Effect of doping parameters on photocatalytic degradation of methylene blue using Ag doped ZnO nanocatalyst

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Abstract

The aim of this study is the synthesis, characterization and photocatalytic degradation of ZnO and Ag doped ZnO nanocatalysts of various compositions synthesized by using co-precipitation method. The nanocatalysts were annealed at the 723.15 K temperature. The obtained nanocatalysts were characterized in concerns their crystalline structure using X-ray diffraction, morphology using scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDS) in concern with their composition. Photocatalytic activity of nanocatalyst was tested by applying it for photocatalytic degradation of Methylene Blue under different experimental conditions. The photocatalytic activity found to increase with the increase of dopant concentration.

Keywords Hexagonal ZnO · Photocatalytic activity · Methylene blue

1 Introduction

Dyes play an important role in waste water effluents because they are discharged in large quantity from various manufacturing industries. They create severe environmental problems due to the presence of organic and inorganic chemicals in it. It creates the attention of many research workers due to the presence of potentially carcinogenic pollutants in contaminated water. Various approaches have been implemented to decontaminate these effluents [1]. Semiconductor photocatalysis is one of the most important photocatalytic processes has a great potential to the contribution of environmental problems. The important aspect of photocatalysis is selection of semiconductor material such as ZnO as an efficient photocatalyst because of its inexpensiveness, chemical stability, non-toxicity, higher efficiency and provides photo-generated holes with high oxidizing power due to their wide band

gap energy for the degradation of wide range of organic chemicals and synthetic dyes [2–4].

Photocatalysis is a promising technique for solving many current environmental issues [5, 6]. Semiconductor adsorbents offer the potential for elimination of organic pollutants [7]. TiO₂ and ZnO are by far the most widely studied transition oxide semiconductors for photochemical and photoelectrochemical applications [8, 9]. Thus they become a sort of common model for research. It is a relatively abundant and stable material, with a more relatively good deal of resistance to photocorrosion than that of other commonly studied oxides. For photocatalysis, ZnO has also been considered as a suitable alternative for TiO₂ due to the band-gap energy of ZnO is similar to that of TiO₂, the most used and typical photocatalytic material, so it hypothetically has the same photocatalytic ability as ZnO and it exhibits better performance in the degradation of organic dye molecule in both acidic and basic media [10].

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Zinc oxide is known as n-type semiconductor with a wide band-gap (2.98 eV) with a large exciton binding energy (60 meV). It is also a promising material for nano-electronics and photonics and an intense interest has been paid to its optical and electronic properties. Pure zinc oxide has transparent properties in the visible range of the spectrum and good absorption of the UV radiation. There are some application where a high photocatalytic activity is desirable [11], but there are also some application where ZnO has capacity to degrade various organic substrate is an impediment, like fabric or paper coating will influence the electronic and optoelectronic properties. Kohan et al. [12] have reported a detailed description of the intrinsic defects usually found in ZnO. These defects are zinc interstitials (Zn_i), zinc vacancies (V_{Zn}), oxygen interstitials (O_i), oxygen vacancies (V_O), oxygen antisites (O_{Zn}), and zinc antisites (Zn_O). All these defects induce changes in the photoluminescence spectra of specific ZnO sample. The UV emission corresponds to the near band edge (NBE) emission (is due to the radiative annihilation of excitons) and the visible emission is commonly referred to as a deep-level or trap-state emission [13]. The relative strength of NBE to deep level defect emissions exhibits a dramatic threshold dependence on surface roughness. Surface optical emission efficiency increases over tenfold as roughness decreases to unit cell dimensions, highlighting the coupled role of surface morphology and near-surface defects for high efficiency ZnO emitters [14]. In view of fundamental studies as well as industrial applications of nanoparticles, chemically pure or compositionally well-defined ZnO is required. Therefore developing a method of obtaining cheap, pure ZnO with small, controlled size is highly desirable. Common synthesis methods include co-precipitation from zinc salts solution with an alkali such as sodium hydroxide, force hydrolysis, sol-gel or pyrosol [15–18]. Out of these methods, co-precipitation method is very facile and convenient method. Also the nanoparticles synthesized by this method are uniform in size. Despite the wide range of applications of ZnO, little is known about the effect of operational parameters on photocatalytic degradation characteristics. Moreover, the research is required for visible light active semiconductor oxides that possess the same stability and versatility of ZnO by either doping or by incorporation with different materials to obtained composites.

