Enhanced Photocatalytic Activity of Silver Doped ZnO for Degradation of Rhodamine 6G†

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Rhodamine 6G is a basic dye used to dye wool, cotton, silk and paper where brilliant shades of fluorescent effects are required. But the release of this complex dye and its products in to the environment is hazardous. Hence the photocatalytic degradation of rhodamine 6G in aqueous solution was studied under visible light irradiation using ZnO and Ag doped ZnO. ZnO was doped with Ag of varying concentrations such as 0.5, 1.0, 1.5 atom percentages by liquid impregnation method in order to improve its photocatalytic activity and the samples were calcined at various temperatures for 2 h. The catalyst was characterized by XRD and SEM. Band gaps of ZnO and silver doped ZnO were calculated from UV-visible diffuse reflectance spectroscopic studies. The photocatalytic activity of ZnO was found to be enhanced by Ag doping. The dye degradation was investigated at different initial dye concentrations and photocatalyst doses.

Key Words: Photocatalysis, Rhodamine 6G, Silver doped ZnO, Dye degradation.

INTRODUCTION

Textile industries produce large volumes of coloured dye effluents, which are toxic and non-biodegradable[1]. Various physical and chemical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra filtration can be used for colour removal from textile effluents[2]. Nevertheless, they are non destructive since they just transfer non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment[3]. Recently, advanced oxidation processes (AOPs) have been proposed as an alternative method for water purification[4]. Among advanced oxidation processes, heterogeneous photocatalysis has been used in the recent years as a promising method for the removal of toxic organic contaminants from industrial wastewater[5,6]. Titanium dioxide is generally considered to be the best photocatalyst but it absorbs only a small portion of solar spectrum in the UV region. Hence, interest has been drawn towards search for other alternatives to TiO_2. Many attempts were made to study the photocatalytic activity of different semiconductors such as SnO_2, ZrO_2, CdS and ZnO[7,8]. The biggest advantage with ZnO is its absorption over a large fraction of solar spectrum than TiO_2. For this reason ZnO is the most suitable catalyst for photo degradation in the presence of sunlight[9].

In this paper an attempt has been made to study the photocatalytic degradation of rhodamine 6G in aqueous solution under visible light irradiation by using Ag doped ZnO. Silver ion doping is done by liquid impregnation method[10].

EXPERIMENTAL

Zinc oxide and rhodamine 6G were obtained from Merck India. All the solutions were prepared using double distilled water. All the chemicals used in the study were of analytical reagent grade.

Preparation of silver-doped ZnO photocatalyst: Silver doped ZnO containing 1 atom % of silver was prepared by the following procedure. Silver nitrate solution containing 105 mg in 100 mL was added to 5 g of ZnO and the mixture was stirred for 4 h. The suspension was allowed to stand for 24 h. The water was then evaporated by heating at 100 ºC for 16 h. The dried solid was grounded to fine powder in an agate mortar and calcined at 200, 400 and 600 ºC for 2 h in muffle furnace. Silver doped ZnO of 0.5 and 1.5 atom per cent were prepared by taking 52.5 mg and 157.5 mg of silver nitrate and following the same procedure.

XRD and SEM: The catalysts were characterized for their structure and morphology by XRD and SEM. The XRD patterns of the powdered samples were recorded by Bruker 8 D advanced X-ray diffractometer and SEM images of the

samples were taken by using Philips XL 30 ESEM Scanning electron microscope.

Ultra-violet diffuse reflectance spectroscopy: UV-VIS spectroscopy was used to characterize the optical absorption properties of ZnO and Ag-ZnO. The UV-VIS absorbance spectra of the samples were recorded in the wavelength range 200-800 nm using Shimadzu UV 3600 UV-VIS-NIR spectrometer in diffuse reflectance mode (DRS) using $BaSO_4$ as reference. Spectra were recorded at room temperature and the data were transformed through Kubelka-Munk function.

