Photoluminescence and photocatalytic activities of Ag/ZnO metal-semiconductor heterostructure

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Abstract. Present article focuses on the photocatalytic activities of ZnO nanorods and Ag/ZnO heterostructure deposited on polyethylene terephthalate (PET) substrate. ZnO nanorods are synthesized by thermal decomposition technique and Ag nanoparticles deposition is done by photo-deposition technique using UV light. X-ray diffraction studies reveal that the ZnO nanorods are of hexagonal wurtzite structure. Further, as-prepared samples are characterized by Scanning Electron Microscopy (SEM), Photoluminescence (PL) spectroscopy and UV-Vis spectroscopy. The surface plasmon resonance response of Ag/ZnO is found at 420 nm. The photocatalytic activities of the samples are evaluated by photocatalytic decolorization of methyl orange (MO) dye with UV irradiation. The degradation rate of MO increases with increase in irradiation time. The degradation of MO follows the first order kinetics. The photocatalytic activity of Ag/ZnO heterostructure is found to be more than that of ZnO nanorods. The PL intensity of ZnO nanorods is stronger than that of the Ag/ZnO heterostructure. The strong PL intensity indicates high recombination rate of photoinduced charge carriers which lowers the photocatalytic activity of ZnO nanorods. The charge carrier recombination is effectively suppressed by introducing Ag nanoparticles on the surface of the ZnO nanorods. This study demonstrates a strong relationship between PL intensity and photocatalytic activity.

Keywords: ZnO nanorods, Ag/ZnO heterostructure, Photo-deposition, Exciton-plasmon system, Photoluminescence, Photocatalysis.

1. Introduction
ZnO is a promising wide band gap semiconductor with direct band gap of 3.37 eV at room temperature and has a large exciton binding energy of 60 meV [1]. ZnO nanostructures have lots of applications in various fields such as varistors, electroluminescent displays, luminescence materials and sensors [2]. ZnO has a lot of importance in the field of photocatalysis. Tan et al reported that the incorporation of Ag on the surface of ZnO could improve the photocatalytic efficiency of ZnO upto a great extent [3]. Due to the large work function, the Ag nanoparticles can slow down the recombination of photogenerated electron-hole pairs. In addition, the surface plasmon resonance (SPR) of Ag nanoparticles can enhance the solar light absorption efficiency of the Ag/ZnO heterostructure.

Photoluminescence spectroscopy (PL) is a powerful technique to investigate the photophysical properties of semiconductor materials. Moreover, PL spectrum provides information about surface defects, oxygen vacancies, carrier capture efficiency etc. A higher PL intensity indicates higher recombination rate of photo-induced electron-hole pairs and vice-versa. Pronin et al reported strong relationship between PL intensity and photocatalytic efficiency [4]. Usually, photocatalyst with lower PL intensity exhibits higher photocatalytic efficiency. This is attributed to the lower recombination rate of photo-induced electron-hole pairs. The semiconductor photocatalysis is environment friendly and cost effective process. The main focus of this work is to study the photophysical and
photochemical properties of ZnO nanorods and Ag/ZnO heterostructure deposited on flexible polyethylene terephthalate (PET) substrate. An attempt has been made to increase the visible light absorption of ZnO through the incorporation of Ag nanoparticles in the Ag/ZnO heterostructure. This process might increase the photocatalytic activity of the Ag/ZnO metal-semiconductor system which is strongly related to the luminescence of the exciton-plasmon system.

2. Experimental section

2.1. Synthesis of ZnO nanorods
The ZnO nanorods are prepared on flexible PET substrate using thermal decomposition method. Ultrasonically cleaned PET substrates are placed inside a beaker to which a mixture of 50 ml each of 10 mM zinc-nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O] and 10 mM hexamethylene tetramine [C$_6$H$_{12}$N$_4$] from Merck are poured. The beaker is placed inside a water bath with constant heating at 90 °C for duration of 3 hours. The prepared film is then rinsed with distilled water and kept inside an oven at 90 °C to dry it up.

2.2. Synthesis of Ag/ZnO heterostructure
Ag/ZnO heterostructures are prepared using photo-deposition technique. The previously grown ZnO is kept in a Petri dish. A mixture of 6 ml ethylene glycol [HOCH$_2$CH$_2$OH] from Merck, 0.10 ml of 20 mM silver nitrate [AgNO$_3$] from Sigma-Aldrich, and 3 ml distilled water is poured over the ZnO nanorods. The Petri dish is kept under UV light irradiation for 1.5 hours. Four UV lamps of 11 W each (Philips) are used for this purpose. The prepared film is then rinsed with distilled water and dried in an oven at 90 °C.

2.3. Photocatalysis experiment
Methyl orange (MO) solution is used for the photocatalytic degradation using ZnO nanorods and Ag/ZnO heterostructure as catalysts. Required amount of MO powder from Merck is dissolved in distilled water to prepare 50 μM concentration of MO solution. 5 ml of MO solution is added to two beakers one containing ZnO nanorods and the other containing Ag/ZnO heterostructure. The beakers are kept under UV-Vis irradiation. This process is carried out for different irradiation time. The absorbance of the degraded solutions is taken for analysis. The degradation efficiency, $\eta$ is measured using the relation:

$$\eta = \frac{A_0 - A}{A_0} \times 100\%$$

where $A_0$ is the absorbance of the MO solution before illumination and $A$ is the absorbance of the MO solution after irradiation time $t$.

