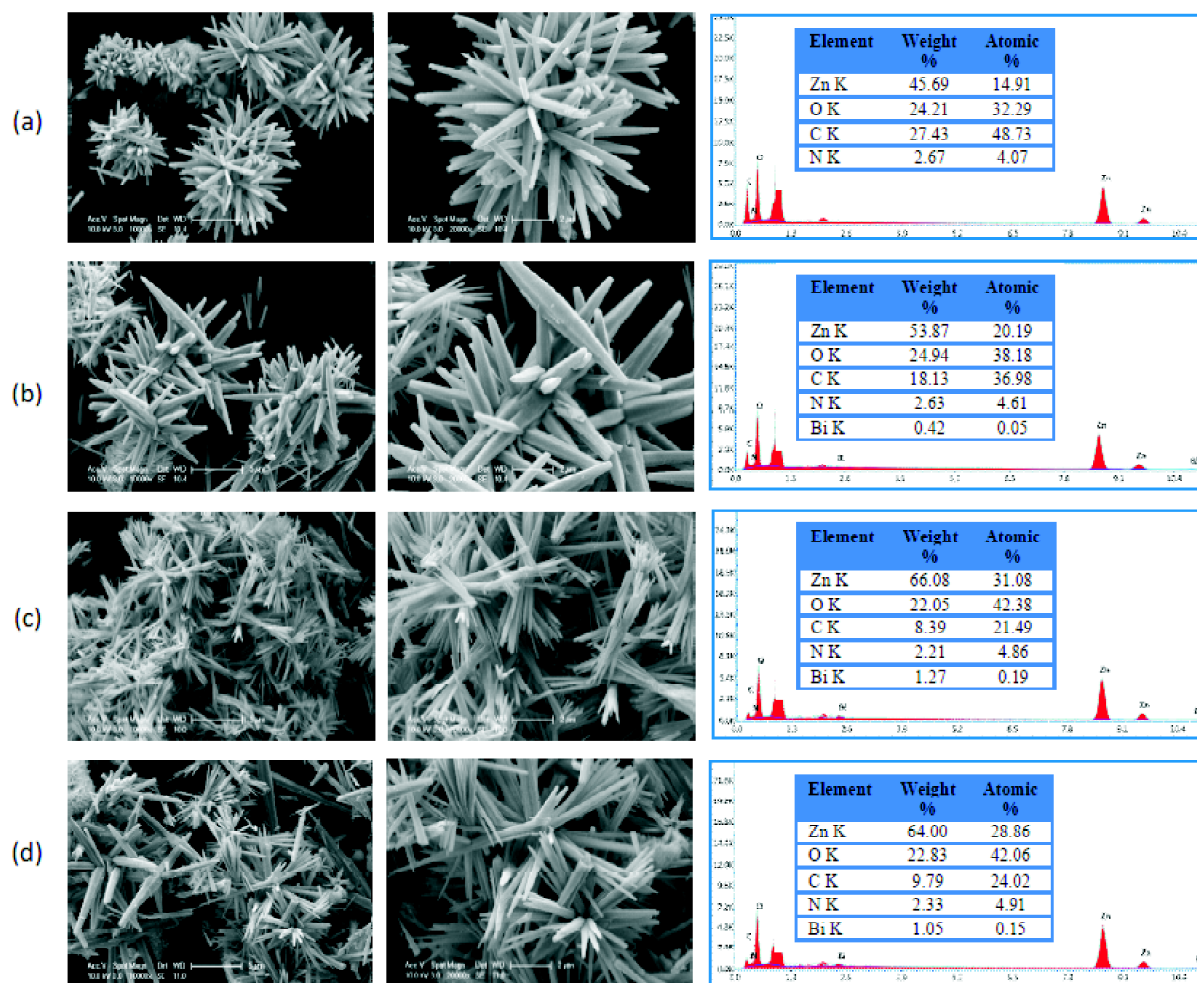


Fig. 4. SEM micrographs x20000 and elemental analysis: (a) ZnO, (b) 0.5-Bi-ZnO, (c) 1.0-Bi-ZnO, (d) 1.5-Bi-ZnO.

tered slightly the thickness of nanorods morphology. In the micrograph of 1.0-Bi-ZnO in Fig. 4(b), the morphology is rather like ZnO. It is clearly seen that morphology of ZnO is changed and the size of aggregates are enhanced with an increase in bismuth concentration especially in 1.0-Bi-ZnO and 1.5-Bi-ZnO. The EDX analysis of ZnO contains Zn, O, C, and N elements, while Bi-ZnO indicates the presence of Zn, O, Bi, C, and N and confirms Bi doping in ZnO. The presence of carbon and nitrogen in samples signifying some organic residues remain in the synthesized photocatalysts²⁶. This finding confirms the existence of acetate groups and is compatible with FTIR results.

The kinetic rate constants calculated under 540 min UV light irradiation for ZnO, 0.5-Bi-ZnO, 1.0-Bi-ZnO, 1.5-Bi-ZnO photocatalysts are 0.39×10^{-4} , 0.35×10^{-4} , 0.54×10^{-4} and 0.32×10^{-4} , respectively. The prepared 1.0-Bi-ZnO photocatalyst exhibits a higher kinetic photocatalytic performance than ZnO.

Conclusions

ZnO and Bi-ZnO photocatalysts were synthesized by using a facile solvothermal method. The presence of phases of ZnO and Bi₂O₃ in XRD spectroscopy confirmed a successful doping. SEM images of the synthesized photocatalysts were nanorod like shape. EDX spectra verified the existence of bismuth in the synthesized photocatalysts. The characteristic modes belong to zincite were obtained in Raman spectra. The photocatalytic experiment results revealed that 1.0-Bi-ZnO photocatalyst exhibited a better photocatalytic activity compared to ZnO.

Acknowledgements

The author expresses her thanks to Kirsehir Ahi Evran University Research Foundation for financial support (Project No. FEF.A4.20.009).

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