

# SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF Cu/Ag DOPED ZnO NANOPARTICLES USING LEDs ILLUMINATIONS

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## ABSTRACT

Nanocrystals of bare and copper doped zinc oxide (Cu/Ag-ZnO) were synthesized by precipitation-decomposition method. Crystalline phases and optical absorption of photo catalyst were determined by Power X-ray diffraction and UV-visible spectrophotometer. The FESEM morphology showed hexagonal wurtzite shape as conformed ZnO Nps. Power X-ray analyses reveals that Cu/Ag doped ZnO crystallizes in hexagonal wurtzite structure. The incorporation of dopant ions in the place of  $Zn^{2+}$  provoked an increase in the size of nanocrystals as compared to undoped or bare ZnO Nps. Optical spectra indicates red shift in the absorption band edge upon Cu/Ag doping ZnO Nps. The band gap decreases from 3.2 eV to 2.92 eV with Cu/Ag doping with ZnO Nps. The photocatalytic activities of the Cu/Ag-ZnO Nps investigated by degradation of methylene blue under LEDs illuminations. The photo-degradation study was find out main reactive species responsible for the degradation of MB dyes.

**Keywords:** Cu and Ag doped ZnO, Methylene blue.

## 1. INTRODUCTION

Photocatalysis could be a promising technique for finding several current environmental problems [1,2]. Semiconductor absorbents offer the potential for elimination of organic pollutants [3]. Semiconductor photocatalysts such as zinc oxide and titanium oxide have been applied to degradation of contaminants in waste water and air [4,5]. For photocatalysis, ZnO has also been considered as a suitable alternative for  $TiO_2$  due to The band-gap energy of ZnO is similar to that of  $TiO_2$ [6]. The photocatalytic activity of nanostructured ZnO is expected to be enhanced because of their

increased surface area [7-11]. The doping of metal ions in ZnO nanostructures will cause effects like sweetening in visible radiation and dominant concentration of surface defects. The doping of Cu and Ag in ZnO is expected to modify absorption, and other physical or chemical properties of ZnO. Recently, simultaneous doping of two kinds of atoms (co-doping) into semiconductor materials has attracted considerable interest, as it could result in a higher photocatalytic activity and special characteristics compared with single element doping into semiconductor oxides. Therefore, in our study, Cu doped ZnO nps, Ag doped ZnO nps and Cu, Ag-codoped ZnO nanostructures were synthesized through the precipitation decomposition method and their photocatalytic activities with completely different doping were evaluated for the degradation of MB.

## 2. Experimental

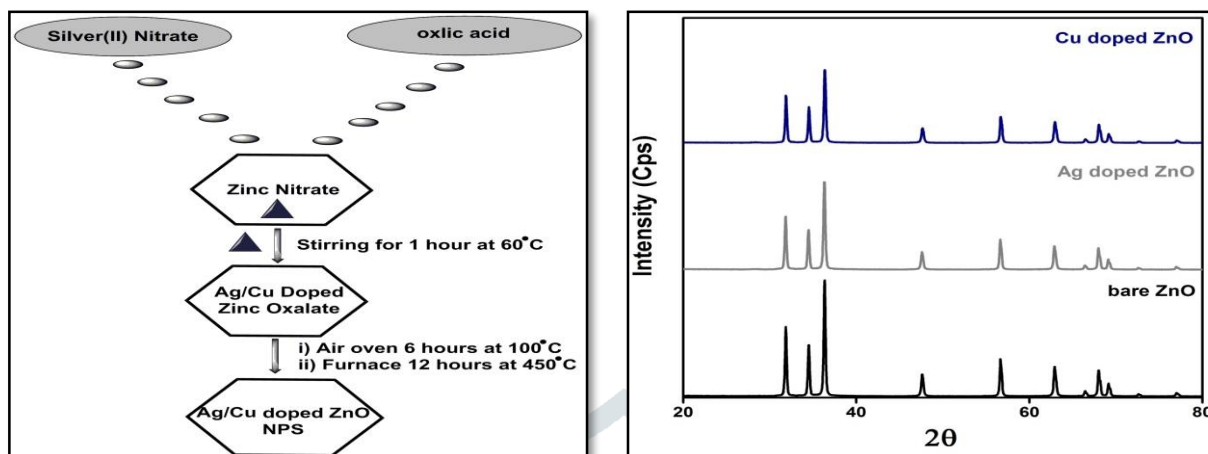
### 2.1. Materials and Methods

All of the Chemicals used in this work were analytical grade reagents and used without further purification. Zinc nitrate, silver nitrate, copper nitrate were purchased from Merck company. Deionized water was used to prepare all solutions. The samples were characterized by X-ray powder diffraction (XRD) using PANalytical X' per PRO X-ray diffractometer with Cu K $\alpha$  radiation. The particle morphologies of the ZnO nano particles a JEOL JSM-6701F scanning electron microscopy (SEM). Optical spectra were prepared via a Shimadzu (2450) spectrophotometer. Photodegradation of dye using LEDs illuminations experiments were early discussed [11].

