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Photocatalytic activity of ZnO and Sr^{2+} doped ZnO nanoparticles

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ABSTRACT

The photocatalytic activity of ZnO and Sr^{2+} doped ZnO nanoparticles was evaluated by photocatalyic oxidation of methyl orange and methylene blue. The results show that the photocatalytic activity of Sr^{2+} doped ZnO was much higher than that of pure ZnO. The sample with mole ratio of Sr/Zn 1:2 show the maximum activity. The effect of heat treatment on photocatalytic activity of the samples was studied in the temperature range 400–800° C and found that the sample calcined at 600° C shows the maximum activity. The dependence of calcination time on the photo-catalytic activity was studied and observed that the best heat treatment time is 7 h.

1. Introduction

The major sources of pollution in water and air are chemicals released from industries. Textile industry is one of the major sources of the pollutants such as coloured organic reagents; the dyes. The presence of such pollutants in ground and surface water are harmful to human as well as aquatic life. Some of them are carcinogenic and mutagenic as well as genotoxic and therefore, a technology for cleaning the water is very important [1]. Use of semiconductor based material as photocatalyst in the detoxification of pollutants has several advantages over any other treatment methods. Major advantage is that it gives complete mineralization in to eco-friendly products without generation of waste [2,3]. Even though anatase TiO_2 is the most studied photocatalyst, many researchers are in search of an alternative to TiO_2. ZnO appears to be one of the promising photocatalysts which has a band gap almost similar to that of anatase TiO_2. Currently zinc oxide is used as a potential photocatalyst due to its powerful oxidation capability, non-toxicity, chemical stability and low cost. High surface reactivity of zinc oxide results in the formation of large number of defect sites arising from oxygen nonstoichiometry which make zinc oxide a good photocatalyst than other metal oxides. Also zinc oxide can generate hydroxyl ions more efficiently than titania [4].

Modification of the surface of zinc oxide plays an important role in making the material useful for numerous applications. The modification should improve the performance of materials like photocatalytic activity, conductivity, etc [5]. The most widely used method for modification of the surface of zinc oxide is doping. Changing the stiochiometric amounts of metal ions within a metal oxide by doping with another metal cation can generate new and interesting properties. Considering the factor electronic structure which affects the doping effects and size of the nanoparticles, alkaline earth metal ions are the best choice for doping than transition metals. Because localized d-levels are absent in alkaline earth metals. These localized d-levels can decrease the photo threshold energy of semiconductors in the case of transition metal doping [6].

Co- precipitation is one of the methods used for the synthesis of nanopowders. The major advantages of this method are; reaction temperature is reduced due to homogeneous mixing of reactant precipitates and metal powders formed are highly reactive in low temperature sintering, which lead to the formation of smaller particles [7–11]. Further in co-precipitation process, the concentration of the solution, pH, temperature and stirring speed of the mixture has a control over the formation of the final product with required properties [12,13]. Extensive investigations have been carried out to study the change in structure, photocatalytic activity, anti microbial activity, etc., of the doped ZnO nanoparticles by co-precipitation method [14–25]. NitiYongvanich reported the synthesis of Sr-doped ZnO based nanopowders by chemical co-precipitation. The effect of Sr doping on the microstructure of ZnO based varistors was also reported [26]. RamnYousefi et al. studied the enhanced visible light photocatalytic activity of Sr-doped ZnO nanoparticles by studying the degradation of methylene blue [27]. Efficient treatment of grey water by solar photocatalysis using TiO2–chitosan film [28], Liquid-phase photocatalytic oxidation of a secondary diazo dye compound, Congo red (CR, C32H22N6Na2O6S2) and pharmaceutical phthalylsulfathiazole, in a cylindrical photochemical reactor on gold-loaded titania systems [29], Photo-catalytic degradation of methyl violet dye using zinc oxide nano particles [30] etc., have been extensively studied.

In the present study, ZnO and Sr^{2+} doped ZnO nanoparticles were prepared by co-precipitation method and the photocatalytic activity of

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the samples was evaluated by photocatalyic oxidation of methyl orange (anionic dye) and methylene blue (cationic dye).

2. Experimental

2.1. Materials

Zinc nitrate, strontium nitrate, ammonium carbonate, methyl orange and methylene blue are used as raw maretials for the synthesis and photocatalytic study of Sr^{2+} doped ZnO nanoparticles. All the chemicals used were of AnalaR grade reagents of Merck India.

2.2. Synthesis of ZnO and Sr^{2+} doped ZnO nanoparticles

ZnO and Sr^{2+} doped ZnO nanoparticles were prepared by simple co-precipitation method. For doping the solutions of $Zn(NO_3)_2$ and $Sr(NO_3)_2$ in distilled water were mixed by vigorous stirring for 30 min, 1 M $(NH_4)_2CO_3$ solution is then added to the mixture drop wise till the formation of colloidal solution. The colloidal solution formed was dried at 70 °C for 24 h in an air oven, kept at 60 °C and then calcined. Different compositions of Sr^{2+} doped ZnO nanoparticles were prepared in a similar way. The calcination temperature ranges from 400 to 800 °C. Calcination time was also changed from 4 to 8 h. Un-doped ZnO was also prepared in the same manner without using $Sr(NO_3)_2$ (Table 1).

