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SYNTHESIS AND CHARACTERIZATION OF AG/ZNO VISIBLE LIGHT PHOTOCATALYST

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Abstract

I this work, we report a heterogeneous Ag/ZnO Photocatalysis absorption in the visible range can be improved by surface modification by adding noble metals such as Ag, Pd, and Au and their alloys. Our work demonstrates the application the synthesis of supported nanoparticle Photocatalyst catalysts for different applications such as water and anti-microbial treatment. Here, we report two step synthesis method of Ag/ZnO Nanoparticle Photocatalyst. The method is based on the synthesis of monodispersed ZnO nanoparticle through chemical reduction and microwave irradiation followed by the deposition of 1 wt. % Ag nanoparticles onto the surface of ZnO nanoparticles through deposition-precipitation method followed by microwave irradiation. The nanostructures of the prepared Ag/ZnO particles have been confirmed using UV-VIS absorbance, XRD, and SEM analysis. Ag/ZnO nanoparticles have been tested as a Photocatalyst for the degradation of Methylene Blue (MB) in water. The Photocatalyst is tested first for discoloration of MB in water under visible solar radiation and then using UV/Ag/ZnO system. Our results indicate that Ag/ZnO nanoparticles remove the color of Methylene Blue (MB) from water. Also, UV/Ag/ZnO system confirms the removal of MB from aqueous solutions containing 5 mg/L MB using small amount of Ag/ZnO Photocatalyst completely. Our kinetic study indicates that the Photocatalytic degradation of MB using UV/ZnO/Ag system follows pseudo-first order kinetics. The increase of Photocatalyst dose enhances both the rate and efficiency of MB degradation. We attributed the photocatalytic activity of the Ag/ZnO Photocatalyst to Plasmon surface effect of Ag nanoparticles and interaction of Ag with ZnO. Ag nanoparticles act as an electron sink, promoting interfacial charge transfer reducing charge recombination.

1. INTRODUCTION

Environmental and water contamination becomes a major issue in recent years due to the discharged of colored and toxic dyes into the water supply system. These dyes are emitted by major industries such as paper, plastic, and pharmaceutical[30], [31]. The presence of dyes such methalyn blue, and other Phenols and phenolic dyes show sever effects on humans, animals, and plants. It was found that the presence of these dyes can affect the nature of water and inhibit the sunlight penetration and reduce photosynthetic reaction[32]. Also, Wastewater contains high levels of pathogenic microorganisms;

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therefore, water disinfection represents a very an important factor in Environmental and water treatment. Various conventional technologies employed different methods for the waste water treatment. These methods are usually inefficient, costly, and did not lead to complete degradation of the dyes and instead transfer it to other phase[33]. Therefore, it is important to develop a new effective method to disinfect and remove dyes from the wastewater.

Recent studies shown that the use of semiconductor photocatalysts offer relatively efficient, simple, and low cost alternative to the conventional methods in removing dyes from waste water[34]. Conventional Metal oxides Semiconductor such as TiO2, ZnO have drawn much attention during the last few years because of their novel photocatalytic activity, availability, stability, strong oxidative capacity, and low cost[35] ,[36] .

Nanomaterials gain much attention in the field of catalysis in recent years due its unique physical and chemical characteristics, Nanomaterials offered cost-effective solutions for many environmental problems such as waste water treatment, pollution, and anti-bacterial treatment. Nanoparticle catalysts are characterized by large surface area, high dispersion and strong interaction with other materials[37] [38] ,[39] [40]. It is therefore, expected that nanoparticles photocatalyst, with controlled particle size and high surface area could potentially provide significantly improved photocatalytic performance over bulk photocatalyst.