Phtocatalytic studies: The experimental setup for the photocatalytic degradation consisted of a 250 mL Borosil beaker with water circulation outside. The beaker was placed on a magnetic stirrer, above which a high pressure mercury vapour lamp (125 W, Philips) emitting visible light was placed. 100 mL of the dye solution was taken in the beaker and photocatalyst ZnO or Ag-doped ZnO at a dose of 1 gL^{-1} was added to it. The distance of the light source from the upper level of dye solution in the beaker was 18 cm. The solution was stirred in the dark for 5 min to establish the adsorption equilibrium. The zero time reading was taken and the solution was then irradiated. Aliquots were taken at regular time intervals and centrifuged to analyse the percent degradation of the dye.

Analysis: The percent degradation of rhodamine 6G was found out spectrophotometrically by measuring absorbance of the dye solution at λ_{max} 523 nm. The decolourization efficiency (%) was calculated as:

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where, C_0 is the initial concentration of dye and C is the concentration of dye after irradiation. Similar experiments were carried out by varying concentration of dye solution and catalyst loading.

RESULTS AND DISCUSSION

Catalyst characterization

XRD and SEM analysis: The XRD patterns obtained for powdered ZnO and Ag-ZnO of various concentrations of silver doping 0.5, 1.0, 1.5 atom % dried at 100 ℃ were shown in Fig. 1(a) indicating well indexed phases of ZnO wurtzite structure. No change in the peak positions was observed in any of the silver doped ZnO samples. This indicates that doping of ZnO with Ag^+ ions doesn't change the crystal structure, may be due to low percent of silver doping and surface deposition. Calcination of samples at 200, 400 and 600 ℃ introduced a small extra peak in XRD pattern [Fig. 1(b)] characteristic of metallic silver[11,12]. The SEM images of ZnO and Ag-ZnO are given in Fig. 2, which shows that ZnO particles are in different shapes and sizes and, silver doping doesn't change the morphology of ZnO.

Diffuse reflectance analysis: Fig. 3 shows UV-VIS absorption spectra of ZnO as well as doped ZnO with 0.5, 1.0, 1.5 atom % of silver ions. All samples have a strong absorbance below 400 nm. The addition of silver ions make a slight shift in the absorption maximum to higher wavelengths in case of 1 atom % silver doped ZnO. The band gap energies of ZnO and Ag-ZnO samples were calculated by extrapolating the linear portion of the plots of modified Kubelka-Munk