The present study emphasizes synthesis of ZnO and Ag doped ZnO by facile, economic co-precipitation method and characterization by different methods like SEM, EDS and XRD. As synthesized nanocatalyst were used to degrade MB dye and its reusability for 4 times. Ag doped ZnO shows a good adsorption and photocatalytic property for the degradation of dye. It has indicates the, possible use of this photocatalyst for the scale-up

of the treatment of textile waste water in bulk volume. Again the present work was undertaken to investigate the effect Ag doping on ZnO and effect of operational parameters, such as dye initial concentration, nanocatalyst load, pH of dye solution on the kinetics of photocatalytic degradation of Methylene blue (MB).

2 Experimental procedure

2.1 Materials

$Zn(NO_3)_2 \cdot 4H_2O$, aqueous ammonia (25%), Silver nitrate and ethanol (99%) were purchased from Merck Specialties Pvt. Ltd. India, MB dye was obtained from Loba Chemie. All chemicals used for synthesis of nano ZnO and Ag doped ZnO were used are of A.R. grade. Concentrations of the Methylene Blue (MB) were estimated using absorbance recorded on UV-Vis double beam spectrophotometer (Systronics model-2203) at the λ_{max} 655 nm. The pH was maintained using 0.1 M NaOH and 0.1M HCl with pH meter (Equiptronics model no. EQ-615).

2.2 Synthesis of ZnO and Ag doped ZnO

Ag Doped and undoped ZnO nanoparticles were synthesized by modified Pechini co-precipitation method. In a typical synthetic procedure 0.5 M of $Zn(NO_3)_2 \cdot 4H_2O$ and 1 M of NaOH were dissolved in double distilled water. The beaker containing NaOH solution was heated to a temperature of about 333.15 K. To this solution of NaOH, the $Zn(NO_3)_2 \cdot 4H_2O$ solution and $AgNO_3$ in appropriate proportion was added drop wise under high speed stirring. The beaker containing the above solution mixture was then securely covered and left aside for 2 h. The precipitated ZnO nanoparticles were then filtered, washed with ethyl alcohol and then with deionized water, dried at 373.15 K for 2 h and annealed at 723.15 K for 2 h in a muffle furnace [19].

2.3 Characterization

The SEM images were taken using the Hitachi S-4800 (Japan) FESEM. The EDS analysis was performed by using Bruker X Flash 5030. The XRD pattern of the samples were measured on PAnalytical X'Pert Pro MPD X-ray diffractometer using monochromatized Cu K α ($\lambda = 0.15418$ nm) radiation under 40 kV and 40 mA and scanning over the range of $20^\circ \leq 2\theta \leq 80^\circ$.

2.4 Photocatalytic experiment

Photocatalytic degradation of MB by ZnO and Ag doped ZnO was carried out in a photocatalytic reactor with a 500 W halogen lamp. The photocatalytic reactor contain cooling water jacket to maintain temperature of the reactor. Different catalyst doses are added to the 50 mL MB solution (10–40 mg/L) and then placed in a photocatalytic reactor. At regular intervals, sufficient amount of sample was withdrawn and then centrifuged in order to determine the changes in the dye concentration by UV double beam spectrophotometer. The percentage removal of MB was calculated by Eq. (1).

$$\text{Percentage removal} = \frac{C_o - C_t}{C_o} \times 100, \quad (1)$$

where C_o (mg/L) is the initial MB dye concentration; C_t (mg/L) is the MB concentration at time t .

3 Results and discussions

3.1 X-ray diffraction characterization

The nanocatalyst was analyzed for the qualitative phase composition by using X-ray diffraction. The XRD patterns obtained for the annealed Ag doped ZnO are presented in Fig. 1. It can be seen that both undoped and Ag doped ZnO were crystalline after annealing at 723.15 K.

in hexagonal structure. The major peaks in ZnO and Ag doped ZnO found that 31.74° , 34.43° , 36.24° , 47.53° , 56.055° , 62.86° , 67.91° and 69.05° (JCPDS: 05-0664). For doped powders peak at 38.11° and 44.27° were appeared showing presence of Ag in phase with crystalline phase (JCPDS: 04-0783). Furthermore these results are in good agreement with other reports [20]. There is no shifting of ZnO peaks, confirming the surface doping or segregation of Ag nanoclusters on the grain boundaries of ZnO [20]. The ZnO and Ag doped ZnO nanocatalysts have an average grain size varying from about 19 nm to 21 nm.

