

Effect of Silver Doping on Structural and Photocatalytic Circumstances of ZnO Nanoparticles

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Abstract

This article describes the synthesis of ZnO nanoparticles (Nps) using the co-precipitation method and then calcinated at 500oC for 2 h. The photo activity of ZnO nanoparticles was examined in photo decolorization of methyl green dye under artificial UV-A light. This prepared photocatalyst (ZnO Np) was modified his surface by 2% Ag doped using the photo deposition method under inert gas for 3h. The characterization of undoped and 2% Ag doped ZnO Nps were estimated by Fourier-transform infrared spectroscopy (FT-IR), X-ray Diffraction (XRD), and Atomic force microscopy (AFM). In FT-IR analysis, the new peaks occurred around 624-778 cm⁻¹ confirmed the Ag really is doped on prepared ZnO Np. Based on data from XRD, the mean crystal size was reduced with doped the 2% Ag. The AFM images for the prepared photocatalysts ensure that the shapes of all samples are semi-spherical with nanometer size. Series of kinetics experiments were performed for the photocatalytic decolourization of methyl green dye using undoped and 2% Ag doped ZnO nanoparticle and found to be pseudo-first-order kinetics.

Introduction

Zinc oxide (ZnO) is one of the important inorganic amphoteric oxides, with pHZPC of approximately 9.0[1, 2], and a boundary between an ionic material and a semiconductor [3, 4]. This oxide is deemed an n-type metal oxide semiconductor, operated at near-ultraviolet and visible spectra regions with direct band gap 3.436 eV at 0 K and (3.37± 0.01) eV at room temperature [5-7]. ZnO is also known as a II-VI semiconductor, which has various forms beyond to lie of zinc atom and the oxygen atom in the 2nd and 6th groups of the periodic table [8] such as cubic zincblende, cubic rock salt, and hexagonal wurtzite [7]. On the other hand, it has been prepared as a nanomaterial in different dimensions such as one dimensional (1D), two dimensional (2D), and three dimensional (3D) structures over the past few years, there are varying procedures for preparing them as physical methods (such as Laser ablation and Chemical vapor deposition(CVD)), chemical methods (such as Precipitation, sol-gel and hydrothermal), and bio methods (such as a green method in employing the extractions of plants and Microbes mediated like bacteria, viruses, and fungi) [9-15]. ZnO bulk or nanomaterial is used in various fields, so, they employed as a photocatalyst to degrade the organic compounds in water [16,17], protection of skin from solar irradiation[18, 19], used in the manufacture of active solar cell [20-22], employed as gas, chemical and biological sensor[23,24], employed in manufactured of cosmetic creams[25]. This research focused on synthesized of ZnO nanoparticles by co-precipitation method, and then changed its surface with doped 2 % of Ag under purged N₂, in order to reduce the recombination process using the photo deposition; under illumination with UV-A light (HPML-400 watt), which have a light intensity equal to 6 x 10⁻⁵ Enstine s⁻¹, that measured by using the chemical actinometry [26].

The employing of FT-IR, XRD, and AFM is used to investigate the properties of these prepared photocatalysts. The efficiency of decolourization of methyl green dye was achieved under the optimum conditions. A reasonable mechanism for dye decolorizing was suggested.

Experimental Work

Chemicals

The used chemicals were employed without any treatment in this work. Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), Sodium hydroxide (NaOH), Absolute ethanol were supplied by BDH -UK. Methyl green dye ($C_{27}H_{35}Cl_2N_3 \cdot ZnCl_2$) was purchased from GEORGE T. GURRL TD -UK and Silver nitrate ($AgNO_3$) was Purchased from AppliChem GmbH-Germany. The chemical structure of Methyl green dye is depicted in Figure 1.

