

## Study on the Photocatalytic Degradation of Methyl Orange in Water Using Ag Doped ZnO Nanowires Under UV Light Irradiation

Seema Gupta<sup>1</sup>, Anjali Oudhia<sup>2</sup>, Neelam Shukla<sup>3</sup>

<sup>1,2</sup>(Govt. Nagarjun PG. Autonomous College, Raipur, Chhattisgarh, India.)

<sup>3</sup>(Govt. V. Y. T. PG. Autonomous College, Durg, Chhattisgarh, India)

**Abstract:** In this work, a high-performance photocatalyst Ag: ZnO nanowires (Ag: ZnO NWs) was synthesized via a chemical bath deposition method for the photodegradation of organic dye under UV light irradiation. The structure, morphology, and photocatalytic activity of as synthesized sample were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-visible absorption spectroscopy (UV-vis spectrum). The XRD result showed that this catalyst was composed of metallic Ag and ZnO. The photocatalytic activity of the as synthesized samples were evaluated by the degradation of methyl orange (MO) in aqueous solution under UV light irradiation. Ag: ZnO NWs show better crystallinity, high specific area, and an increased area of contact. Hence they are better photocatalysts than undoped ZnO NWs. The Ag: ZnO NWs has influenced the photocatalytic activity of nanocrystalline photocatalysts because of its enhanced optical and electronic properties. A suitable mechanism was proposed to explain better photocatalytic activity in Ag: ZnO NWs as compared to ZnO NWs under UV irradiation, which shows that presence of Ag facilitates conduction band electrons for this reaction. The photocatalytic degradation efficiency (PDF) is 97% of Ag: ZnO NWs in the 60 min whereas PDF of ZnO NWs is 77% at the same time.

**Keywords:** Photocatalyst, Ag: ZnO NWs, photodegradation, crystallinity, water treatment.

Date of Submission: 29-11-2017

Date of acceptance: 11-12-2017

### I. Introduction

Removal of various organic pollutants from wastewaters is of a great importance nowadays, because these compounds usually are toxic and carcinogenic, posing a serious hazard to aquatic living organism [1, 2]. Physical methods such as adsorption on various adsorbents, ultra filtration and coagulation only succeed in transferring the pollutants from water to another phase, thus creating secondary pollution [3]. Heterogeneous photocatalysis process has been established as an efficient technique for the mineralization of toxic organic compounds, bacteria elimination, self-cleaning, etc. and thus, constitutes a potential process for environmental remediation. This is achieved by the strong oxidative ability of the photocatalyst, due to the ease of OH• radical formation [4,6]. Semiconductor materials such TiO<sub>2</sub> and ZnO micro/nanoparticles are the most promising materials for mediation and destruction of organic pollutants under UV-irradiation [7]. Both metal oxides exhibit very similar band gaps (ZnO, 3.37 eV and TiO<sub>2</sub>, 3.2 eV) and their physicochemical properties are tunable by controlling the structure and surface area of the particles [8, 10]. The interest in ZnO is because it is a low cost alternative photocatalyst with photo degradation capacity comparable and in some cases better than that of titanium dioxide (TiO<sub>2</sub>), which is one of the most efficient photocatalyst for degradation of organics in aqueous solutions [18]. Several reports refer to the synthesis and properties of ZnO nanoparticles, powders and colloids giving very high photocatalytic efficiencies and good stability [11, 12]. But for water treatment applications, thin films are preferred to avoid the separation of the catalyst after the detoxification process. Different developments has been carried out to increase the surface area of these photocatalytic particles [13, 14]. Decreasing particle size is one effective way to increase the surface area of photocatalyst. However the agglomeration of such extremely nano-sized particles and difficulty of their recovery from the reaction system after photocatalysis hinders their application in this field [15,17]. Furthermore, the photo excited electron and holes can also recombine to reduce photocatalytic activity of pristine semiconductor particles. The Ag nanoparticles have been mostly extensively investigated as the important candidate for wide band gap material to absorb light. Ag nanoparticles can offer high performance absorption in visible light without using any highly toxic elements. The strategy of doping silver (Ag) NPs on the surface of ZnO NWs could further enhance the photocatalytic activity by preventing the fast electron-hole recombination process [19, 21]. Moreover, doping of Ag NPs might process good antibacterial property even in the absence of UV-light. Ag:ZnO is now an exciting area in research for developing photocatalytic applications [22]. In this present work, a simple and effective strategy of

simultaneous crystal growth of Ag: ZnO particles from the CBD method is reported. The variation of semiconductors with metals has attracted major attention especially in heterogeneous photo catalysis. Although, there are many reports about the effect of Ag NPs on photochemical properties of semiconductors.