2.4. Characterization
X-ray diffraction (XRD) data are recorded using an X-PERT PRO X-ray diffractometer with a Cu $K_\alpha$ (1.5406 Å) radiation source at a tube voltage of 40 kV and a current of 35 mA. UV-Vis absorbance spectra are measured using UV-Vis spectrophotometer (CARY EL02086586). SEM images are taken using SIGMA-Zeiss Field Emission Scanning Electron Microscope (FE-SEM). The room temperature PL spectra are recorded using Eddinburg FSP920 spectrometer with xenon lamp as an excitation source. The excitation wavelength is set at 300 nm.

3. Results and discussion

3.1. X-ray diffraction studies
XRD patterns of ZnO nanorods and Ag/ZnO heterostructure deposited on PET substrate are shown in Figure 1. The diffraction peaks are indexed to hexagonal wurtzite ZnO (ICDD 36-1451). The Ag diffraction peak is indexed to face centred cubic (fcc) metallic Ag (ICDD 04-0783). XRD patterns
show that both the samples are crystalline in nature. No change of diffraction peaks is observed for ZnO after Ag deposition. The diffraction peaks for ZnO nanorods are found at 2θ values 31.66°, 34.31°, 36.12°, 47.50°, 56.46°, 62.84°, 66.34°, 67.88°, 69.10°, and 77.05° corresponding to the diffraction planes (100), (002), (101), (102), (110), (103), (200), (112), (201), and (201) respectively. The intensity of (100) peak is maximum which indicates most of the ZnO nanorods are oriented along $a$-axis. The intensity of Ag diffraction peak is very weak and it is seen at 2θ value 38.03° and the corresponding diffraction plane is (111).

The crystallite size of Ag nanoparticles is calculated using the Scherrer formula [6]

$$t = \frac{k\lambda}{\beta \cos \theta}$$

Here, $t$ is the crystallite size, $k$ is the Scherrer constant, $\lambda$ is the wavelength of X-ray, $\beta$ is the full width of the peak at half-maximum and $\theta$ is the half of the diffraction angle. The crystallite size of the Ag nanoparticle is found to be 18 nm.

### 3.2. FE-SEM studies

The crystallite size of Ag nanoparticles is calculated using the Scherrer formula [6]

$$t = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

Here, $t$ is the crystallite size, $k$ is the Scherrer constant, $\lambda$ is the wavelength of X-ray, $\beta$ is the full width of the peak at half-maximum and $\theta$ is the half of the diffraction angle. The crystallite size of the Ag nanoparticle is found to be 18 nm.

**Figure 1.** XRD patterns of (a) ZnO nanorods, (b) Ag/ZnO heterostructure.

**Figure 2.** FE-SEM images of (a) ZnO nanorods, (b) flower-like structure formed by ZnO nanorods, (c) Ag/ZnO heterostructure, and (d) higher magnification image of Ag/ZnO heterostructure.
In order to investigate the morphologies of the as prepared ZnO nanorods and Ag/ZnO heterostructure FE-SEM investigation is carried out. Figure 2(a) shows the FE-SEM image of the ZnO nanorods. The rods are oriented along different directions. The average length and diameter of the ZnO nanorods with well defined hexagonal facets is found to be 6 μm and the 700 nm respectively. The rod has tapered ends with diameter 500 nm. The flower like structure formed by the ZnO nanorods is shown in Figure 2(b). Figure 2(c) shows the SEM image of the Ag/ZnO heterostructure. Ag nanoparticles are seen on the surface of the nanorods. Self nucleated or isolated Ag nanoparticles are hardly seen. Ag nanoparticles are almost entirely covering the ZnO nanorods. Free areas on the ZnO nanorods are very less. A higher magnification image of Ag/ZnO heterostructure is shown in Figure 2(d). The average sizes of the Ag nanoparticles are 60 nm. Slight variations in the sizes of the Ag nanoparticles are observed.

3.3. UV-Vis spectroscopy studies
The absorption properties of ZnO nanorods and Ag/ZnO heterostructure are investigated with UV-vis spectroscopy in the wavelength range 200-800 nm. Figure 3 shows the absorption spectra for both ZnO nanorods and Ag/ZnO heterostructure. Both the samples show strong absorption in the UV range. A broad band centering at 420 nm is seen in the absorption spectra of Ag/ZnO heterostructure. This is the characteristic of surface plasmon resonance absorption of Ag nanoparticles. The optical band gap of ZnO nanorods is found to be 3.20 eV which is smaller than the band gap of bulk ZnO. The band gap narrowing of ZnO nanorods is attributed to the formation of oxygen vacancies [7].