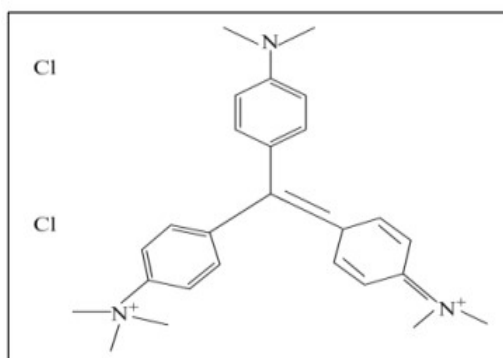


Figure 1. The chemical structure of Methyl green dye.

Synthesis of ZnO nanoparticles

The ZnO-NPs were prepared directly by the co-precipitation method from two aqueous solutions NaOH and $ZnSO_4 \cdot 7H_2O$ with molar ratio (4:1) [27, 28]. The precursor solution was prepared by completely dissolving ($ZnSO_4 \cdot 7H_2O$) in distilled water. The precipitation agent was also prepared from dissolved NaOH in distilled water. 100 mL of NaOH solution added slowly as drop by drop to the precursor solution with vigorous stirring for 20 min at 25 °C. A solution with pH=7 containing a white precipitate can be observed as shown in Figure 2.



Figure 2 Real images for preparing ZnO in the co-precipitation method.

Then the white precipitate was collected, filtered, washed several times with distilled water, and then with absolute ethanol to ensure removal of all remaining sulfate particles. The white wet precipitate was dried in an oven at 86 °C and then kept overnight in a desiccator. The resulting powder was calcined at 500°C for 2h. The preparation of ZnO-Nps can be explained by the following equations,





Synthesis of Ag doped ZnO nanoparticles

After calcined, the modification of the ZnO NPs surface is necessary to depress the recombination by 2% Ag doped using the photo deposition method: under purged N₂ [29]. In a closed Pyrex photoreactor, exactly 2 g of ZnO NPs was dispersed in 20 mL from absolute ethanol and then mixed with suitable volume from the stock solution (1% Ag NO₃) under purged nitrogen gas. This solution was illuminated with UV-A light for 3h. The leaden color precipitates were formed; as shown in figure 3. This leaden precipitant was filtered; washed using absolute ethanol and dried at 80 oC in an oven. The photo deposition mechanism [29,30] was used, which is basically based on the use of Philips High-Pressure Mercury Lamp (HPML) 400 watt as a UV-A light and the ZnO's photoelectron to conduct Ag⁺ to Ag metal photoreduction on its surface.

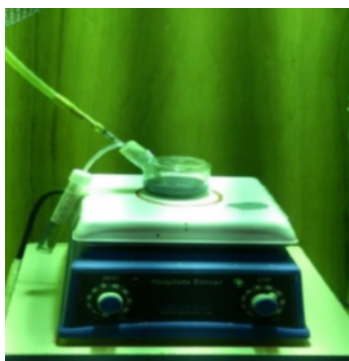


Figure 3. Real image for doped 2% from Ag on ZnO Np surface in the photo deposition method.

Characteristics of synthesis samples

Series of techniques were used to conduct this work, such as Atomic absorption (AA-6300-Shimadzu) analysis, which applied to estimate if all amount of Ag was doped. FTIR model 8400S -Shimadzu employed the KBr disc in the ranged of 400 - 4000 cm⁻¹. XRD analysis style Lab X XRD 6000-Shimadzu was used to investigate whether the samples were successfully prepared and then measure the mean crystal sizes for all prepared samples by using the Scherrer's formula [31-33] with use 2θ ranging from 20o to 80o. Moreover, the AFM model, AA 3000 was employed to represent the shape of the samples prepared.

Photoreaction of methyl green dye with synthesis photocatalysts

In order to check the efficiency of prepared photocatalysts, the undoped ZnO Np and 2 % Ag doped ZnO NPs were applied to the solution of methyl green dye. Series of preliminary experiments were performed with employed the ZnO nanoparticles (NP) in dye aqueous solution. The undoped or 2 % Ag doped ZnO NPs were dispersed in 200 mL of 25 ppm of methyl green dye solution.

At outset, the dark reaction is a vital step to reach for the homogenous equilibrium at 30 min, the adoption on the ZnO surface has happened as physical adsorption [34, 35]. Under moderate stirring, the UV-A light was focused on the produced suspension solution. In intervals, time of illuminated; 2.5 mL of samples were collected and twice separated using a centrifuge to remove all the fine catalyst particles.