In this paper, we report a systematic comparative study on the effect of silver doping in ZnO NWs and undoped ZnO NWs and consequent photocatalytic activity due to the presence of silver, studied by characterization of the materials and optimization of the reaction conditions.

## II. Materials and Methods

### 2.1 Materials

AR grade Zinc acetate dihydrate, Zinc Nitrate, Silver Nitrate, and Ethanol and were used without further purification. The dye used for the photocatalytic study (methyl orange) was of AR grade and used without further purification.

### 2.2 Preparation of ZnO NWs on glass substrate

The ZnO seeded substrates were kept in a chemical bath at 95°C prepared by dissolving 0.743 gm Zinc nitrate and 0.3504 gm hexamethylenetetramine (HMTA) in 100ml double distilled water. After 2.5 hrs the bath was replenished by fresh source solution and the substrates were kept in the bath for another 2.5hrs. This double bath deposition helped in the growth of densely populated NWs on ZnO seed layer substrates.

### 2.3 Preparation of Ag: ZnO NWs on glass substrate

The ZnO seeded layer substrates were kept in a chemical bath at 95°C prepared by dissolving 0.722 gm Zinc Nitrate, 0.350gm hexamethylenetetramine (HMTA) and 0.02 gm Silver Nitrate in 50ml double distilled water. After 2.5 hrs the bath was replenished by fresh source solution and the substrates were kept in the bath for another 2.5hrs.

## III. Result and Discussion

### 3.1 Characterization

Fig. 1 shows the XRD pattern of the undoped ZnO NWs and Ag: ZnO NWs. The XRD pattern indicates that apart from ZnO and Ag, no other reaction phases are present. All the samples were crystalline and were of hexagonal wurtzite phase. However, the Ag doped samples indicate some additional diffraction peaks associated with the face-centered-cubic (fcc) phase of metallic Ag (JCPDS card no. 04-0783). The appearance of Ag peaks in the peaks in the diffraction pattern clearly indicates the formation of crystalline silver clusters in the nanoparticles [23]. A decrease in the peak position value is generally observed when a doping element with a larger ionic radius than  $Zn^{2+}$  is replaced at the substitution sites of the ZnO crystal lattice.  $Ag^+$  ion (1.22Å) has a higher ionic size than a  $Zn^{2+}$  ion (0.74Å), probably substituting  $Zn^{2+}$  ions, and the appearance of Ag peaks in the diffraction patterns clearly indicates the formation of crystalline silver clusters in the nanoparticles. Therefore, the increment in the XRD peak position in this case suggests that the Ag ion has occupied the interstitial site of ZnO, which is consistent with the reported data by Ahn et al. [24]. This is possible, since Ag acts as an amphoteric dopant, having a tendency to occupy both substitution Zn and interstitial sites. However, it has been predicated theoretically that the incorporation of  $Ag^+$  ions at the interstitial sites is a difficult proposition owing to their high formation energy, ~ 3eV [25]. Moreover, the large size difference between  $Zn^{2+}$  and  $Ag^+$  ions limits the solubility of Ag in ZnO lattice [24]. Fig 1b) Shows the characteristic wurtzite peaks of Ag: ZnO NWs corresponding to (101), (002), (100), (111), (200) and (102) etc. planes for as-prepared Ag: ZnO NWs Fig. 1a) shows the XRD patterns of the nanowires in range  $2\theta = 15-80^\circ$ . All detectable peaks are from the ZnO wurtzite structure. There are no other peaks related to Ag, or other mixed compounds. ZnO NWs should be assigned to the (100), (002), (101), and (102) crystal planes of ZnO NWs with wurtzite crystal structures. An average grain size of undoped ZnO NWs and Ag: ZnO NWs are obtainable using the Scherrer's formula for crystallite size broadening of diffraction peaks:

$$D = 0.9\lambda/\beta \cos \theta$$

Where  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg diffraction angle and  $\beta$  is the full width at half-maximum intensity (FWHM) of the diffraction peak [25, 26]. Using the FWHM of (101) diffraction peaks, crystallite size of 30.26 nm was obtained for Ag: ZnO NWs and 35 nm for ZnO NWs.