function[13], $[F(R)h\nu]^2$ *versus* the photon energy (hν). There is no much change in the band gap energy of ZnO by silver doping. But a slight decrease is observed in 1 atom % Ag-ZnO, which supports the red shift in absorption maximum.
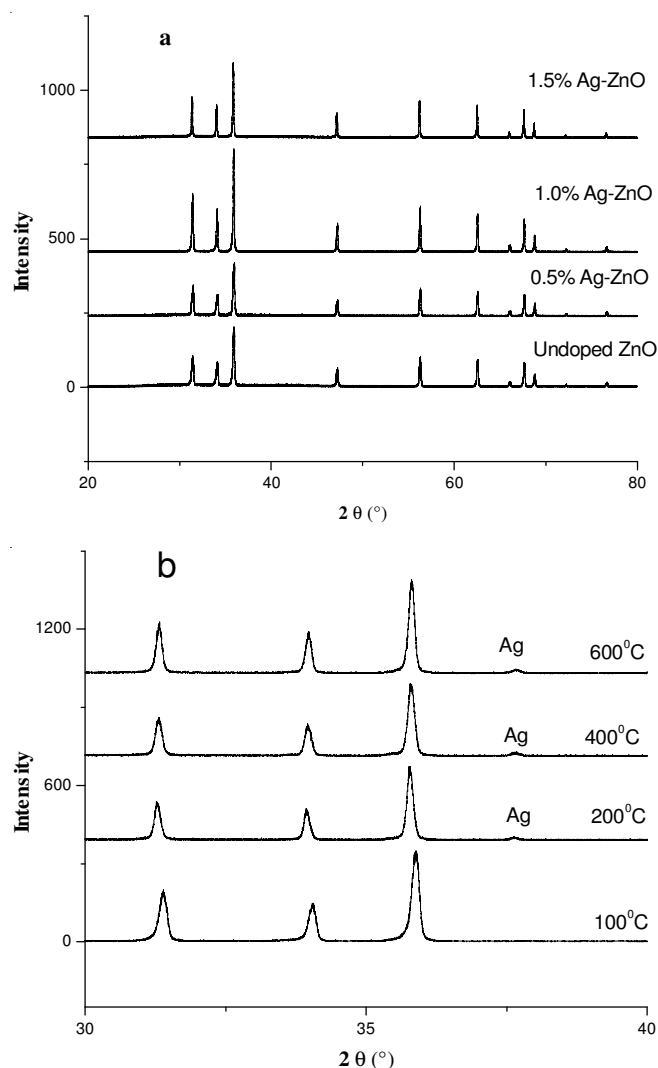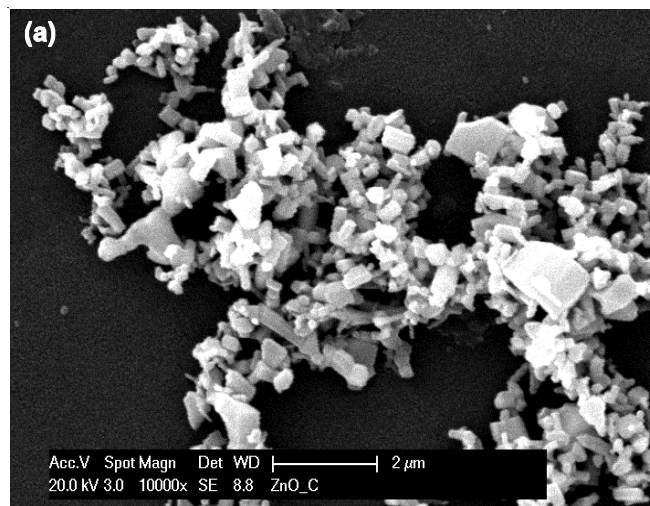

Fig. 1.   Powdered XRD patterns of ZnO and various atom% of Ag-doped ZnO samples; a) Dried at 100 ℃ and b) 1 atom % Ag-ZnO calcined at various temperatures
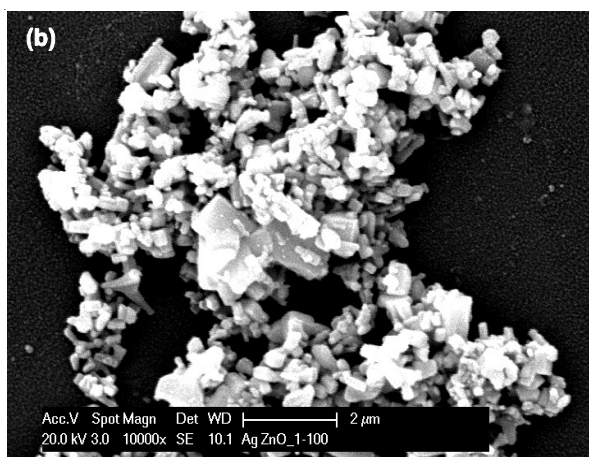
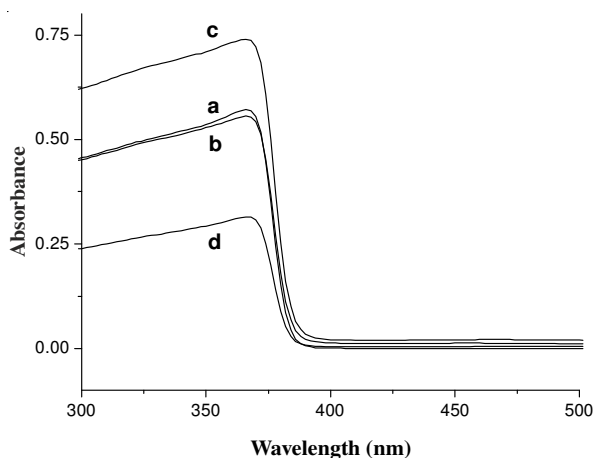Fig. 2. SEM images of a) Undoped ZnO and b) 1 atom % Ag doped ZnO