### 2.2 Preparation of Cu/Ag doped and bare ZnO Nanoparticles.

A Precipitation-decomposition method to prepare catalyst (Scheme-I). A 100 mL of zinc nitrate hexahydrate (0.8 M) and 100 mL of oxalic acid (1.2 M) in triple distilled water used to homogenous was boiled separately. Both are 5 mL of AgNO<sub>3</sub> (4 % Ag) solution or 5 mL of Cu(NO<sub>3</sub>)<sub>3</sub> (4 % Cu) solution added slowly one by one with constant stirring of zinc nitrate bulk solution were heated for 1 h at 60–70 °C. Further adding of oxalic acid into bulk solution. Finally precipitation of zinc-Ag oxalate occurred when the solution was cooled to room temperature. The zinc-Ag oxalate powder washed with triple distilled water and dried at 100 °C for 6 h. The Zinc-Ag oxalate powers were calcinated at 10 °C per mints in a muffle

furnace reach the decomposition (450 °C) temperature. The ZnO–Ag catalyst was collected and used for further analysis.



Scheme-1 Preparation of bare and Cu/Ag doped ZnO Nanoparticles. Fig. 1 XRD pattern of bare and doped ZnO Nanoparticles.

### 3. RESULTS AND DISCUSSION

#### 3.1 The X-ray powder diffraction

Fig. 2a shows the XRD pattern of bare and doped ZnO nanoparticles. It can be seen that all these peaks are in good agreement with hexagonal (wurtzite) ZnO (JCPDS Card, No. 36-1451)

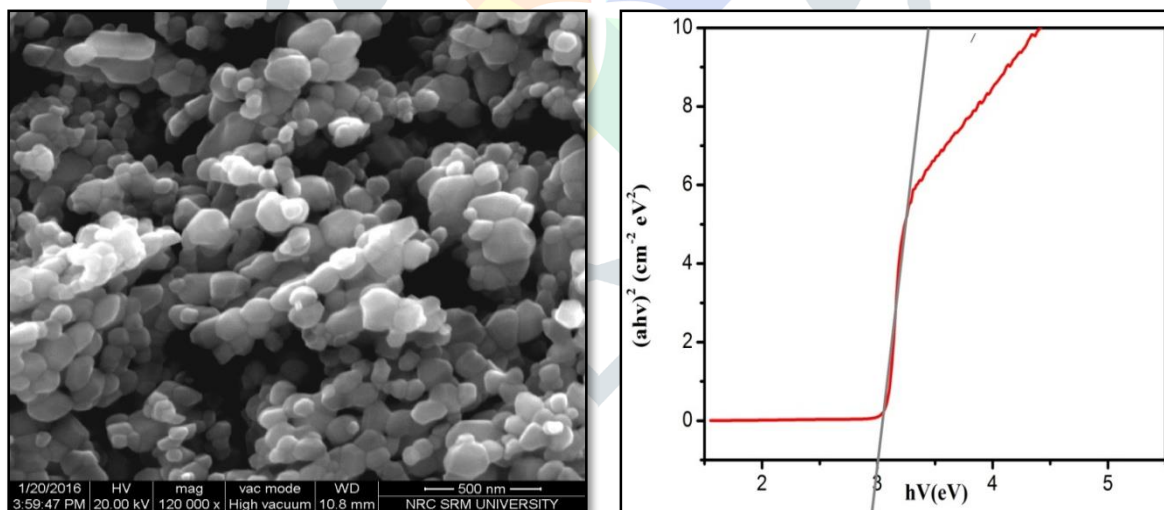


Fig. 2a SEM Image of Co doped ZnO Nanoparticles, Fig. 2b band gap of Ag doped ZnO Nanoparticles

#### 3.2 Morphological characterizations

The morphology of the Ag doped ZnO particle was examined from SEM images, as shown in Fig. 2b. It was found that all synthesized ZnO nanoparticles were quite uniform in size.

#### 3.3. Optical properties of catalyst

The Diffuse reflectance spectra (DRS) of the synthesized ZnO nanorods and Cu-doped ZnO, Ag-doped ZnO Nanoparticles. The spectrum reveals a characteristic absorption peak of ZnO at wavelength of 368, which can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band [11].