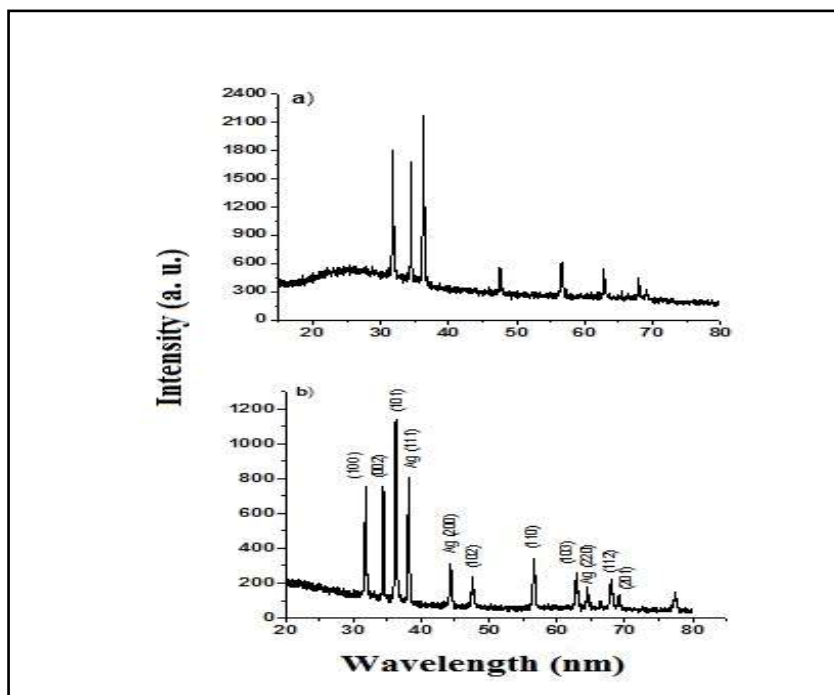


Fig.1 XRD pattern of a) undoped ZnO NWs and b) Ag:ZnO NWs

Fig.2 shows the SEM images of the undoped and Ag doped ZnO NWs, respectively. The orientation of NWs growth is, preferentially, in the direction of the c-axis ([0001]). Fig. 2a) shows the dense undoped ZnO NWs. Fig. 2b) shows that Ag NPs sitting on the top of the ZnO NWs. The flower like ZnO NWs emerging out from single base can be observed. This striking change in morphology of Ag: ZnO NWs introduces many fold increase in the specific area as compared to the undoped ZnO NWs. The Ag: ZnO NWs possess extremely large surface-to-volume ratio as compared to a catalyst deposition on a flat surface [27].

