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Synthesis and characterization of plasmonic visible active Ag/ZnO photocatalyst

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Abstract Ag deposited ZnO nanoparticles (NPs) have been synthesized by simple sol–gel method for visible light active photocatalytic application. X-ray diffraction (XRD), TEM, UV–DRS and PL studies have been used to characterize the photocatalyst. The results show that Ag/ZnO NPs are wurtzite phase (WZ) of ZnO with Ag NPs in the surface region forming a hetero-interface of Ag–WZ (ZnO). Visible light activity of the material has been studied using photocatalytic degradation kinetics of methylene blue as a probe pollutant. Ag/ZnO NPs exhibit five times higher visible-light driven photocatalytic activity than pristine ZnO and four times than the reference Degussa P-25, under identical conditions. The high visible activity of Ag/ZnO may be attributed to the surface plasmon effect complemented sensitization in the presence of metallic Ag and effective charge separation through Ag–WZ hetero-interfaces.

1 Introduction

The semiconductors such as ZnO and TiO_2 have wide applications in the area of photocatalysis because of their physical and chemical stability, high oxidative capacity, low cost and ease of availability [1]. Among these nanomaterials ZnO has promising applications in electronics, energy, environment, photonics, and spintronics due to its multifunctionality and high efficiency attributed to its direct wide band gap (3.37 eV) and large exciton binding energy of $\sim$60 meV [2]. However, optical absorption in the ultraviolet region and low photonic efficiency are factors that prevent the wide scale use of ZnO for photo catalytic activities under sunlight. Numerous studies report on improvement of visible-light photocatalytic activity of metal oxide semiconductors by introducing bulk modification doping metals [3], and non-metals [4] and surface modifications [5]. Here surface modifications may be preferable than bulk modification because sometimes dopant may act as a recombination center of photogenerated electrons and holes, subsequently, reducing the activity of the photocatalyst [6]. Noble metals are used as surface modifiers [7, 8], primarily because they possibly inhibit charge recombination by accelerating transfer of photo-excited electrons from zinc oxide. Surface plasmon resonance (SPR) effect using noble metals can enhance the generation of electron and hole as well, through increase in the absorption in the visible light region. In such SPR assisted photocatalysis, with the use of resonant visible light wavelengths, the charge carriers are directly injected from excited plasmonic-metal into the semiconductor surface. The metallic plasmonic nanoparticles act as a sensitizer, which absorb the resonant photons and transfer the electron, generated through the process of the SPR excitation, to the nearby semiconductor [9].

In the present study, the Ag induced SPR assisted photocatalytic activity of Ag loaded ZnO NPs has been investigated under visible light.

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2 Experimental

2.1 Material synthesis

The chemical used for synthesis of Ag/ZnO were zinc acetate dihydrate $(CH_3COO)_2$ Zn · $2H_2O$, silver nitrate ($AgNO_3$), oxalic acid and ethanol. All these materials were purchased from Merck (India). Double distilled water was used in all the processes. In this method, zinc acetate (0.01 M) was dissolved in ethanol at 60 °C and stirred for 30 min. Oxalic acid (0.002 M) dissolved in ethanol at 60 °C was slowly added to the warm ethanolic solution of zinc acetate. The mixture was stirred for 4 h. The thick white colloidal semi-gel formed was allowed to dry at 80 °C overnight. The material was further calcined at temperature 450 °C for 2 h to form ZnO powder. Ag/ZnO nanoparticle was synthesized by same process using $AgNO_3$ (1 wt%) for deposition of Ag in ZnO.

2.2 Characterization

X-ray diffraction (XRD) pattern was recorded on diffractometer (Rigaku Miniflex, Japan) at a scan rate of 0.05 2θ/s. The transmission electron microscope (TEM, model Tecnai G2, F2OS-Twin, FEI, USA, 200 kV), was used to study the internal structure and morphology. The spectral response of the catalyst material was evaluated using UV–visible diffuse reflectance spectra using a UV–DRS spectrophotometer (Shimadzu UV-2200, Japan). The photoluminescence spectrum was recorded using a photoluminescence spectrometer (Perkin Elmer LS55, USA) for studying the trap states.

2.3 Photocatalytic activity test

The photocatalytic activity of the prepared nano-material was studied by using aqueous probe pollutants—methylene blue (MB). The degradation kinetics was studied under visible light irradiation (source: Radium, Relogen PAR30, China, Fig. 5c). The visible irradiance at the reactor surface was 121 W/m^2 (measured by Research radiometer International light, USA with detectors SD 005 and SD 033). The adsorption–desorption equilibrium was ensured by keeping the catalyst loaded MB solution in dark for one hour. The sample was exposed to visible light and the samples were collected after every 15 min of exposure. The spectral response of the centrifuged sample solution was recorded by UV–Vis spectrophotometer (Shimadzu 1700, Japan).