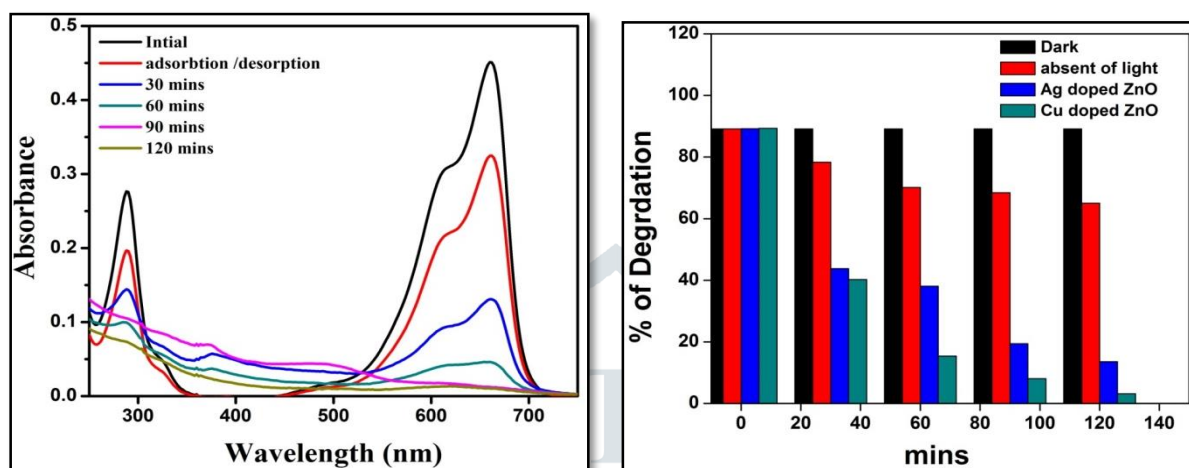


Fig 3. Photodegradation of methylene blue with LEDs light illuminations and different catalysts

### 3.4. Photocatalytic degradation of methylene blue

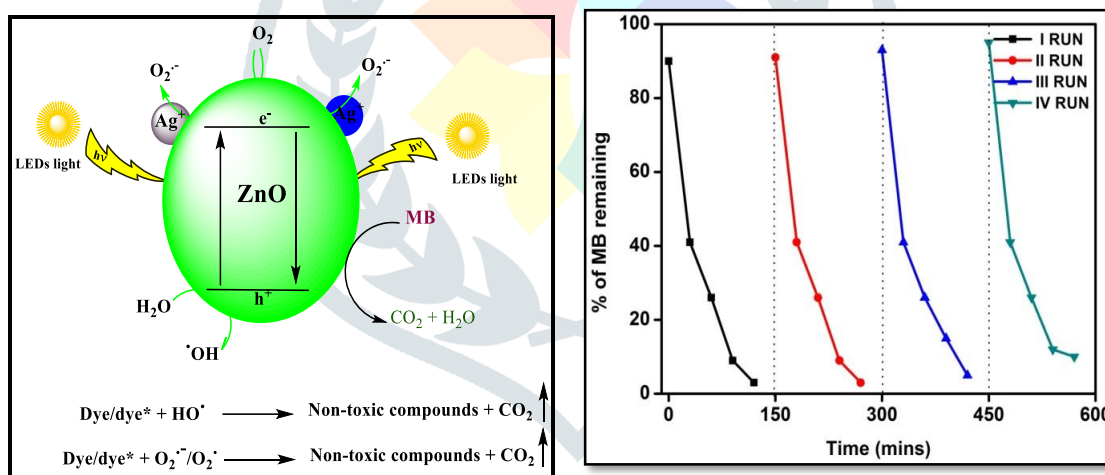


Fig.4 Mechanism of photodegradation of MB in present of Ag doped ZnO nps and catalyst reusable.

The photocatalytic activities of as-synthesized four kinds of catalysts were evaluated by the degradation of organic dyes methylene blue in aqueous solution under LEDs light irradiation. The ZnO nps and Cu-doped ZnO, Ag-doped ZnO and Cu,Ag-codoped ZnO nps with a high specific surface area, were used as photocatalysts for the decomposition of methylene blue by the superoxides and/or hydroxyl radicals formed at their interface. The characteristic absorption of MB at 664 nm was chosen to monitor the photocatalytic degradation process. Fig. 3 and 4 shows a typical photocatalytic degradation process of MB (initial

concentration: 10 mg/l, 50 ml) using ZnO nps and Cu-doped ZnO, Ag-doped ZnO nps (0.05 g) under visible light irradiation.

#### 4. CONCLUSION

A precipitation–thermal decomposition method for prepared of Ag/Cu–ZnO photocatalyst. The SEM images reveal the presence of the hexagonal wurtzite structure of ZnO. The presence of Ag/Cu increases the absorption of ZnO to the entire visible region. The Ag doped ZnO is found to be more efficient than Cu–ZnO, bare ZnO for degradation of MB under LEDs at neutral pH. This catalyst was found to be reusable.

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