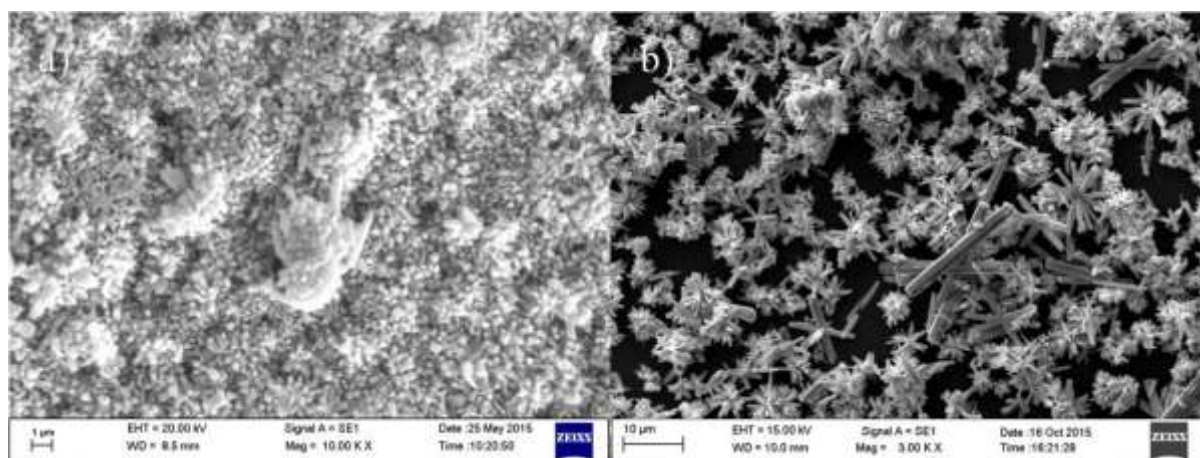


Fig. 2 Scanningelectronmicroscopy(SEM) images of undoped ZnO NWsand Ag:ZnO NWs grown by the aqueous chemical bath deposition method.

### 3.2 Photocatalytic activity test

The photocatalytic activity of the ZnO films was evaluated by studying the photo degradation kinetics of MO under UV light irradiation in a photocatalytic reactor. The thin films with various layers deposited on glass substrates were placed in a photocatalytic reactor. The photo-catalytic experiments were carried out using an indigenously made photo-reactor (100cm × 100 cm × 100 cm), and using a 340 W mercury lamp for UV irradiation. The distance between the solution surface and the light source was about 5cm. In a typical experiment, 100 mL of aqueous Methyl Orange (MO) were placed in an outer jacket, the photocatalyst film was also placed in MO solution and the suspension was stirred for 30 min in the dark, at room temperature, to ensure the establishment of the adsorption/desorption equilibrium. The photocatalytic reactor temperature was 25°C when the UV lamp was turned on. At fixed intervals of time, 3mL of the sample were withdrawn, centrifuged,

and the supernatant transferred into a spectrophotometer cell for measurement of the absorbance of MO. Absorbance measurements were also recorded in the range of 300-700nm, using a UV-Vis spectrophotometer. Since the contaminant molecules need to be adsorbed on the photocatalytic surface before the reactions take place, the surface area plays a significant role in the photocatalytic activity. Although NPs offer a large surface area, they have mostly been used in water suspensions, which limit their practical use due to difficulties in their separation and recovery. Moreover, additional equipment is needed for catalyst NPs separation. Photocatalyst supported on a steady substrate can eliminate this issue. One dimensional nanostructures, such as NWs grown on a substrate, offer enhanced photocatalytic efficiency due to their extremely large surface-to-volume ratio as compared to a catalyst deposition on a flat surface [28]. Silver can trap the photo generated electrons from the semiconductor and allow the holes to form hydroxyl radicals which results in the degradation reaction of organic species present. The increased photocatalytic activity of Ag: ZnO is reportedly due to the change in the surface properties such as oxygen vacancies and crystal defects [29].

### 3.3 Photocatalytic mechanism

Fig.1 illustrates the process of photocatalysis. When photons with energies greater than the band gap energy of the photocatalyst are absorbed, the valence band (VB) electrons are excited to the conduction band to facilitate a number of possible photoreactions. The photocatalytic surface with sufficient photo energy leads to the formation of a positive hole (h+) in the valence band and an electron (e-) in the conduction band (CB). The positive hole could either oxidize organic contaminants directly or produce very reactive hydroxyl radicals (OH•). The hydroxyl radicals (OH•) act as the primary oxidants in the photocatalytic system [27], which oxidize the organics. The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst. Heterogeneous photocatalysis using semi-conductors is an effective method to destroy a wide range of organic pollutants at ambient temperatures and pressures [25, 26].

