Visible active silver sensitized mixed phase ZnO photocatalyst

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The present work reports synthesis of highly photoactive silver-sensitized mixed phase ZnO nanoparticles. The structural, optical and chemical characterizations of the prepared materials were done using XRD, TEM, UV–DRS, PL and EPR. The photoactivity of the nanoparticles was assessed through photocatalytic degradation kinetics of methylene blue. The rate constant of the photocatalytic degradation of methylene blue using silver sensitized mixed phase ZnO was found to be 3.7 and 1.2 times higher than monophasic (wurtzite) ZnO without and with silver sensitization, respectively, under visible light. The increase in the activity is mainly attributed the synergy of the interacting phases at the homojunction and the surface plasmon resonance due to the metallic silver.

Keywords: Photocatalyst, surface plasmon resonanace, mixed phase

1. Introduction

Two of the most investigated semiconductor photocatalysts-TiO_2 and ZnO, have some inherent constraints in achieving high photocatalytic activity due to their large band gap, which restricts the photo-absorption only to the UV region of solar spectrum and low separation probability of photo-generated charge carriers leading to high recombination. To overcome these constraints different techniques such as doping [Vazquez et al. 2015, Kumar et al. 2015], formation of nanocomposite [Wenga et al. 2014], sensitization [Pawar and Sunyong, 2014] and mixed phase transformation [Nair et al.2011] had been implemented for such semiconductor photocatalysts. Recently, it has been reported that these problems can also be alleviated by plasmonic/ semiconductor photocatalyst [Chiu et al. 2015 and Rajbongshi et al. 2014a]. Surface plasmon resonance of metal at UV and visible region can extend photo activity in higher wavelength also. Further, noble metal Ag acts as electron scavenger which enhances the life time of energetic charge carriers by reducing their recombination probability. Also many researchers have reported that mixed phase TiO_2 shows photocatalytic activity under visible light. Recently Rajbongshi et al. reported that like TiO_2, mixed phase (wurtzite and zincblende) of ZnO also shows higher photocatalytic activity under visible light [Rajbongshi and Samdarshi, 2014b]. But the main challenge of synthesis of mixed phase ZnO is in ensuring the suitable synthesis conditions in addition to an appropriate matching substarte for the formation of metastable zincblende phase of ZnO [Ashrafi,2007]. The challenge of synthesis of metastable zincblende (ZB) phase with wurtzite (WZ) subdomian has been recently solved by a single-step and simple synthesis procedure using dopant as a substrate. But none of the dopants used were known to show plasmonic resonance under visible light. This encouraged the present work to study the photocatalytic activity of the mixed phase ZnO with Ag sensitization to take the advantage of surface plasmon resonance; and wurtzite and zincblende homojunction. The basic investigation suggest that Ag can act as a sensitizer and a substrate for the formation of mixed phase ZnO as reported earlier[Rajbongshi and Samdarshi, 2014b]. Some studies on the role of Ag in formation of mixed phase have been reported earlier in the case of ZnS [Synnott,2013; Tsuji,2006].

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In this present study Ag sensitized mixed phase ZnO photocatalyst was synthesized by sol-gel co-precipitation method. The photocatalytic activity was studied under visible light for methylene blue degradation for the synthesized photocatalyst.

2. Material and Methods

2.1. Material synthesis

The chemicals used for synthesis of Ag doped ZnO were zinc acetate dihydrate $(CH3COO)_2$ Zn. $2H_2O$, silver nitrate, sodium hydroxide pellets (NaOH) and ethanol. Sol-gel co-precipitation method was used as reported earlier [Rajbonghi and Samdarshi 2014b] to synthesize the sample. The calcinations temperatures were 400 and 425^oC for Ag-senistized single phase (AZ(M)) and Ag-sensitized mixed phase ZnO (AZ(S)), respectively. For comparison single phase ZnO(without Ag sensitization)was also synthesized and calcined at a temperature of 400^oC.