ZnO show excellent photocatalytic activity to reduce contaminants in the environment. However, due its wide band gap (about 3.2 eV at room temperature) and high excitation binding energy (about 60 meV), it is only allows absorption the UV region of solar spectrum. Li-Yun Yang et.al report a novel synthesis of dumbbell-shaped ZnO photocatalyst using microwave heating with extremely high photocatalytic activity toward Methylene Blue degradation[41]. Photocatalytic activity of ZnO nanoparticle photocatalyst can be enhanced to allow absorption in the visible range of solar spectrum. Several studies report improvement of visible-light photocatalytic activity of metal oxide by cationic or anionic doping or adding metals or none-metals[42], [43] [44]. It has been reported that doping ZnO with

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noble metals such as Ag or Au enhanced the photocatalytic activity, improve charge separation, and prevent the electro-hole recombination in ZnO due to its electron storage properties[45]. The creation of a local electric field and the optical vibration of surface Plasmon in silver induce enhancement in this electric field and hence enhance the photocatalytic activity[46]. Numerous studies report the synthesis of Ag/ZnO using various synthetic routes for waste water treatment and disinfection[47] [48] [49] [50] [51] [52] [53] [54] [55]. In this paper, we report the synthesis and characterization of a heterogeneous Ag/ZnO visible light photocatalyst for different applications such as water and anti-microbial treatment. Ag/ZnO nanostructure was prepared using Microwave Assisted Deposition- Precipitation method. The photocatalytic activities of Ag/ZnO system were investigated and compared to ZnO nanoparticles. The morphology, optical properties of the Ag/ZnO photocatalyst was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis absorption spectrum (UV-Vis) methods. We attribute the enhanced photocatalytic activity of Ag/ZnO nanoparticles to the synergetic effect, improved charge-transfer, and the prevention of the electro-hole recombination in ZnO.

2. EXPERIMENTAL

All the chemicals were used as received without any further purification. Zinc nitrate (Zn-$(NO3)_2$; Alfa Aesar), Silver nitrates (AgNO3;Sigma-Aldrich), 10 N NaOH (Alfa Aesar), and Glucose (C6H12O6; Natura). Distilled water was used in all the preparation.

2.1 Synthesis of ZnO Nanoparticles

In a typical synthesis, the precursor solutions of zinc is prepared by dissolving 5 g of Zn-$(NO3)_2$ 100 mL of ethanol in 250 ml reaction flask. The solution is kept under stirring, while 10 N NaOH was added to the solution drop wise until the pH of the resulting solution reaches 10. The Obtained solutions then placed into a domestic microwave oven were the microwave power was adjusted to 1/3 of full 650 W power setting. The solution placed in the microwave and irradiated for approximately 10-15 minutes and is removed from the microwave before reaching the boiling point. The resulting

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solution was left to cool down naturally. Finally, the particles were collected and filtered and then washed thoroughly several times by distilled water and ethanol.

2.2 Synthesis of Ag/ZnO nanoparticles

Ag/ZnO was synthesized using Deposition Precipitation method (DP) by dissolving 4 g of as prepared ZnO nanoparticles in 100 ml solution of 2 wt. % of reducing agent (glucose) dissolved in distilled water and kept under vigorous stirring for 10 minutes while 1 wt. % Ag nanoparticles onto the surface of ZnO nanoparticles through precipitation of Ag on the surface of ZnO nanoparticles. Were Ag (NO3)2 is reduced using Glucose as a reducing agent. The silver nitrates AgNO3 was added to the solution drop wise until the pH of the solution reaches 7. The resulting solution contains 1wt% of silver precipitated on the surface of the ZnO nanoparticles. Finally, the solution placed in the microwave oven and irradiated for 10 minutes and removed before the solution reaches the boiling point. After that, the resulting particles were left to cool down naturally and collected by filter and washed thoroughly several times by distilled water.

Ag/ZnO nanoparticles have been confirmed using UV-VIS absorbance, XRD, and SEM analysis.

2.3. Characterization

The crystalline structure of obtained ZnO and Ag/ZnO photocatalysts were characterized by X-ray diffraction (XRD) technique operating at 40 kV and 30 mA in the diffraction angle range 2θ) 1-70° and step 0.16°.

The morphology of the products was imaged by scanning electron microscope (SEM) with beam acceleration of 10 kV voltages.

The optical properties, the absorbance spectra of samples were measured using a UV-Vis Perkin-Elmer spectrophotometer.