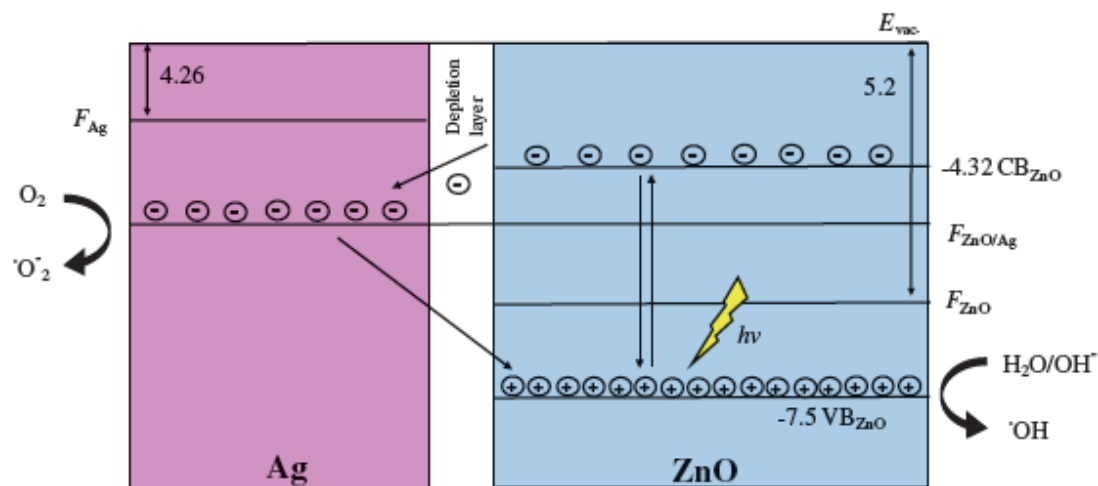
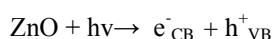


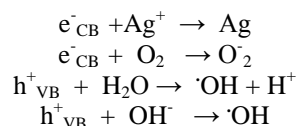
Fig.3 Schematic mechanism of photocatalysis process onAg:ZnO nanoparticles under UV irradiation.

The mechanism for the photo degradation of MO on the Ag:ZnO photocatalyst is represented in a schematic diagram in fig.3. ZnO and Ag have the work function of 5.2 and 4.26 eV, respectively (lin et al, 2009). The Fermi energy level of Ag ( $F_{Ag}$ ) is higher than that of ZnO ( $F_{ZnO}$ ) because of the larger work function of ZnO. This leads to the transfer of electrons from Fermi level of Ag ( $F_{Ag}$ ) to Fermi level of ZnO ( $F_{ZnO}$ ), until the two levels attain equilibrium and form the new Fermi energy level ( $F_{ZnO/Ag}$ ) (saravanan et al, 2013). The process can be expressed as:



Upon UV irradiation, electrons are excited from the valence band of ZnO is higher in energy than the new equilibrium Fermi energy level ( $F_{ZnO/Ag}$ ) of Ag:ZnO, the photoexcited electrons on the conduction band are transferred from ZnO react with water and hydroxyl groups to form hydroxyl radical, which lead to the photocatalytical oxidation of the dye. At the same time, the photogenerated electron electrons react with  $O_2$  to form the active oxygen species, which also participate in the photocatalytic oxidation of the dye. This process can be expressed as follows:





Finally, photocatalytic degradation efficiency (PDE) of MO solutions was calculated with the following formula:

$$PDE(\%) = \frac{A_0 - A}{A_0} \times 100\% \quad \text{----- (1)}$$

Where,  $A_0$  and  $A$  are the UV-Vis absorption of MO solution and MO solutions in suspension after time  $t$ .