2.2. Characterization

Structural and morphological analysis was done by XRD (Rigaku Miniflex, Japan) and TEM (model JEM-100CX II (JEOL Japan). The spectral response of the material was evaluated using a UV–DRS spectrophotometer (Shimadzu UV-2200, Japan) with diffuse reflectance attachment. The photoluminescence spectrum was recorded using a photoluminescence spectrometer (LS55, Perkin Elmer, USA) for studying the trap states. Further study on oxygen vacancy and defects on the material was done using ESR spectrometer (JEOL, Model: JES-FA200).

2.3. Photocatalytic activity test

The photocatalytic activity of the synthesized nano-material was studied using probe pollutant - methylene blue (MB) with visible irradiance at the reactor surface of 14.5 W/m^2 at 28^oC. The adsorption-desorption equilibrium was ensured by keeping the catalyst loaded MB in dark for one hour. The change in the concentration of the sample was recorded by correlating it with the absorbance of the sample, measured using UV-Vis spectrophotometer (Shimadzu 1700, Japan) at the wavelength of 650 nm for MB.

3. Result and discussions

XRD spectra of pristine ZnO and Ag doped ZnO are shown in Fig.1a,b. Pristine ZnO is monophasic wurtzite(Fig.1a). Among the Ag-sensitized samples, AZ(M) shows the mixed phase of wurtzite (JCPDF: 891397) and zincblende (JCPDF: 652880) phases of ZnO while AZ(S) is single phase of wurtzite (Fig.1b). The diffraction peak (111) at $\theta = 38^o$ is identified for metallic Ag which matches with the JCPDS file No: 893722. Another extra peak can be identified for AgO in Ag doped ZnO sample. The particle size that has been calculated using Scherrer formula [Zachariah et al.,2008] is given in Table 1. From the Table it can be seen that mixed phase sample AZ(M) posses higher particle size for zincblende ([111] plane) phase.

Table 1: Particle size and band gap of the synthesized sample

Sample	Particle size (nm)		Band gap (eV)
	WZ	ZB	
ZnO	14.2	-	3.12
AZ(M)	13.3	18.6	2.93
AZ(S)	12	-	3.03

Fig.1c shows the TEM image of the sample AZ (M) wherein the presence Ag of about 20nm in size is clearly visible. The particle size from TEM analysis accords well with XRD results. The formation of wurtzite (WZ) and zincblende (ZB) polymorph of ZnO with an additional phase for metallic silver is shown in Fig.1d. The d-spacing for wurtzite and zincblende is found to be 0.25 and 0.23nm, respectively, and that of Ag to be 0.21nm. So AZ (M) is a combination of homo- and heterojunction of wurtzite-zincblende ZnO and ZnO-Ag, respectively.