2.3. Photocatalytic study

The photocatalytic activity of ZnO and Sr^{2+} doped ZnO were investigated by the degradation of methyl orange (MO) and methylene blue (MB) solution under UV light. A concentration of 10^{-5} M (MO and MB) was used in all experiments. For a typical experiment, 50 mL of 10^{-5} M solution of the dye was taken in a 100 mL beaker, added 0.1 g of calcined ZnO, stirred for 10 min in the dark and then irradiated under UV light in a Luzchem LZC-4X reactor containing 16 lamps. Degradation was monitored by taking aliquots at different time intervals. It was then centrifuged for 30 min, after recovering the catalyst the clear solution was subjected to absorption spectra analysis. The same experimental procedure was adopted for each sample of Sr^{2+} doped ZnO.

The rate constant of degradation, k was obtained from the first-order plot according to Eq. (1):

$$\ln A_0/A = kt \tag{1}$$

2.4. Characterization

The X-ray diffraction (XRD) patterns of the samples were obtained in a scanning range of 20–75° by an X-ray diffractometer (Model: RIGAKU MINIFLEX 600) with Cu Kα radiation (λ = 0.15406 nm). The XRD was used to examine the nature of crystalline state of the samples. Optical properties of the samples were characterized at room temperature by using a UV–visible spectrometer; Model: JASCO V 570. The surface morphology of the samples was observed by using a scanning electron microscope (SEM); Model: Hitachi SU-6600 FESEM. The chemical structure of the different samples were characterized by KBr disc method with a Fourier transform infrared (FTIR) spectrometer (JASCO FT-IR-4100) and analyzed over the range 3500–500 cm^{-1}.

Table 1
Preparation of different compositions of Sr^{2+} doped ZnO nanoparticles.

Sample	Sr/Zn molar ratio	Mass of Sr $(NO_3)_2$ (g)	Mass of Zn $(NO_3)_2$ (g)
SZO-14	1:4	2.1163	11.8988
SZO-12	1:2	2.1163	7.097
SZO-11	1:1	2.1163	5.9494
SZO-21	2:1	4.2326	2.9747
SZO-41	4:1	8.4652	2.9747

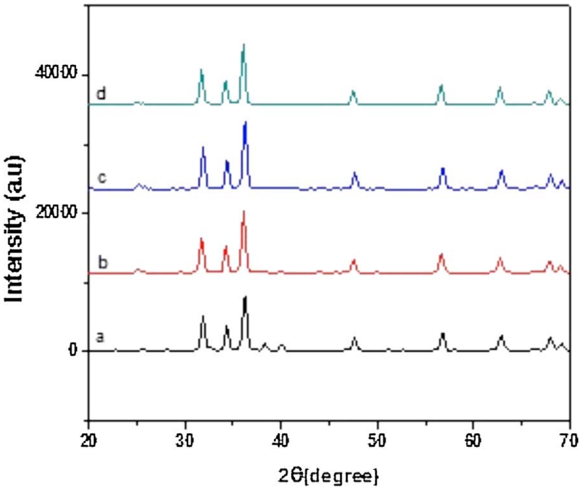

Fig. 1. XRD patterns of ZnO (a), SZO-12-400 (b), SZO-12-600 (c) and SZO-12-800 (d).

Table 2
The average crystalline size of pure and doped ZnO.

Sample	2θ (degree)	Distance between planes (Å)	Full width at half maximum (degree)	Particle Size (nm)
ZnO	36.27	2.4744	0.417	20.9
SZO-12-400	36.14	2.483	0.412	21.2
SZO-12-600	36.13	2.4841	0.410	21.3
SZO-12-800	36.06	2.489	0.328	26.6

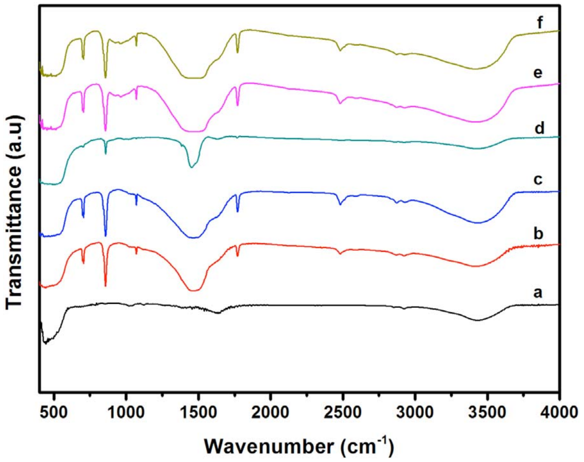

Fig. 2. FT-IR spectra of ZnO (a), SZO14 (b), SZO12 (c), SZO11 (d), SZO21 (e) and SZO41 (f) calcined at 400° C for 3 h.

3. Results and discussion

The XRD patterns of the prepared samples are shown in Fig. 1. The XRD peaks are located at angles (2θ) of 31.81, 34.45, 36.27, 38.36, 40.20, 47.49, 56.65, 62.85, 67.95 and 69.13° corresponding to (100), (002), (102), (110), (110), (103), (112), (201), (004) and (202) planes of ZnO nanoparticles respectively. The standard diffraction peaks shows the hexagonal wurtzite structure of ZnO nanoparticles with P63mc space group. This is also confirmed by the JCPDS data (Card No. 36-1451).

The Sr^{2+} doped ZnO sample (SZO-12), calcined at 400° C, shows