3.2 EDS analysis

The elemental analysis of material surface layer is obtained by electron dispersive X-ray spectroscopy (EDS). Figure 2a–d shows that ZnO and Ag doped ZnO nanocatalyst. ZnO contains Zn K 80.70%, O K 19.30%. The 1% Ag doped ZnO contains Zn K 67.90%, O K 32.08% and Ag 0.02%, The 2% Ag doped ZnO contains Zn K 79.61%, O K 20.61% and Ag 0.07% and the 4% Ag doped ZnO contains Zn K 81.50%, O K 18.29% and Ag 0.21% in EDS of ZnO and Ag doped ZnO micrograph proves existence of ZnO and Ag doped ZnO in the nanocatalyst.

3.3 SEM analysis

The SEM image of ZnO and Ag doped ZnO nanocatalyst are shown in Fig. 3a–d. The SEM image of ZnO and Ag doped ZnO nanocatalyst shows nanorods with crystal

Fig. 1 XRD of ZnO and Ag doped ZnO

Fig. 2 EDS analysis of ZnO and Ag doped ZnO

structure having irregular size and shape. It was revealed that the particle size increases with increasing doping concentration of Ag due to Ag ions in ZnO. The average crystallite size is increasing from about 24 nm to 90 nm.

3.4 Photocatalytic activity

3.4.1 Effect of pH

The effect of pH on the degradation of MB was studied in the pH range from 2 to 12 with 50 mg/L dye concentration and 1 g/L catalyst loading (Fig. 4). For doped and undoped photocatalyst, the photocatalytic degradation efficiency increases from pH 2 to 8. At pH 8, higher degradation was observed. Further increase in pH from 9 to 12 photocatalytic degradation observed to be decreases. The degradation efficiency was found to be optimum at a pH of 8. At $pH_{ZPC} = 7.6$ catalyst has zero charge; it becomes positively charged at pH less than pH_{ZPC} while it becomes negatively charged at pH greater than pH_{ZPC} . Hence being a catalytic dye, MB gets attracted to the catalyst surface at pH 8. Thus adsorption and consequently photocatalytic degradation is found to be higher. In more alkaline medium there is

a Coulombic repulsion between the negatively charged photocatalyst surface and the hydroxide anions. This could prevent the formation of $\cdot OH$ and hence decrease the photooxidation. Therefore % degradation decreases on increase in pH from 8 to 12. Further photocatalytic study was carried at optimum pH 8.

3.4.2 Effect of initial dye concentration

The degradation of MB with different initial concentrations (10, 20, 30 and 40 mg/L) for a catalyst dose of 1 g/L of 4% Ag doped ZnO nanocatalyst was investigated and shown in Fig. 5. The degradation efficiency was to be inversely proportional to the increase in concentration. This is due to the fact that as the dye concentration increases, the equilibrium adsorption of the dye on the catalyst surface active sites increases, therefore resulting in the lower formation rate of $\cdot OH$ radicals which is the principle oxidant in this process [21]. The maximum degradation 95% was found for 10 mg/L for Ag doped ZnO nanocatalyst and 65% was found to at 40 mg/L for Ag doped ZnO nanocatalyst it indicates that increasing

Fig. 3 SEM of ZnO (a), 1% Ag doped ZnO (b), 2% Ag doped ZnO (c), 4% Ag doped ZnO (d)

Fig. 4 Effect of pH on photocatalytic degradation of MB

concentration of dye decrease the percentage degradation. The equilibrium time for degradation was reached at 100 min.

In order to find the efficiency of the photocatalysis by Ag doped ZnO nanocatalyst, the Total Organic Carbon (TOC) of dye solution was determined. The TOC of MB dye solution before treatment was observed to be 336.7 mg/L and that decreases down to 11.6 mg/L after treatment with Ag doped ZnO nanocatalyst. This reflects the photocatalytic degradation of MB by Ag doped ZnO.

Fig. 5 Effect of initial dye concentration on MB (Catalyst dose 1 g/L)

3.4.3 Effect of catalyst on initial dye concentration

The effect of catalyst on initial dye concentration of MB was investigated by changing the doping amount Ag in ZnO as 1%, 2% and 4% using 1 g/L of ZnO and Ag doped ZnO nanocatalyst at pH 8. The results showed that dye concentration decreases with increasing in doping concentrations

from ZnO 20 mg/L to 1.3 mg/L, 1% Ag doped ZnO 20 mg/L to 1.0 mg/L, 2% Ag doped ZnO 20 mg/L to 0.86 mg/L, 4% Ag doped ZnO 20 mg/L to 0.76 mg/L (Fig. 6). This was due to the reason that, as doping concentration increased; the concentration of unabsorbed dye in the solution decreases which lead to more penetration of light through the solution on to the surface of ZnO and Ag doped ZnO thereby increase the concentration of $\cdot\text{OH}$ radicals on the surface and hence increases the percentage degradation.