The XRD diffraction patterns of ZnO and Ag/ZnO photocatalysts are shown in Figure 1. The XRD pattern of and Ag/ZnO samples show peaks similar to the peaks reported by Pillai et al. [48]. The intensity of silver peaks is consistent with 1w% concentration of Ag. Furthermore, the XRD patterns confirm the formation of the metallic silver and at least Ag (111) peak is evident. There is no shift in the peak location was observed in for Ag/ZnO sample which indicates the positioning of Ag particles on the surfaces of ZnO nanoparticles than going into the lattice of ZnO or substitute Zn site as observed by Blinks et al.[56]. The other Ag peaks was not observed in the XRD patterns. This is probably due to the presence of small and highly dispersed Ag particles.

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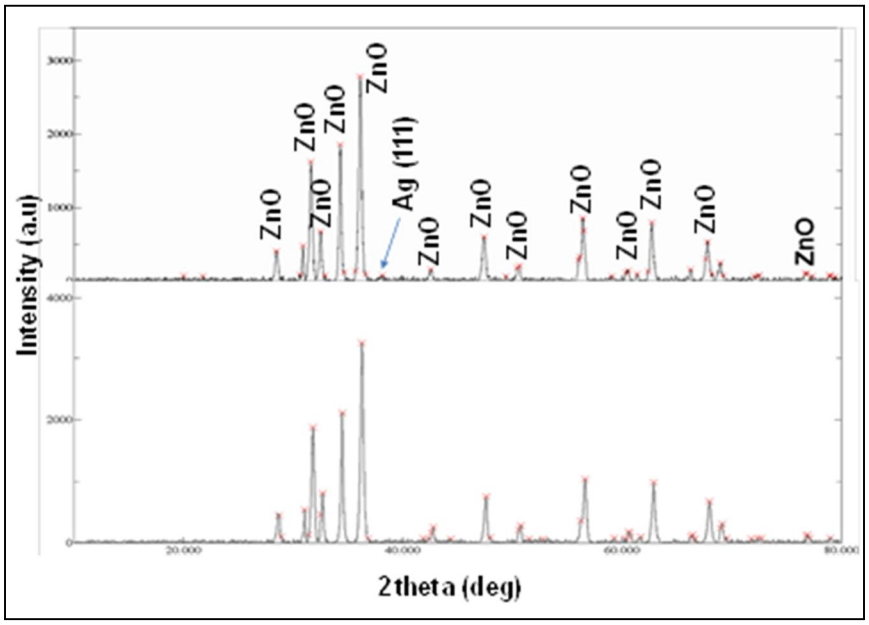


Figure 1. XRD patterns of ZnO and Ag/ ZnO photocatalysts.

SEM microphotographs are shown in Figure 2a and 2b. There were no significant differences in particle shapes and sizes of both samples. The structure is consistent with structures obtained by Microwave synthesis as reported by many groups[57] or dumbbell-shaped reported by [41]. However, the high electron reflectance of our samples prevents further magnification.