In photoreaction, the residue concentration of this dye was monitored at 630 nm using UV-Vis analysis. From based on equations 5 and 6 [36- 38], the apparent rate constant (k_{app}) and the photo decolourization efficiency % (PDE %) were determined.

$$\ln \left(\frac{C_o}{C_t} \right) = k_{app} \cdot t \quad (5)$$

$$PDE \% = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \quad (6)$$

Where: C_o and C_t are the concentration of methyl green dye without and with irradiation respectively.

Results and Discussion

Atomic absorption analysis

The result of this analysis was indicated that the concentration of Ag that needed to doped as 2% Ag is equal to 1723.336 ppm, but the residue of Ag in solution after irradiation the colloid solution of ZnO for 3h was reached 0.36 ppm, that ensure the 2 % Ag was doped successfully on ZnO surface.

FTIR analysis

Based on the FT-IR spectra for undoped and 2% Ag doped on ZnO-NP surface was investigated as shown in figures 4 (a) and (b). The essential peaks of ZnO are obtained at around 3446-3450 cm^{-1} for stretching vibrations of O-H and appearance two peaks approximately at 1120 and 1577 cm^{-1} . On the other hand, the narrowband around 410 - 500 cm^{-1} are assigned to the stretching vibration band of Zn-O [28,39]. Moreover, the new peaks occur in the region ~ 624 -778 cm^{-1} , when Ag doped on ZnO NP, this result is approximately agreed with T. S. Vijayakumar et al [40].

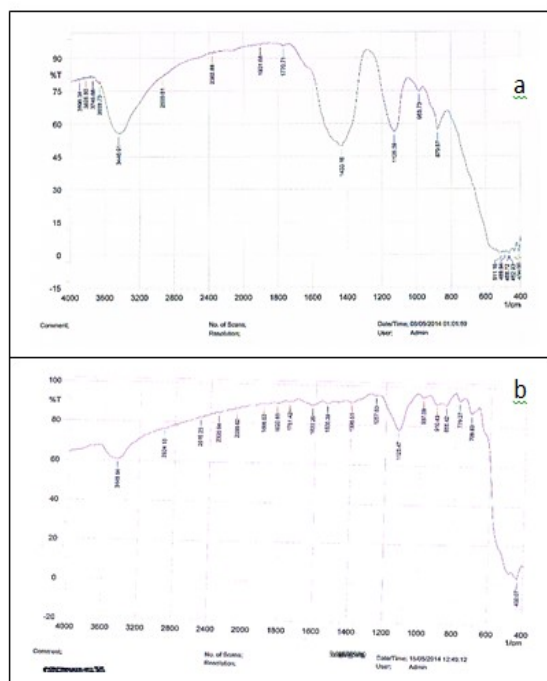


Figure 4. FT-IR Spectra for prepared a) undoped ZnO NP and b) 2% Ag doped ZnO NP

XRD analysis

Based on the indexed [JCPDS no. 36-1451] and [JCPDS card no. 04-0783] of the ZnO hexagonal wurtzite structure and the face-centered cubic structure of Ag [41], the XRD peaks in figure 5 were indicated the undoped and Ag doped ZnO Np samples are successfully formed. The XRD spectra were evidenced that the nine broad bands at 2θ values 31.6°, 34.4°, 36.15°, 47.45°, 56.5°, 62.7°, 66.4°, 67.8° and 69° are beyond the miller indexes equal to (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively [28, 42]. Moreover, a new broad peak has confirmed the Ag doped on ZnO NP surface, and noticed at 44.50° with miller index (200); this result did not form a silver oxide.