Fig. 3.   UV-VIS absorption spectra of ZnO and Ag doped ZnO; (a- Undoped, b-0.5 % Ag-ZnO, c-1.0 % Ag-ZnO, d-1.5 % Ag-ZnO)

Photocatalytic degradation: The aqueous solutions of Rhodamine 6G dye (1.04×10^{-4} M) were found to degrade by 72 % and 90 % on visible light irradiation for 1 h in the presence of ZnO (1 gL^{-1}) and Ag-ZnO (1 gL^{-1}), respectively. The degradation efficiency of Ag-ZnO was found to be higher than ZnO (Fig. 4).
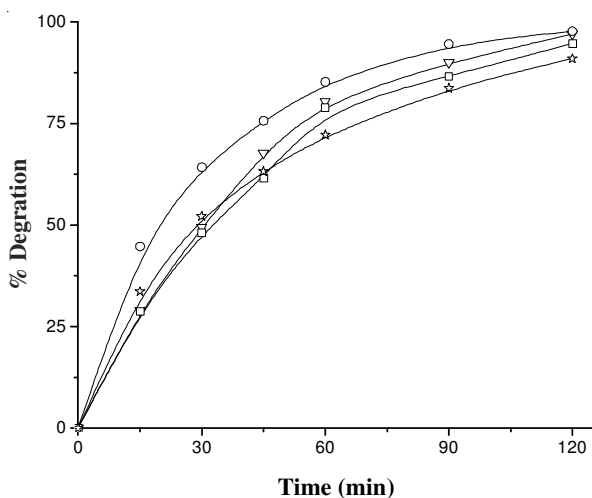

Fig. 4.   Effect of silver doping on degradation of rhodamine 6G, [R6G] = 1.04×10^{-4} M, [Catalyst] = 1gL^{-1}; (☆) Undoped ZnO, (▽) 0.5 % Ag-ZnO, (O) 1.0 % Ag-ZnO, (□) 1.5 % Ag-ZnO

The per cent degradation decreased with increase in calcination temperature. Samples heated at 100 and 200 ºC have high activity than samples calcined at 400 and 600 ºC for 2 h. Higher temperature calcinations have a negative effect on photocatalytic activity because the presence of silver promotes the densification and grain growth of ZnO at higher temperatures by forming a silver island in the ZnO matrix, which causes the reduction in active surface sites of the photocatalyst for the adsorption of dye and for the absorption of light[14]. With increase in silver doping from 0.5 to 1.5 atom percent, the degradation efficiency was found to be maximum for 1 atom percent of silver doping on ZnO. This is the optimal concentration of Ag doping on ZnO by this method.

The enhancing effect of Ag doping may be explained by its ability to trap electrons and this process reduces the recombination of charges and favours the oxidation of the substrate. Higher concentrations of silver doping could be unfavourable to photocatalytic efficiency. It is assumed that silver doping below optimum value acts as electron-hole separation center[15], whereas above optimum value it can also act as charge carrier recombination center.