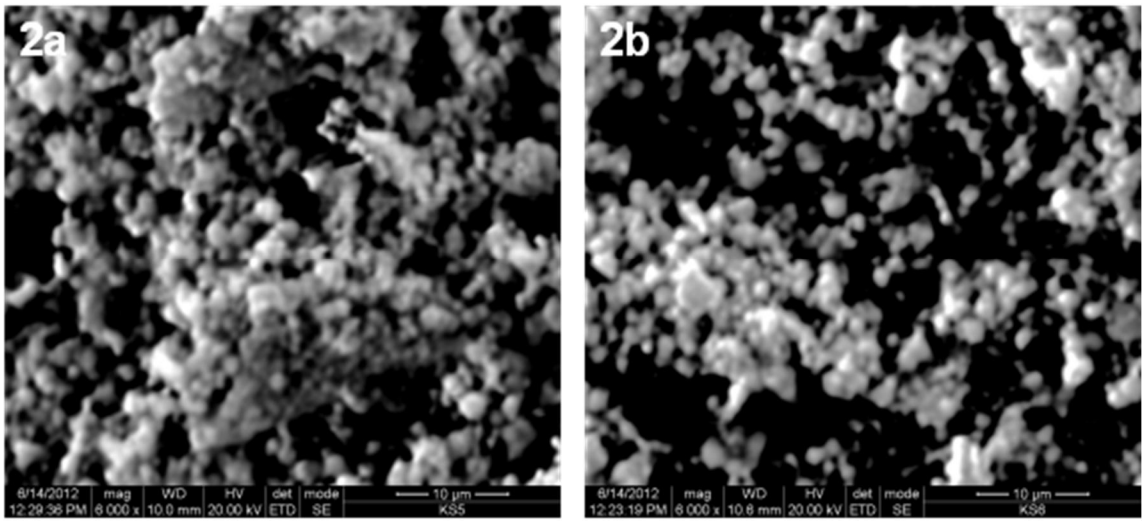


Figure 2. (a) ZnO, (b) Ag/ZnO nanoparticles

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UV-Vis absorption spectra of ZnO and Ag/ZnO photocatalysts are shown in Figure 3. The UV-Vis results indicated that the presence of Ag nanoparticles significantly increases the ZnO nanoparticles absorption in the visible light range of solar spectrum when compared with the Ag/ZnO synthesized by microwave[58]. These results are attributed to Plasmon surface effect of Ag nanoparticles.

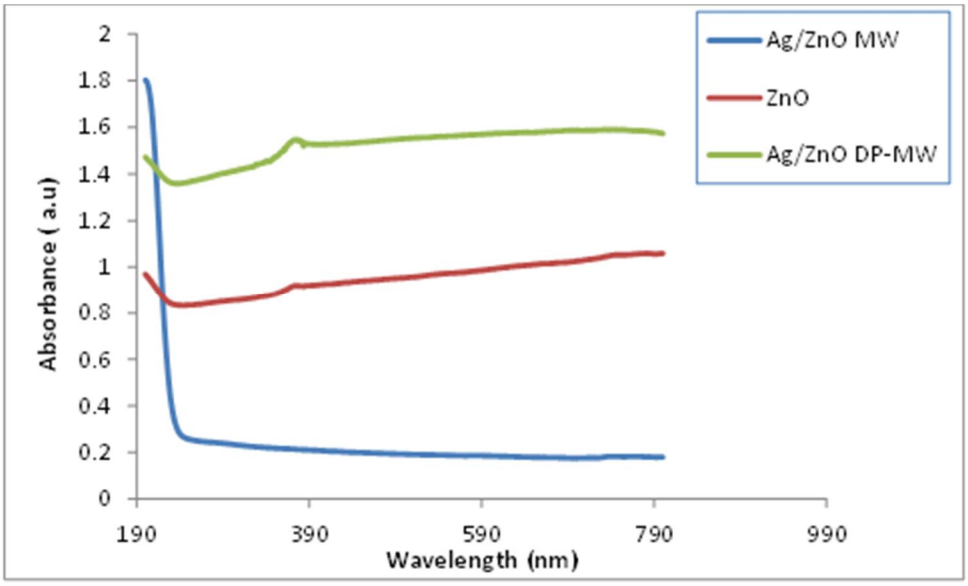


Figure 3. UV-visible absorption spectra of (a) ZnO, (b) Ag/ZnO using microwave synthesis, and (c) Ag/ZnO Deposition-Precipitation (DP) and microwave synthesis (MW).

2.4 Photocatalytic Activity

The MB degradation under UV light irradiation using Ag/ZnO nanoparticles as photo-catalyst at room temperature was investigated. Figure 4 presents the influence of photo-catalyst dose on the changes of MB concentration with time during photocatalytic degradation of MB by UV/Ag/ZnO (ZnO nanoparticles doped with Ag). It is obvious that MB degradation is enhanced by the addition of Ag/ZnO compared to UV irradiation alone. The increase of Ag/ZnO dose enhances MB removal from and increases the rate of MB degradation. UV/Ag/ZnO photocatalytic process leads to complete removal of MB for doses of the photo-catalyst higher than 0.5 g/L within less than 60 min. However, for lower doses of Ag/ZnO nanomaterial than 0.5 g/L, even high MB removals can be reached within 120 min; significant amounts of MB remain in solution higher than maximum contaminant levels regulated by environmental agencies.