![Figure 3. UV-Vis absorbance spectra of (a) ZnO nanorods, (b) Ag/ZnO heterostructure.](image)

3.4. Photoluminescence studies
Figure 4 shows the PL spectra of ZnO nanorods and Ag/ZnO heterostructure at an excitation wavelength of 300 nm. Figure 4(a) shows two emission peak centered at 391 nm and 447 nm. The former is attributed to the near band edge emission (NBE) and the latter is defined as the deep level emission (DLE) [8,9]. The NBE originates due to the recombination of free excitons formed when excited by radiation of energy greater or equal to the band gap energy. The DLE is a result of several intrinsic defects such as zinc interstitials (Zn\(_i\)), interstitial oxygen (O\(_i\)), zinc vacancies (V\(_{Zn}\)), oxygen vacancies (V\(_O\)), etc [10,11]. The DLE is mainly attributed to electron transition from shallow donor level formed by Zn\(_i\) to the top of valance band (V\(_{Zn}\)) [12]. Several defects are responsible for the high intense long range green emission from 500-700 nm.
The combination of O\textsubscript{i} and V\textsubscript{Zn} emissions results in the red band forming at 773 nm \[13\]. The intensity of NBE, DLE and the green emission decreases for Ag/ZnO heterostructure (Figure 4(b)) with no change in peak position. This accounts for the interaction between excitons of ZnO and surface plasmons of Ag nanoparticles. The recombination rate of electrons and holes decreases which results in low PL intensity \[14\]. The Ag nanoparticles attached over ZnO nanorods act as traps for photogenerated electrons and quench the PL emission. As the ZnO nanorods and Ag nanoparticles are in direct contact, electron transfer takes place between the energy levels of ZnO and Ag.

3.5. Photocatalytic activity studies

The photocatalytic performance of Ag/ZnO heterostructure is superior to ZnO nanorods. Figure 5 shows the absorbance spectra of MO solution using ZnO nanorods and Ag/ZnO heterostructure as catalyst for 8 hours of irradiation time. The photodegradation efficiency is 37.17% for ZnO as catalyst and 40.46% for Ag/ZnO as catalyst for 8 hours UV-Vis irradiation.

The degradation of MO follows first order kinetics. Therefore the rate equation is:
Here \( k' \) is the first order rate constant, \( C_0 \) is the initial concentration of MO solution, \( C \) is the concentration of the MO solution after irradiation and \( t \) is the irradiation time. The \( (C/C_0) \) versus \( t \) curves for MO solution with ZnO nanorods and Ag/ZnO heterostructure are shown in Figure 6. The degradation rate constants for ZnO nanorods and Ag/ZnO heterostructure are found to be 0.0007 min\(^{-1}\) and 0.0009 min\(^{-1}\) respectively.

Electrons and holes are produced as a result of UV irradiation in ZnO. The photogenerated electrons react with dissolved oxygen to form superoxide anion radicals (\( \cdot O_2^- \)) and holes react with hydroxide ions (OH\(^-\)) to produce hydroxyl radicals (\( \cdot OH \)) [9]. The presence of Ag nanoparticles acts as a sink for electrons in the Conduction Band (CB) of ZnO and decreases their recombination rate with the holes allowing the photocatalytic process to continue further. These reactions result in decolorization of the MO solution. The reactions as proposed by Zheng et al [14] are listed below:

\[
\begin{align*}
Ag & \rightarrow Ag^+ + e^- \\
e^- + O_2 & \rightarrow \cdot O_2^- \\
ZnO + h\nu & \rightarrow e^-_{cb} + h^+_{vb} \\
e^-_{cb} + Ag^+ & \rightarrow Ag \\
h^+_{vb} + OH^- & \rightarrow \cdot OH
\end{align*}
\]

PL studies suggest the decrease in intensity with the incorporation of Ag nanoparticles. Moreover, photocatalytic studies confirm the increase in photocatalytic activity due to the presence of Ag nanoparticles. These two facts describe an inherent relationship between PL and photocatalytic activity. The lower the PL intensity, the greater is the photocatalytic activity and vice-versa.

**Figure 6.** Plot of normalized concentration of MO solution versus irradiation time with (a) ZnO nanorods and (b) Ag/ZnO heterostructure as catalyst.
4. Conclusions
ZnO nanorods are prepared by thermal decomposition method and Ag deposition is done by photo-deposition technique. XRD studies show that the as prepared ZnO nanorods are of hexagonal wurtzite structure. Ag diffraction peak in the XRD pattern of Ag/ZnO heterostructure is very weak and this can be indexed to face centered cubic (fcc) metallic Ag. FE-SEM studies reveal that the ZnO nanorods are randomly aligned and this forms flower-like structures. In the Ag/ZnO heterostructure Ag nanoparticles are seen on the surface of the ZnO nanorods. The band gap narrowing of ZnO nanorods is attributed to the oxygen vacancies. Quenching in the PL emission has been observed in the Ag/ZnO heterostructure. This could be attributed to the exciton plasmon interaction in the Ag/ZnO heterostructure. The photocatalytic activity of the Ag/ZnO heterostructure has been found to be better than that of ZnO nanorods. A strong relationship exists between PL intensity and photocatalytic activity. When PL intensity is weak, the photocatalytic efficiency is high and vice versa. Again the degradation rate of MO increases with increase in irradiation time.

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