Effect of catalyst concentration: In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from 0.25 to 2.0 gL^{-1} for dye solution of 1.04×10^{-4} M at natural pH of dye solution 5.97. The percent degradation of rhodamine 6G for various doses of catalyst has been shown in Fig. 5. The percent degradation increases with increase in catalyst dose and higher concentrations of catalyst beyond 1 gL^{-1} doesn't have much effect on degradation. This can be explained on the basis of increased total active surface area with the catalyst dose and availability of more active sites on the surface. At the same time due to increased turbidity of the suspension with high dose of photocatalyst, penetration of light and photoactivated volume of suspension decrease. Hence an optimum catalyst dose of 1 gL^{-1} was selected for further studies.
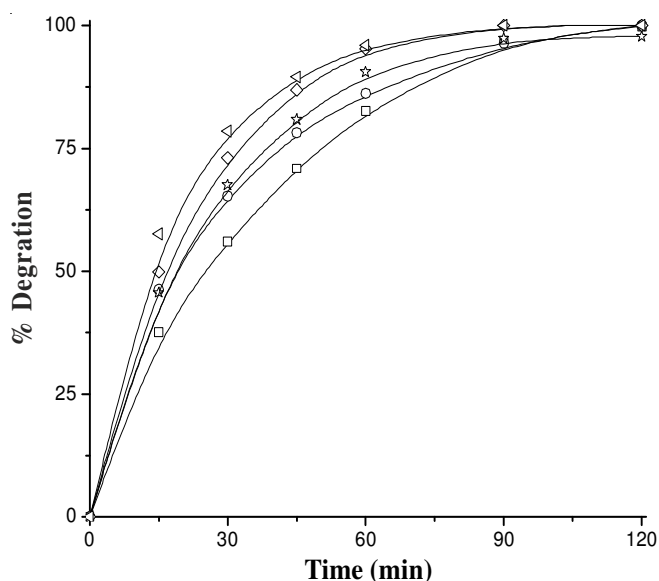

Fig. 5.   Effect of catalyst loading on degradation of rhodamine 6G, [R6G] = 1.04×10^{-4} M; (□) 0.25 g L^{-1}, (O) 0.50 g L^{-1}, (☆) 1.00 g L^{-1}, (◇) 1.50 g L^{-1}, (◁) 2.00 g L^{-1}

Effect of dye concentration: The effect of initial dye concentration on the photodegradation of rhodamine 6G was studied at different concentrations in the range of 1.04×10^{-5} M to 4.17×10^{-4} M (Fig. 6). It was observed that the percent degradation gradually decreased with increase in initial dye concentration. As concentration of dye solution increases, the colour of the reaction mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amounts of OH^- and O^{2-} on the surface of the catalyst decreases. Thus the dye degradation efficiency decreases as the dye concentration increases[16].
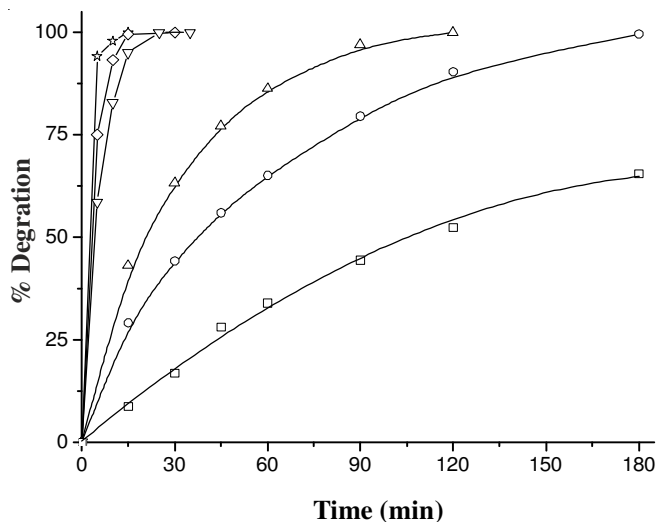

Fig. 6.   Effect of dye concentration on degradation of rhodamine 6G, [Ag-ZnO] = 1 gL^{-1}; (☆) 1.04×10^{-5} M, (◇) 2.08×10^{-5} M, (▽) 4.17×10^{-5} M, (△) 1.04×10^{-4} M, (O) 2.08×10^{-4} M, (□) 4.17×10^{-4} M

Conclusion

The doping of silver ions drastically enhanced the photocatalytic activity of ZnO. The optimum concentration of silver doping in this method was found to be 1 atom %. Calcination of the samples at higher temperature has a negative impact on photocatalytic activity. The characterization of samples by XRD and SEM analysis indicated that silver doping did not change the crystal structure and morphology of ZnO, but diffuse reflectance spectra studies indicate a small decrease in band gap of 1 % Ag-ZnO. This may be one of the reasons for higher activity of 1 % Ag-ZnO samples over others in visible region. The percent degradation of rhodamine 6G increased with increase in catalyst dose up to an optimum loading. Further increase in catalyst dose showed a little effect.

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