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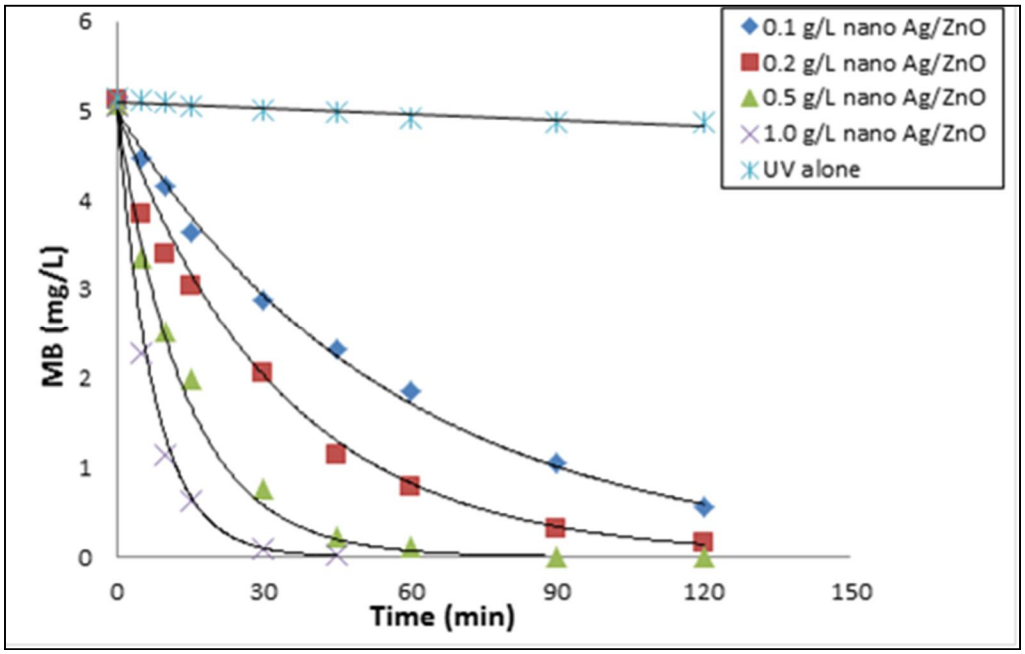


Figure 4. Influence of Photocatalyst dose on the kinetics of MB removal during photocatalytic degradation of MB by UV/Ag/ZnO (ZnO nanoparticles doped with Ag). Experimental conditions: UV-L (254 nm): 15 W, 5 mg/L MB, natural pH 5.8, room temperature (23-25 ◦C).

The plots of MB concentration vs. time indicate in a first approach, that degradation of MB can be described by a pseudo-first-order kinetics as given by the following equation (Eq(1)):

$$-\frac{d[MB]}{dt} = k_{app} \times t \qquad (1)$$

where [MB] is the concentration of MB at instant t, kapp is the apparent MB degradation rate constant, and t is the time. According to this assumption, the rate equation can be integrated (Eq. (2)) with the boundary conditions [MB] = [MB]0 for t=0 and [MB] = [MB]t for t = t, leading to Eq. (3):

$$-\int_{[MB]_0}^{[MB]_t} \frac{d[MB]}{dt} = \int_0^t k_{app} \times t \qquad (2)$$

$$Ln\left(\frac{[MB]_0}{[MB]_t}\right) = k_{app} \times t \qquad (3)$$

The plots of $Ln\left(\frac{[MB]_0}{[MB]_t}\right)$ *vs.* time (t) at different Ag/ZnO doses are presented in Figure 5. The plots are straight lines pass by the original point with correlation coefficients (R^2) higher than 0.99. The

linearity of $Ln\left(\frac{[MB]_0}{[MB]_t}\right)$ = f(t) curves confirms that MB degradation rate is a pseudo-first-order reaction. In accordance with Eq. (3), each line has a slope equal to k_{app} which is the apparent MB degradation rate constant. All k_{app} values were calculated for a same initial concentration of MB (5 mg/L) and at various Ag/ZnO doses. Figure 3 represents the variation of k_{app} with Ag/ZnO dose. The profile of k_{app} values vs. Ag/ZnO dose suggests that MB degradation rate by UV/Ag/ZnO process increases linearly with the increase of Ag/ZnO dose. L.-Y. Yang et al. reported photocatalytic degradation kinetics of MB fitted the pseudo-first-order kinetics and the Langmuir–Hinshelwood model [41].

