Effect of Transition Metal Dopant on the Physical and Photocatalytic properties of BiOCl

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Abstract: Hydrolysis method has been used to prepare Mn-BiOCl by taking different amount of $MnCl_2.4H_2O$ i.e. 1%, 2% and 3%. Aggregation of particles after doping was confirmed from SEM analysis. In XRD results, the perfect incorporation of Mn ion in the crystal lattice was investigated. Band gapwas reduced from 3.6 eV to 3.3 eV by adding 1% to 3% dopant. The photocatalytic activity was evaluated by performing degradation of methylene blue dye with pure and 2% Mn-BiOCl. It was found that 72 % of the methylene bluewas degraded with pure whereas 91 % of degradation was observed with doped BiOCl within 115 min irradiation time.

INTRODUCTION

Tunable material "Bismuth oxychloride (BiOCl)"having band gap of 3.4eV, has many industrial applications such as a pigment in cosmetic industry, photoluminescent material and also used as a photocatalystfor degradation of organic contaminants [1,2]. A number of studies have reported that introduction of a small percentage of impurityelementsinto wide gap semiconductormakeit receptive for dramatic alteration in the optical and structural properties[3, 4]. Metal ion doped semiconductors have potential industrial applications. Transition metal doped semiconductors have drawn interest to the new confront that arise in different properties when doping into the crystal lattice [5,6,7]. Mangnese, a transition metal element is considered as a good candidate for doping for industrial applications due to low cost and its easy preparation[8, 9]. For the treatment of dye waste water, BiOCl modified with manganese loading enables the catalyst more effective and shortens the illumination period.This study also looks into the influence of manganese doping on the microstructure and photocatalytic activity of BiOCl. From the obtained results, it was found that suitable amount of manganese dopant can enhance the activity mainly endorsed to alteration of grain size. The prepared material of Mn-doped BiOCl was characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and diffuse reflectance spectroscopy (DRS). In addition, photocatalytic activity of Mn-doped BiOCl has been evaluated by degrading methylene blue under visible light irradiation.

EXPERIMENTAL

For the preparation of Mn doped BiOCl, $MnCl_2.4H_2O$ was added to HCl along with pure BiOCl under vigorous stirring condition. For 1%, 2% and 3% doped Mn-BiOCl samples, different amount of $MnCl_2.4H_2O$ was added. After complete mixing, pH was adjusted between 2 to 3 with ammonia and white precipitates were separated from liquid using centrifugal machine. The obtained sample was dried in oven at 373 K for 2 h and used for further characterization. .

X-RAY DIFFRACTION ANALYSIS

Figure 1 shows the XRD spectra of BiOCl and Mn-BiOCl. The spectra give us information of the structure, crystal size and extent of doping. For pure BiOCl, the peak obtained in (001) is sharp and of higher intensity, which supports that the crystalline structure is well defined. The peak intensity of (001) was found to be decreased when 1% and 2% Mn was added into BiOCl. By addition of 3% Mn peak intensity found to be very low, this signifies that Mn well incorporated in BiOCl crystal lattice. On the other hand the intensity of (102) diffraction peak increased upto 3% Mn doping. In addition, the shifting of the (102) peak of ~2.4 degree from pure BiOCl shows the insertion of Mn in the crystal lattice. It can be attributed that the smaller ionic radii, Mn^{2+} (0.080 nm) can easily substitute Bi^{3+} (0.096 nm) in BiOCllattice. [10,11]