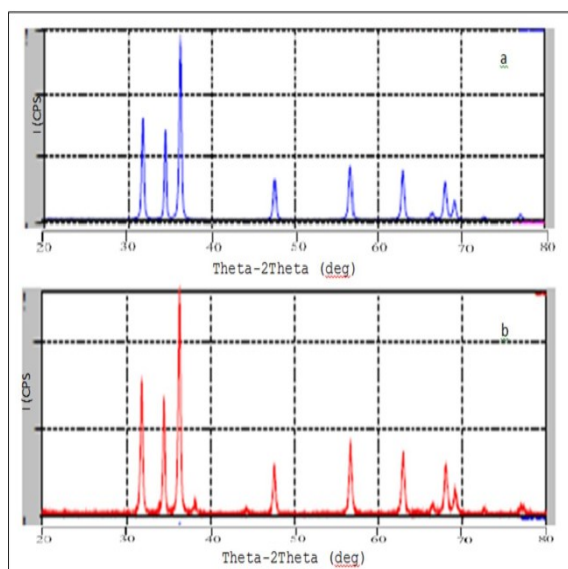


Figure 5 The XRD Spectra of a)Undoped ZnO Np, b) 2 % Ag doped ZnO Np.

Using the Scherer equation [31,43], the highest three peaks at 2θ 31.6°, 34.4°, 36.15° were selected to calculate the mean crystallite size of ZnO NPs. The magnitudes of mean crystallite size of undoped and 2% Ag doped ZnO NP were proved the Ag doped ZnO NPs is less value than it's for ZnO NP that due to incorporate of Ag(I) (with ionic radius 0.115 Å) with Zn(II) (with ionic radius 0.74 Å) in ZnO lattice [44]; these values were displayed in table 1.

Table1. The Mean Crystallite Sizes of Undoped ZnO and 2% Ag doped ZnO NP.

Mean Crystallite sizes /nm	Crystal components
29.0090	(0)% Ag doped ZnO NP
28.2010	(2)% Ag doped ZnO NP

AFM analysis

Figures 6 and 7 display, that the undoped and 2% Ag doped ZnO Nps are semi-spherical and nanoparticles. The particle size of prepared ZnO Np increased with 2% Ag doped on ZnO Np from 7.28 nm to 22.6 nm, which leads to improvement in the agglomerated process when metal-doped [45,46].

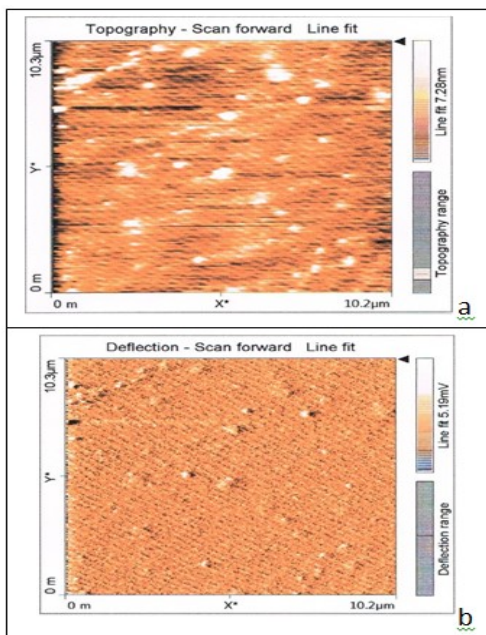


Figure 6 . AFM images for a) 2- Dimensions Image (Topography) and b) 2- Dimensions Image(Deflection) of Udoped ZnO Np.

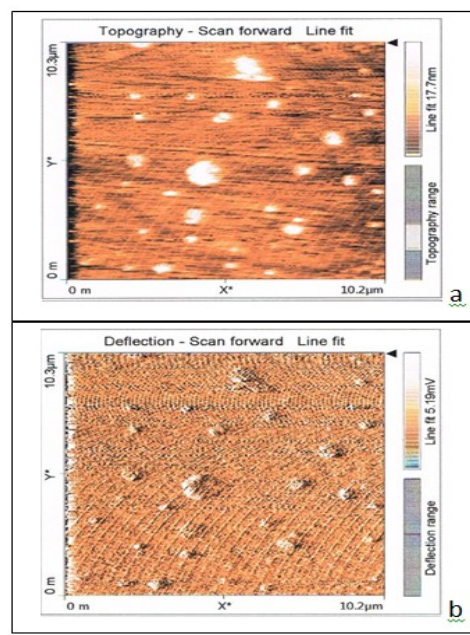


Figure 7 . AFM images for a) 2- Dimensions Image (Topography) and b) 2- Dimensions Image(Deflection) of 2% Ag doped ZnO NP.