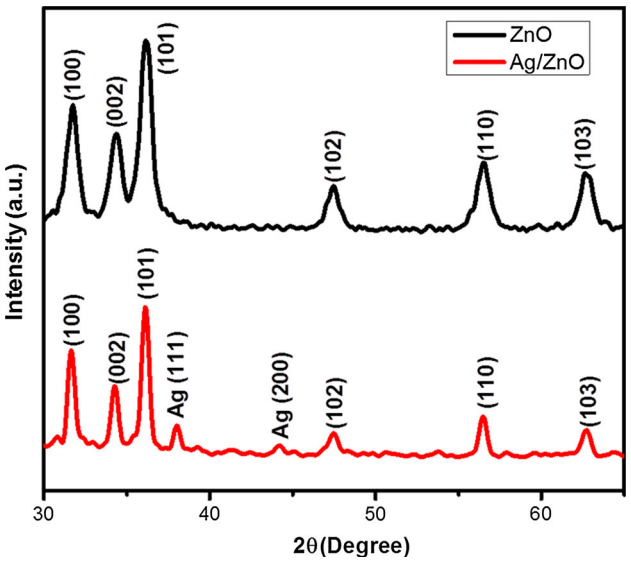

Fig. 1 XRD spectrum of ZnO and Ag/ZnO

3 Results and discussion

3.1 Structure and morphology

Figure 1 shows the X-ray diffraction (XRD) of ZnO and Ag/ZnO calcined at 450 °C. From the figure it can be observed that ZnO and Ag/ZnO are in wurtzite phase (WZ) of ZnO (JCPDF = 891397). The presence of cubic phase of metallic Ag (JCPDF = 893722) is clearly visible in the Ag/ZnO and the intensity of these peaks is very weak because the amount of Ag is very small. The average crystallite sizes, evaluated by the Scherrer formula are about 11.3 and 15.6 nm for ZnO and Ag/ZnO, respectively.

The morphology of Ag/ZnO was studied by TEM micrograph (Fig. 2). Figure 2a shows the presence of small Ag NPs with ZnO. The high-resolution TEM image of Ag/ZnO confirmed that the Ag was deposited on ZnO making a hetero-interface of Ag and WZ–ZnO with *d* spacing of Ag 0.21 nm and 0.25 for WZ–ZnO (Fig. 2b). The average crystalline size of Ag/ZnO NPs are well accords with the X-ray diffraction (XRD) results. The SAED pattern of Ag/ZnO (Fig. 2c) confirms the crystallinity of the material.

3.2 Optical properties

The diffuse-reflectance of nanocrystals (Fig. 3) shows two prominent absorption bands in the UV–visible region. The former can be assigned to the absorption of the ZnO semiconductor, and its corresponding absorption edge is located at around 375 nm. The latter can be attributed to

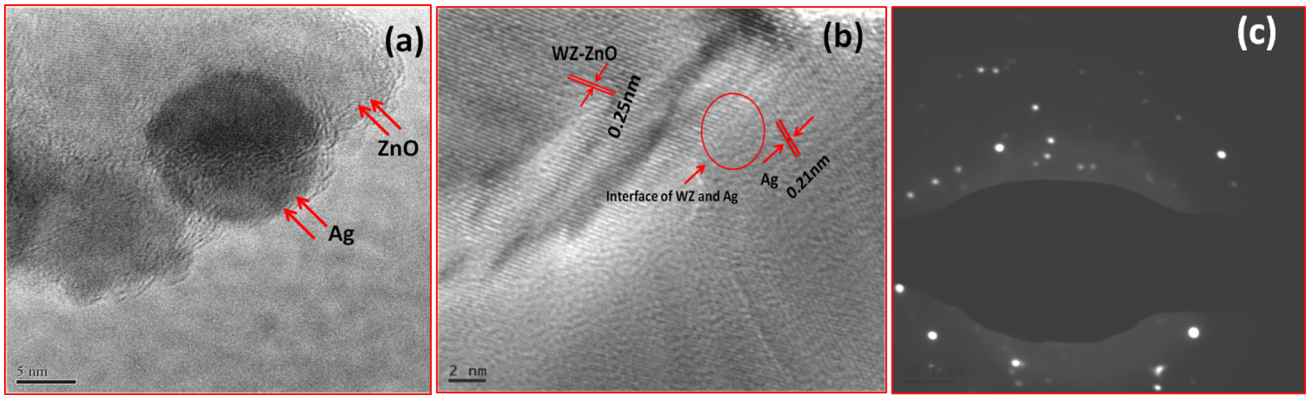

Fig. 2 TEM micrograph of Ag/ZnO (**a**, **b**) and SAED pattern (**c**)