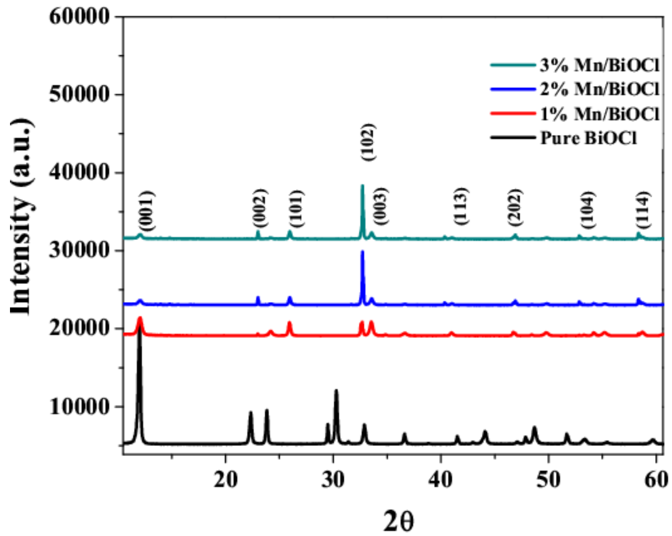

FIGURE 1. XRD pattern of Pure, 1 wt%, 2 wt% and 3 wt% Mn/BiOCl

MORPHOLOGICAL STUDIES (SEM ANALYSIS)

The surface morphology of the as-prepared samples was examined by scanning electron microscopy. Figure 2 shows the SEM images of pure, 1%, 2% and 3% Mn-BiOCl. Figure 2(a) demonstrates that the pure BiOCl crystals are well differentiated from each other. In Fig. 2(b) it can be observed that the BiOCl particles get aggregate by adding 1% dopant concentration. This aggregation was found to be increased when more amount of dopant added up to 2%. But as the concentration of dopant was increased to 3%, the crystal structure gets distorted. The SEM image (Fig. 2(d)) of 3% showed that neither aggregation for crystals took place nor well defined crystals formed. The reason for deformed structure of crystal is exceeding the limit of dopant concentration. It can be seen that dopant concentration played a critical role in controlling the crystal structure and morphology of the Mn/BiOCl nanoparticles.[12,13]

ULTRAVIOLET–VISIBLE ABSORPTION MEASUREMENT ANALYSES

Figure3 shows UV-vis spectra for prepared samples. The plot shows the obtained bandgap of pure BiOClwas 3.6 eV and for 1% doping the band gap reduced to slightly less than 3.5 eV. The least band gap was obtained for 3% Mn doped BiOCl i.e. 3.3 eV and band gap of 2% was 3.4 eV. The reduction in band gap occurred possibly due to the substitution of Mn (0.080 nm) with Bi (0.096 nm) in the crystal lattice, as ionic radii of Mn is smaller than Bi[12]. Band gap can decrease also due to formation of new energy level in between conduction and valance band. By formation of new energy level, electron require less energy for excitation from valance band to conduction band so it can be used as an effective photocatalyst under visible light irradiation.

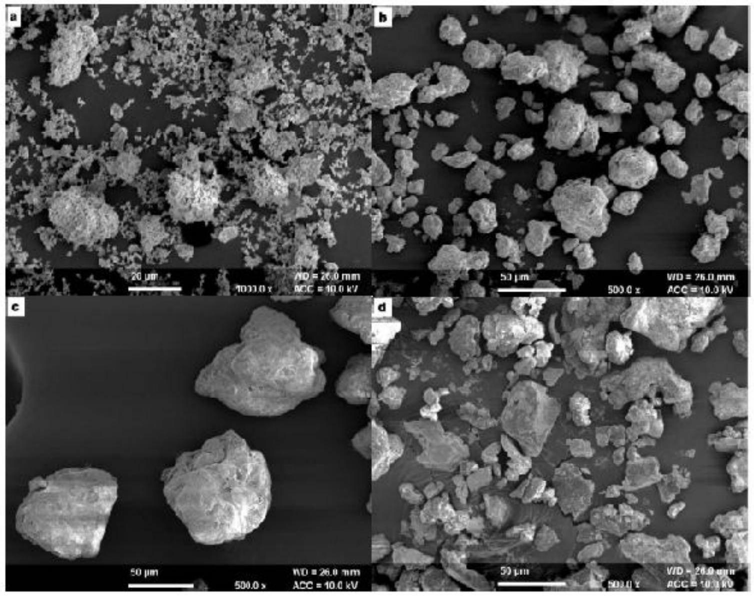

FIGURE 2. Scanning electron micrographs of (a) pure BiOCl (b)1% Mn-BiOCl (c) 2% Mn-BiOCl and (d) 3% Mn-BiOCl