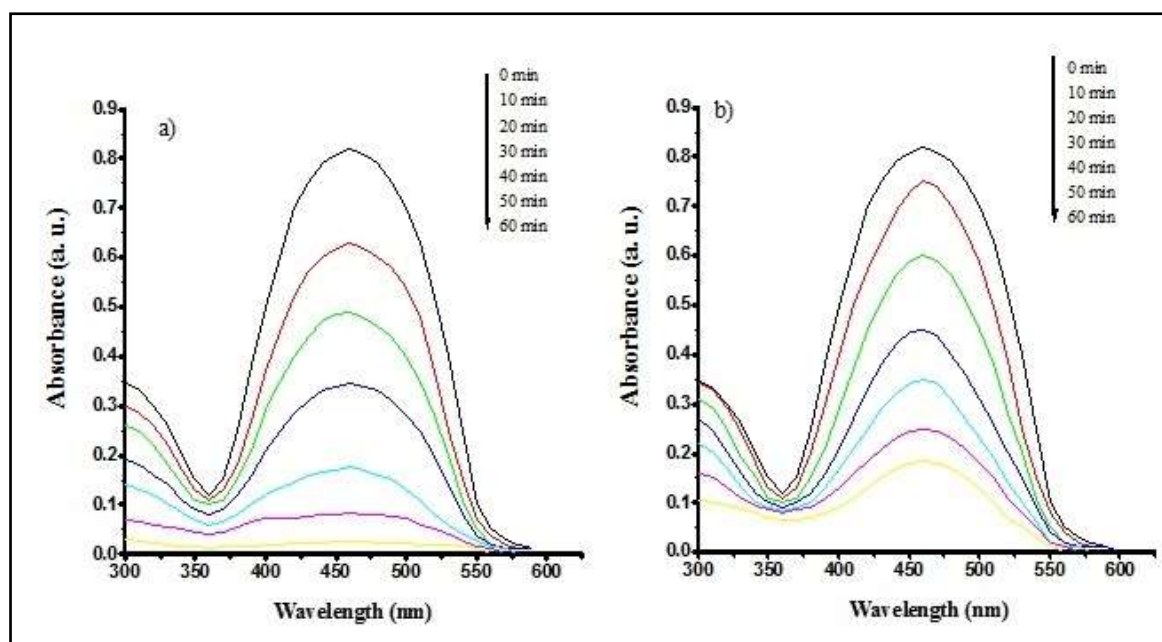


Fig.4 UV-vis spectra in various times for degradation of MO with (a) undoped ZnO NWs and (b) Ag: ZnO NWs.

To evaluate activity of the as prepared samples, degradation of MO under UV light irradiation was considered. Fig. 4 shows the plots of absorbance versus wavelength for the degradation reaction on undoped ZnO NWs and Ag: ZnO NWs. It is evident that MO has some small absorption peaks in visible range and a large absorption peak in the UV range. Under the light irradiation, intensity of the absorption peaks gradually decreases without any changes in position of the peaks. Fig. 3 shows a typical photocatalytic degradation process of MO using Ag:ZnO NWs under UV light irradiation. Ag: ZnO NWs shows the highest photocatalytic activity and more than 97% of MO molecule was decomposed in just 60 min. It can be observed that the maximum absorbance at 470 nm.

#### IV. Conclusion

Highly active Ag: ZnO NWs and undoped ZnO NWs photocatalysts were prepared through a chemical bath deposition route, which has shown that photocatalytic degradation of MO can be readily performed in the presence of Ag doped ZnO NWs in an aqueous suspension system, leading to the complete mineralization of the MO. The required time for an entire degradation of MO using Ag doped catalyst is less than 60 min, much shorter than the corresponding value by other catalysts (ZnO NWs). The PDF is 97% of Ag: ZnO NWs in the 60 min whereas PDF of ZnO NWs is 77% at the same time. The material synthesized shown to have a high crystal quality. The mechanism of Photocatalytic activity shows that the presence of silver facilitates the CB electron for enhancing the photocatalytic activity. This trapping of electrons in these materials, could be extend to the development of a photocatalyst which is applicable in both environmental purification and energy production processes.

#### Acknowledgments

The authors acknowledge CCOST, Chhattisgarh for funding this work through 1219/CCOST/MRP/2014 dt.24/09/2014.



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IOSR Journal of Applied Physics (IOSR-JAP) (IOSR-JAP) is UGC approved Journal with SI. No. 5010, Journal no. 49054.

Seema Gupta "Study on the Photocatalytic Degradation of Methyl Orange in Water Using Ag Doped ZnO Nanowires Under UV Light Irradiation." *IOSR Journal of Applied Physics (IOSR-JAP)*, vol. 9, no.6, 2017, pp. 28-33.