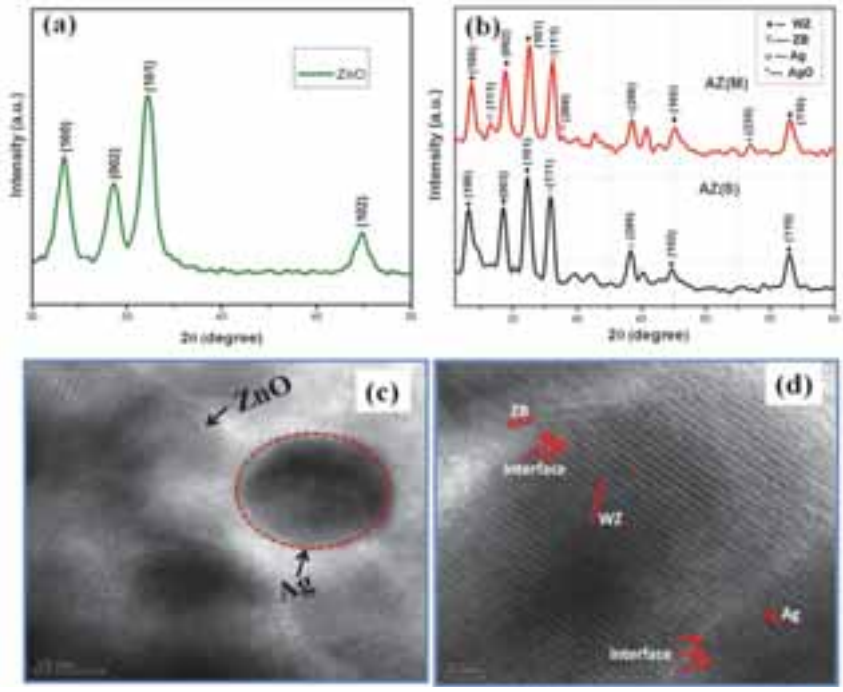

Fig.1: XRD spectrum of (a) Pristine ZnO (b) AZ(M), AZ(S); (c) and (d)TEM micrograph of AZ(M)

UV-DRS spectrum of pristine and Ag-ZnO sample is shown in Fig. 2a. All the Ag-sensitized samples show red-shift compared to the pristine ZnO. The band gap of the materials calculated using Tauc's equation [Xu, H., and Zhang, L., 2009.] is found to be 3.03 and 2.93 eV for AZ(S) and AZ(M), respectively while that of the pristine ZnO it is 3.12 eV (Table 1). In UV-DRS spectrum it can be observed that samples AZ(S) and AZ(M) show absorption peak near at 410 and 550nm, respectively. It has been reported that Ag shows a typical absorption peak in the range 400-550 nm due the surface plasmon resonance [Ansari et al., 2013; Logar et al., 2010]. So the peaks at 410 and 550nm are ascribable to the surface plasmon resonance of metallic silver. The emission centered at 370nm is due to the near band edge emission for ZnO. The PL spectra measured at excitation wavelength 325nm are shown in Fig.2b. The visible emission intensity of Ag doped ZnO sample was lower than the pristine ZnO ascribing the quenching of fluorescence due to the Ag, which increases the electron hole pair life time. The quenching of PL intensity (Fig.2b) is higher in AZ(M) which may due to synergistic effect of WZ-ZB homojunction and also Ag-ZnO heterojunction. PL spectra also reveal the increase of oxygen vacancies after Ag doping in ZnO.

Oxygen vacancy and the local environment of Ag are also investigated through EPR analysis (Fig.2c). Both pristine ZnO and AZ(S) show the EPR signal with g value 1.9 but AZ(M) shows a shift with g value at 1.8. These signals are ascribed to impurities or defects due to oxygen vacancies and broadening of the signal

for AZ(M) sample indicates increase in the oxygen vacancy. The g value 2.1 is assigned to zinc vacancy in the sample. The EPR signal at g value 2.35 in the sample AZ(M) is assigned to the Ag^{+} which indicates the presence of high amount of AgO in the sample [Deng et al.,2008]

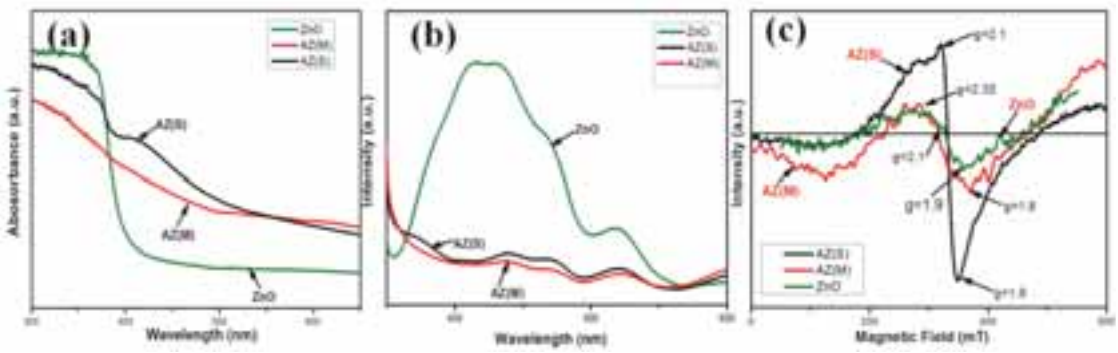

Fig. 2: (a) UV-DRS (b) PL and (c) EPR spectrum of the samples.