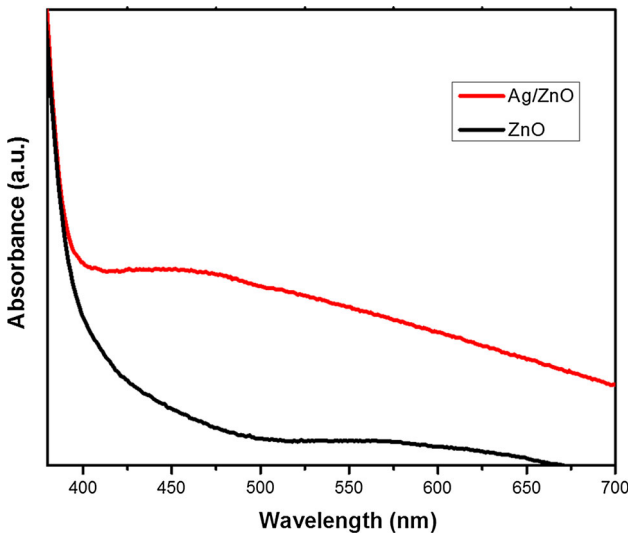

Fig. 3 UV–DRS of ZnO and Ag/ZnO

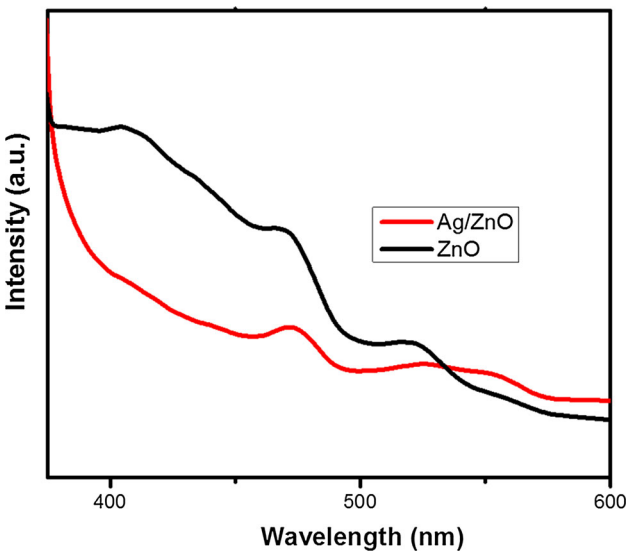

Fig. 4 PL of ZnO and Ag/ZnO

the characteristic absorption of SPR resulting from the metallic Ag in the Ag/ZnO [1]. The band gaps of the samples were calculated using Tauc's equation and it was found to be 3.25 and 3.16 eV for ZnO and Ag/ZnO, respectively. Incorporation of Ag in the ZnO does not change the band gap significantly but SPR effect enhances the absorption of material in the visible region also.

In a photocatalytic process, the generation and recombination of photo-induced electron and hole are competitive pathways, and photocatalytic activity is effective when the recombination is prevented. From the photoluminescence spectrum (Fig. 4) of ZnO and Ag/ZnO we can investigate the recombination phenomenon and the defects in the material. The weak blue bands at 421 and 480 nm correspond to the band edge free carriers and bound excitons, respectively, of the samples [10]. The green emission centered at 530 nm can be attributed to the oxygen vacancy and Zn^{2+} vacancy. The considerable increase in the oxygen vacancy of the sample Ag/ZnO indicates that the surface defects in the ZnO photocatalyst are greatly reduced after the Ag loading, suggesting that the metallic Ag is deposited on the defect sites [11]. The low PL intensity of Ag/ZnO compared to ZnO signifies less recombination of the charge carriers due to SPR effect of Ag.

3.3 Kinetic study for degradation of dye

The photocatalytic activity study of the materials was performed by investigating the kinetics of degradation of aqueous MB dye solutions under visible light. For comparison the results of the studies carried out on commercial TiO_2, Degussa P-25 (Make:) is shown in Fig. 5a, b. The adsorption equilibrium was established in all the cases by