3.4.4 Effect of doping percentage

The effect of different doping ratio on the photocatalytic degradation of MB is performed with catalyst dosage 1 g/L, pH 8 and the MB concentration 20 mg/L. As shown in Fig. 7, the MB degradation efficiency (%) was increased slightly with the increase of doping ratio from 1 to 4%. Photocatalytic activity of doping concentration increases with decreasing the band gap energy. In addition, rapid transfer of the electrons from the ZnO to the Ag may

improve the photocatalytic activity and increase the efficiency of photodegradation.

3.5 Kinetic degradation study

The photocatalytic degradation of the MB was found to obey first order kinetics at low dye concentration. A plot of $-\ln C_0/C$ Vs irradiation time t , as shown in the Fig. 8. Figure 8 was found to be linear, confirming first order kinetics adherence. The first order rate constant k , was found to be 0.0102 min^{-1} from the plot shown in the Fig. 8.

3.6 Thermodynamic study

The thermodynamic study of photocatalytic degradation of MB was performed by performing the reaction at different temperatures in the range 298.15–318.15 K using 20 mg/L initial dye concentration and 1 g/L catalyst loading. Average value of rate constant k was determined considering pseudo first order behavior of the photocatalytic

Fig. 6 Effect of catalyst on initial dye concentration (MB 20 mg/L, catalyst dose = 1.0 g/L)

Fig. 8 First order kinetics plot of MB degradation (MB conc. = 20 mg/L, catalyst dose = 1 g/L)

Fig. 7 Effect of doping percentage on percentage degradation of MB (catalyst dose 1.0 g/L, MB conc. = 20 mg/L)

Fig. 9 Plot of k versus temperature

Fig. 10 Plot of $\ln k$ versus $1/T$

degradation reaction [22, 23]. The plot of k vs temperature was plotted Fig. 9.

The straight line nature of the graph with positive slope indicates the endothermic nature of the reaction. An increase in temperature helps the reaction to compete more efficiently with decreasing the chances of e^-/h^+ recombination [24, 25]. The energy of activation, E_a , was calculated from the value of intercept of Arrhenius plot of $\ln k$ vs $1/T$ (Fig. 10).

The other thermodynamic parameters viz. enthalpy of activation (ΔH), entropy of activation (ΔS) and free energy

of activation (ΔG) were calculated using Arrhenius equation are shown in Table 1.

The possible mechanism of the photocatalytic degradation of MB dye is given by Fig. 11.

The proposed reaction mechanism is also supported by the fairly high positive values of the free energy of activation and enthalpy of activation, which indicates that the transition state is highly solvated. While the small ΔS suggests that the intermediate complex is less ordered than the reactants, which supports higher degree of degradation of the dye molecule into simple products.

The band gap energy of ZnO is 2.98 eV is decreased for Ag doped ZnO to 2.80 eV [26, 27]. The metallic Ag contributes in narrowing the band gap and that ultimately results into extending the absorption edge to visible region. Thereby Ag doped ZnO becomes the promising candidate for visible light induced photocatalysis.

It was clear from Table 2 that, the reported method found to exhibit good MB removal efficiency, in less operational time and photocatalyst dose with higher initial dye concentration as compare to other literature studies. Therefore this method could be potential method for the waste water treatment.

3.7 Scavenging study

The purpose of scavenging study is to detect main active species in the photocatalysis for evaluation of mechanism of photocatalytic degradation of MB by Ag doped ZnO. Photocatalytic degradation of MB using Ag doped ZnO proceeds by advanced oxidation process. Primarily the process involves generation of photoelectron (e^-)–hole pair. This e^- –hole pair again generates highly reactive $O_2^{\cdot-}$ and $\cdot OH$ radicals in succeeding steps which causes oxidative degradation of the dye [32]. Also water generated hydrogen atoms cause reductive degradation of the dye. The scavenging study was performed under similar conditions by addition of scavenger into the dye solution during photocatalysis. The oxidative species like $\cdot OH$, h^+ and $O_2^{\cdot-}$ are trapped by using isopropanol (i-PrOH), methanol (MeOH), ethylene diamine tetraacetic acid (EDTA) and Potassium iodide (KI). These are used as $\cdot OH$ scavenger, $O_2^{\cdot-}$ scavenger, h^+ scavenger, and $\cdot OH$ and