Photocatalytic activity reaction of undoped and Ag doped on ZnO NPs

Figures 8 (a,b) illustrates, that the Ag doped ZnO Np indicates to increase the photoreaction with increment the apparent rate constant and PDE% values. Since Ag acts as a sink of electrons, so, the recombination process will reduce [41,47, 48]. The best PDE% with using ZnO Np increases from 37.000 % to 87.368 % with 2% Ag doped on ZnO NP for 40 min at 25 ppm dye, 0.7g. /200 mL catalyst, pH 5.4, and 298.15 K.

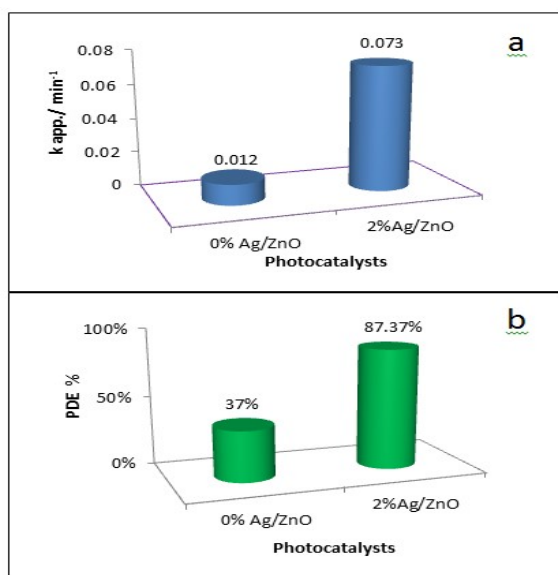
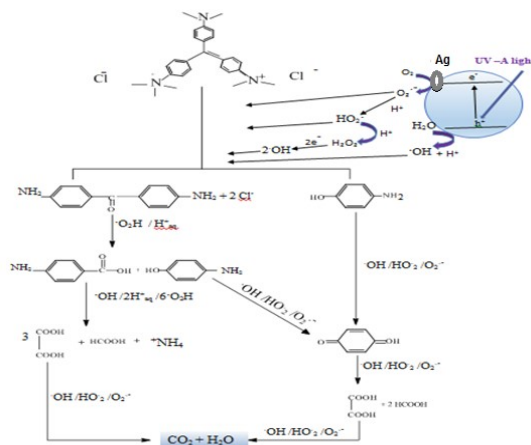


Figure 8. The relation between a) Kapp verse photocatalysts, b) PDE % verse photocatalysts.

Suggested mechanism

According to scheme 1, the more acceptance mechanism for photo decolourization of methyl green dye was suggested to use the undoped ZnO NP or Ag 2% ZnO NP. This mechanism was based on a series of redox processes [49-51], which leading in essential to produce a hydroxyl free radical as a key to starting the photo decolourization of this photoreaction[52-56].



Scheme 1. The schematic diagram for decolorization mechanism in (methyl green Dye/undoped or Ag 2% ZnO NP/ UV-A light) system.

Conclusions

The main conclusions in this work can be summarized by the undoped ZnO NP and 2% Ag doped ZnO NP, respectively, which were successfully prepared by using co-precipitation and photodeposition. That was evidenced by FT-IR, XRD, and AFM. The mean crystal size at Ag 2% doped on ZnO Np was found to be reduced compared without doping. All prepared photocatalysts have been shown in the AFM images as semispherical. The FT-IR spectra were conformed to ZnO NP and Ag-Zn bond form. At working conditions, the photocatalytic decolorization of methyl green dye using prepared samples was performed and obeyed to pseudo-first-order. with 2% Ag doped on ZnO Np surface, the PDE % was found to be increased.

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