MB photocatalytic degradation experiments proved that synthesized samples of Ag/ZnO nanoparticles have excellent activity on decomposition of MB under UV irradiation. Furthermore another set of experiments was performed under sunlight irradiation using Ag/ZnO nanomaterial as photo-catalyst and showed that more than 90 % of MB can be removed by Sunlight/Ag/ZnO system with 4 hours. This work is still underway and the results will be published later.

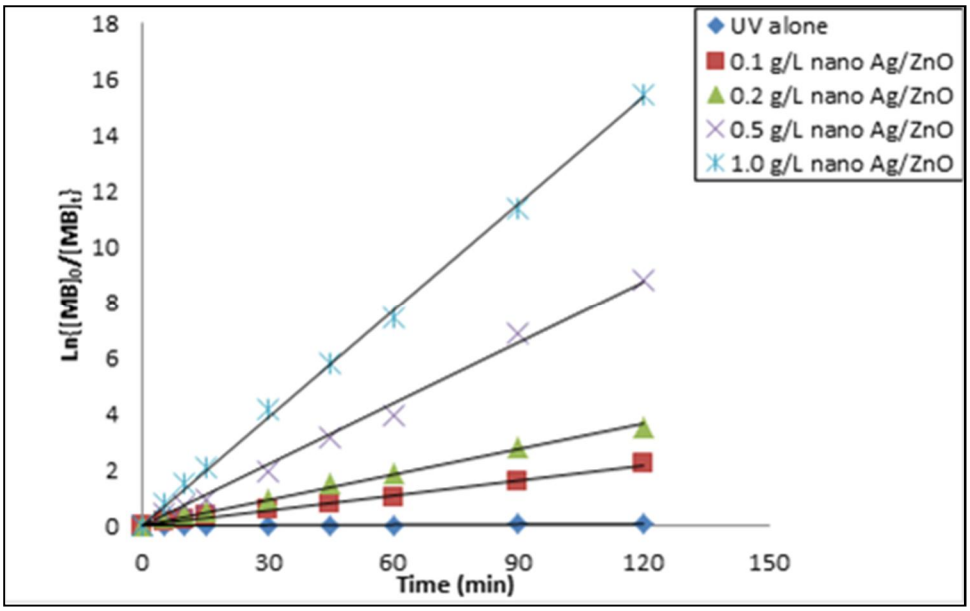


Figure 5. Pseudo-first order fitting of the kinetics of MB removal during photocatalytic degradation of MB by UV/Ag/ZnO (ZnO nanoparticles doped with Ag) using different doses of Photocatalyst. Experimental conditions: UV-L (254 nm): 15 W, 5 mg/L MB, natural pH 5.8, room temperature (23-25 ◦C).

CONCLUSION

These results showed that Ag/ZnO nanoparticles have high photocatalytic activity compared to conventional photocatalysts for color removal of MB. The high photocatalytic activity of the Ag/ZnO photocatalyst is attributed to the presence of surface Plasmon effect of Ag nanoparticles and the interaction of Ag with ZnO were Ag nanoparticles act as an electron sink, promoting interfacial charge transfer reducing charge recombination. Future direction is to explore the photocatalytic activities of different metals such as Au, Pd and their Alloys on ZnO will be tested for deactivating pathogenic microorganisms in water. Our results indicate that Ag/ZnO nanoparticles have excellent activity on

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decomposition of MB under UV and under sunlight irradiation. Ag/ZnO nanomaterial showed that more than 90 % of MB can be removed by Sunlight/Ag/ZnO system with 4 hours.