3.1. Photocatalytic activity test

To evaluate the photocatalytic activities of Ag-ZnO photocatalyst the degradation of methylene blue (MB) was investigated under visible light. Fig.3a shows the degradation kinetics of MB over Ag-sensitized ZnO samples. It is evident from the Fig.3 that the Ag-sensitized ZnO samples show excellent visible light activity compared to the pristine ZnO for methylene blue degradation. The degradation rate constant was calculated using $\ln(C/C_o)$ vs. time curve (Fig.3b) and it is found to be 0.007 and 0.006 min^{-1} for AZ(M) and AZ(S), respectively. But pristine ZnO shows a rate constant of 0.002 min^{-1}. So, AZ(M) shows 3.7 and 1.2 times higher photocatalytic activity under visible light compared to monophasic sensitized and unsensitized ZnO. The higher photocatalytic activity of AZ(M) compared to pristine ZnO and AZ(S) indicates the synergistic effect of mixed phase homojunction which increases the charge carrier migration and separation; and Ag nanoparticles anchored surface plasmon effect on ZnO nanoparticles. SPR of Ag enhances the photocatalytic activity by increasing electron concentration in ZnO. Besides these, increase in the life time of the photogenerated charge carrier also reduces due to the reduction in probability of the recombination of the charges which again helps in the enhancement of photocatalytic activity.

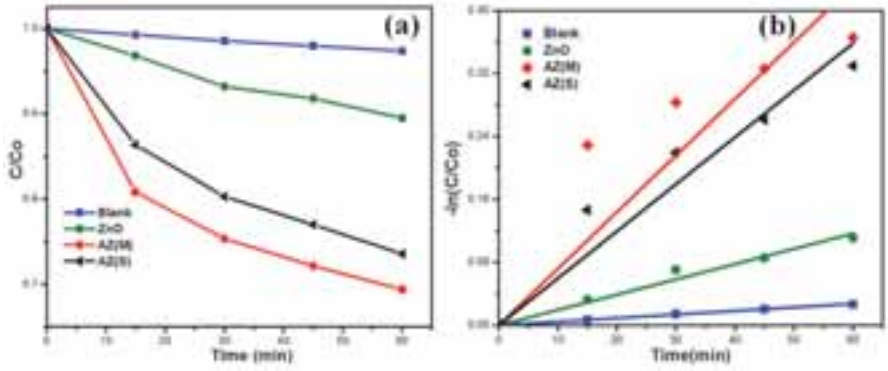

Fig. 3: (a) photocatalytic degradation of MB, (b) $\ln(C/C_o)$ vs. time curve for determination of rate constant

4. Conclusion

In conclusion, we have demonstrated synthesis of Ag-doped ZnO having mixed phase(wurtzite and zincblende) ZnO with an advantage of surface plasmon resonance of noble metal Ag. Surface plasmon resonance helps in extending the absorption spectrum of the photocatalyst in the visible region. Homo-junction interface of wurtzite-zincblende of ZnO helps in the separation and migration of the charge carrier to the surface. Photocatalytic activity study concludes that the mixed phase Ag-sensitized ZnO shows higher photocatalytic activity compared to pristine and single phase ZnO with and without sensitization due to the presence of homojunction of wurtzite-zincblende ZnO and heterojunction of Ag-ZnO on multiple aspects of the photocatalytic activity.

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