Table 1 Thermodynamic properties of photocatalytic degradation of MB

Temperature (K)	$K \times 10^{-2} \text{ (min}^{-1}\text{)}$	$-\ln k$	$1/T$	$E_a \text{ (KJ mol}^{-1}\text{)}$	$\Delta H \text{ (KJ mol}^{-1}\text{)}$	$\Delta S \text{ (JK mol}^{-1}\text{)}$	$\Delta G \text{ (KJ mol}^{-1}\text{)}$
298.15	0.0154	4.1733	0.003335	27.43	12.23	19.02	79.43
303.15	0.0205	3.8873	0.003300			19.11	80.56
308.15	0.0265	3.6306	0.003246			19.23	81.48
313.15	0.0315	3.4577	0.003194			19.28	82.52
318.15	0.0387	3.2519	0.003144			19.35	83.21

Fig. 11 Mechanism of the photocatalytic degradation of MB

Table 2 MB removal efficiencies (%) of various methods

Nanomaterial	Removal efficiency (%)	Operation time (min)	Catalyst Dose (g/L)	Initial dye Concentration (mg/L)	Reference
UV/ H_2O_2 / TiO_2	97.6	50	1.5	20	[28]
ZnO/UV	95	–	2.5	10	[29]
ZnO	76	120	4.0	50	[30]
ZnS:CdS	73	360	1.0	10	[31]
ZnO	92	180	1.0	20	This study
Ag doped ZnO	95	100	1.0	50	This study

h^+ scavenger respectively. The photo-generated holes also causes oxidation of smaller alcohols like i-PrOH. But the extent is negligible, hence omitted. Figure 12 gives the results in terms of MB degradation by Ag doped ZnO with and without scavengers. By addition of MeOH, EDTA, i-PrOH and KI; the photocatalytic degradation of MB decreases down to 63.43, 56.46, 28.45, and 23.74% respectively as compared to photocatalytic degradation carried out in aqueous medium (95%). From Fig. 12 it was clear that, MeOH has very little impact on MB degradation. However, the photocatalytic performance of Ag doped ZnO largely suppressed due to addition of $\cdot OH$ and h^+ scavenger i.e., KI. It indicate that the photo-generated holes and $\cdot OH$ are the major species of Ag doped ZnO while, the $O_2^{\cdot-}$ radical acts as supportive species in the degradation of MB.

Fig. 12 Photocatalytic degradation of MB using Ag doped ZnO with and without scavenger

Fig. 13 Reusability study of Ag doped ZnO nanocatalyst

3.8 Recyclability and photostability of catalyst

In any catalytic process, catalyst lifetime is one of the important factors that directly affect the cost of process. Some researchers [33] reported that ZnO undergoes photo corrosion according to the following reaction which results in a decrease of its photocatalytic activity in aqueous media.

Therefore, in this study, the recyclability of Ag doped ZnO catalyst was tested. The catalysts were separated by centrifuging, washed 3 times with deionized water to remove any adsorbed organic compounds and dried in an oven. The catalyst stability was tested for 4 cycles. At the end of 1st cycle % degradation was upto 95% and it decreases down only to 89.5% at the end of 4th cycle. As is obvious from Fig. 13 synthesized ZnO-Ag photocatalyst shows good photostability. The obtained results are in a good agreement with other reports [33].

4 Conclusions

ZnO was synthesized by the simple and modified Pechini method. The obtained ZnO and Ag doped ZnO nanocatalyst have an average grain size from about 19 to 21 nm, while the average crystallite size is increasing from about 24 to 90 nm. The method produces a nanopowder that contains only crystalline ZnO, with no detectable secondary phases. FESEM, EDS and XRD data sustain the formation of a single phase, monodisperse ZnO nanocrystal. The photocatalytic degradation of MB in the presence of nano ZnO and nano Ag-doped ZnO were show promising results towards Degradation of MB. The photocatalytic degradation followed first order kinetics with respect to MB. The

percentage degradation of dye increased with an increase Doping percentage of Ag and decrease with increase in initial concentration of dye. The pH 8 found to be suitable for photocatalytic degradation of MB. A comparative study shows that 4% Ag doped ZnO nanophotocatalyst is effective than bare ZnO, 1% Ag doped ZnO, 2% Ag doped ZnO for photocatalytic degradation of MB. The reusability study shows the stability of the Ag doped ZnO catalyst.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no Conflict of interest.

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