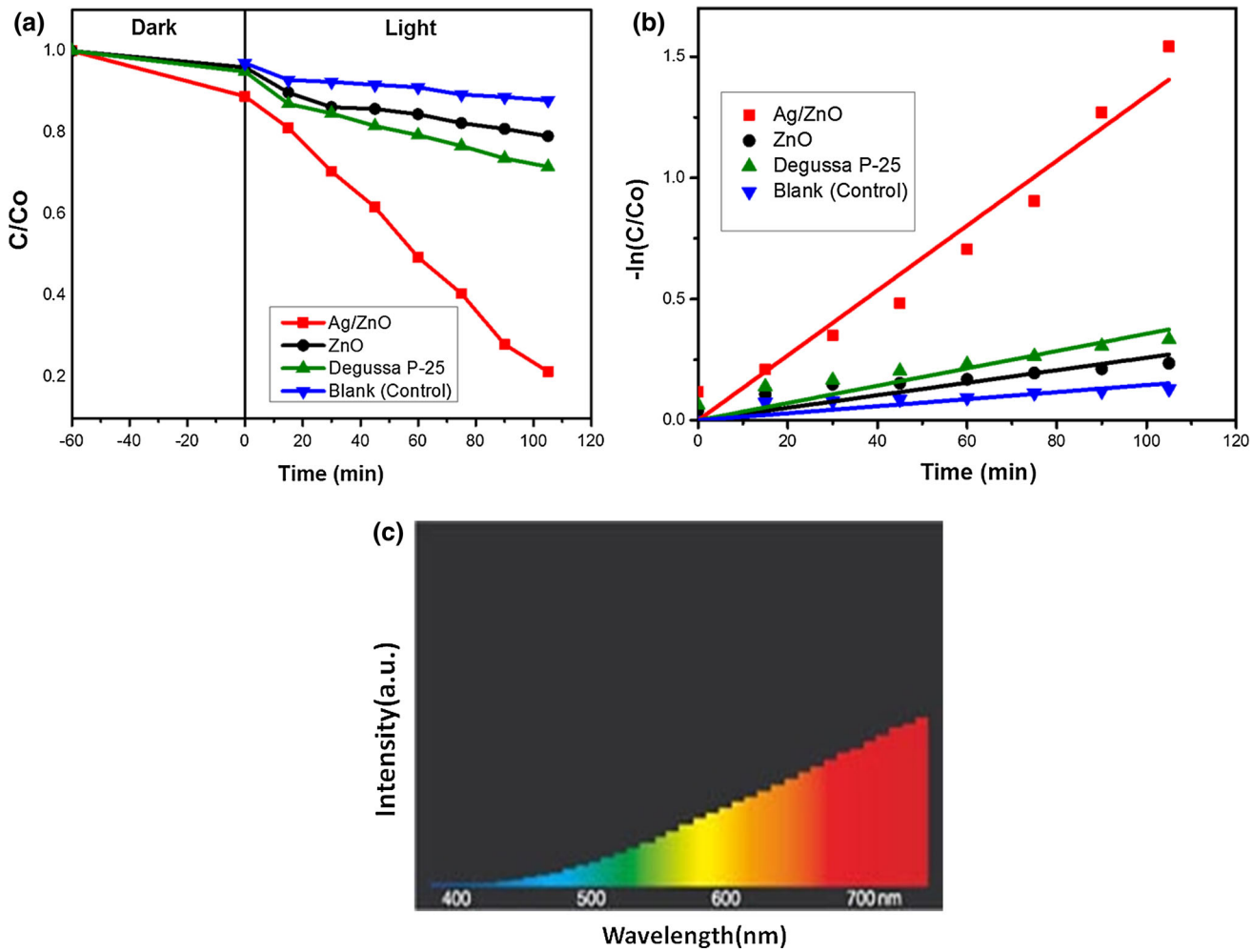

Fig. 5 **a** Photocatalytic degradation of MB under visible light. **b** lnC/Co versus time plot to determine the rate of constant. **c** Source spectrum in visible range [Radium, Relogen PAR30, China]

keeping the samples in dye solution in dark for one hour (Fig. 5a). The variation in concentration of MB dye is given in Fig. 5a. The rate of degradation of MB was calculated using the plot of lnC/Co versus time graph (Fig. 5b). The rate constant of Ag/ZnO (0.014 min^{-1}) shows higher activity (in terms of rate constant) compared to pristine ZnO (0.0026 min^{-1}) and Degussa P-25 (0.0035 min^{-1}) under visible light. The degradation of the control (blank) is also given for reference in Fig. 5a, b and it shows low degradation rate constant (0.001 min^{-1}) under visible light. The enhanced activity of Ag/ZnO is due to the Ag loading. As stated the SPR effect of Ag increases the absorption spectrum of ZnO in the higher wavelength side and reduces the charge carrier recombination as well. In Ag/ZnO photocatalytic system photo-induced electrons are generated from Ag due to SPR and are, subsequently, transferred from Ag to ZnO particle. Thereafter the electrons interact with adsorbed oxygen, finally forming hydroxyl radicals, thus, enhancing the visible-light driven photocatalytic efficiency.

4 Conclusions

The present work, demonstrates that Ag loaded ZnO nanoparticle had higher photocatalytic activity compared to pristine ZnO for MB dye degradation under visible light. The results have been supported with the help of experimentation done using the reference Degussa P-25. The enhancement of the photocatalytic activity is finally attributed to the SPR effect of metallic Ag which increases the generation of photo-induced electrons and holes and reduces the recombination losses.

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