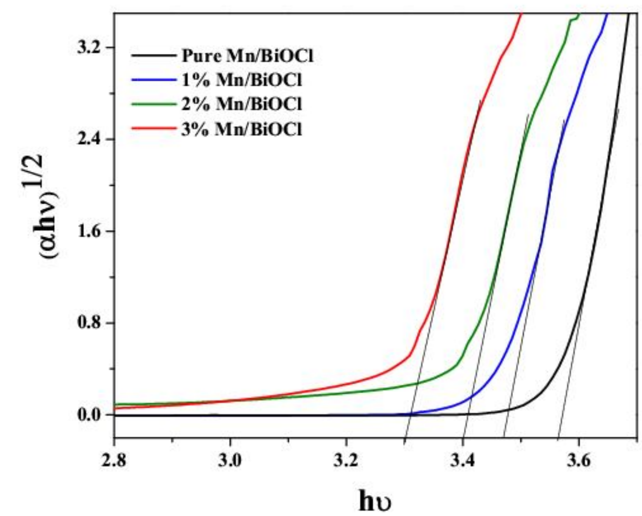

FIGURE 3. UV-vis spectra of Pure, 1 wt% Mn/BiOCl, 2 wt% Mn/BiOCl and 3 wt% Mn/BiOCl

PHOTOCATALYTIC ACTIVITY

The photoactivity of as prepared photocatalysts was evaluated by photo degradation of 10^{-5}M methylene blue by using 50 mg of pure BiOCl and 2% Mn doped BiOCl under visible irradiation (see Fig. 4). It was found that 57 % of the MB was degraded with pure whereas 72 % of degradation was observed with doped BiOCl within 115 min irradiation time. Rate constant was found to be 4.66 x 10^{-5} Sec^{-1} and 9.33 x 10^{-5} Sec^{-1} for pure and Mn-doped BiOCl, respectively. From these observations, it can be concluded that Mn-doped BiOCl is more active under visible light illumination than that of pure BiOCl.

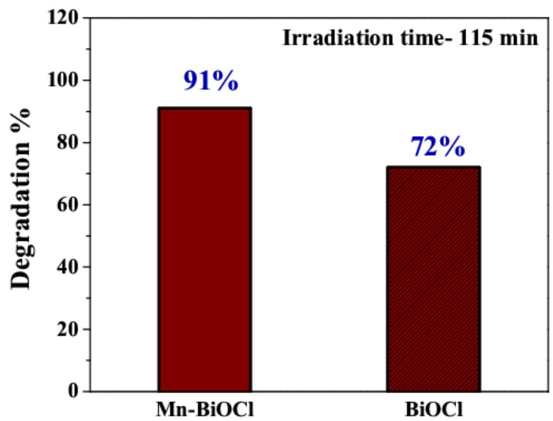

FIGURE 4. Photocatalytic activity of pure BiOCl and 2 wt% Mn-doped photocatalyst

CONCLUSION

The Mn-BiOClwas prepared with different amount of $MnCl_2.4H_2O$to obtain 1%, 2% and 3% Mn-BiOCl by hydrolysis method. The doping has great effect on the morphology of the photocatalyst. SEM images showed that as the doping concentration was increased, aggregation of particles occurred. XRD graphs indicated the incorporation of Mn ion in the crystal lattice. UV analysis showed the decrease in band gap as concentration was increased from 1% to 3%. The photocatalytic activity was evaluated by performing degradation of methylene blue dye with pure and 2% Mn-BiOCl. It was found that 57 % of the MB was degraded with pure whereas 72 % of degradation was observed with doped BiOCl within 115 min irradiation time. Thus, Mn doping in BiOClenhances the rate of degradation process and 2% Mn-BiOCl showed the best result out of the rest.

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