Degradation of Congo Red Solution by Zinc Oxide/Silver Composite Preheated at Different Temperatures

Amjed Mirza Oda*, Salih Hadi Kadhum1, Ahmed Salih Farhood2 and Hussain Abdul alkadhum2

1Science Department, College of Basic Education, University of Babylon, Iraq
2Chemistry Department, Science College, University of Babylon, Iraq

Abstract

Zinc oxide-silver composite was prepared by photodeposition process. The composite was treated with different temperature 373, 573 and 773 K. Characterization the catalysts by XRD and FTIR analysis was studied. All the analysis showed the modification of zinc oxide surface after doping. The XRD analysis showed Ag2O was the only phase found with ZnO at 373 K while Ag metal was formed after heat treatment. Photocatalytic degradation was tested for all prepared catalyst compared with ZnO. The photocatalytic degradation tested by using congo red dye and the experiment was efficient in sun light without focusing and the reaction last 50 minutes of time and loading was 1 gm./L. The sequence of Photocatalytic efficiency was ZnO/Ag 373> ZnO> ZnO/Ag 573 > ZnO/Ag 773.

Keywords: Zinc oxide; Photodeposition; Photocatalytic degradation; Congo red dye

Introduction

Industrialization and agricultural development, together with population growth, has drastically reduced clean water resources. Various kinds of contaminants enter water, most of them in industrial wastewater. Developments in the field of chemical water purification have led to an improvement in oxidative degradation processes applying catalytic and photochemical methods [1,2]. In recent years, photocatalytic degradation attracts increasing attention as a promising technology for the removal of toxic organic and inorganic contaminants that are recalcitrant to biodegradation from water and wastewater [3]. Heterogeneous photocatalysis based on TiO2 is one of the most active and the most promising advanced oxidation processes. In order to obtain a high reaction rate, the recombination rate of photogenerated electrons and holes must be kept low [4]. In the past two decades, photocatalysis by semiconductor materials such as TiO2 and ZnO has attracted public concern as a promising tool among the advanced oxidation processes to substitute the traditional wastewater treatment due to their high photosensitivity, non-toxic nature, high stability, and the possibility of using sunlight as the source of irradiation [5,6]. While TiO2 is probably the most frequently used photocatalyst, ZnO is an alternative photocatalyst with low cost. It has a similar band gap energy compared to TiO2 (3.2 eV) [7].

To expand the usage of this photocatalyst, many studies employed modifications onto ZnO in order to improve its catalytic efficiency through enhancements of absorbance in the visible-light region. The advantages of photocatalysts modifications are to ensure the separation of electron–hole pairs, broadening the absorption spectrum, and to facilitate some specific reactions on the surface of catalysts. Those methods consist of doping ZnO with manganese, cobalt, silver, polymer-modification, and so forth [8-10]. Rapid recombination of photo-excited electrons and holes greatly impedes the photocatalytic efficiency of ZnO. To overcome this limitation, modification with Ag is considered to be an interesting doping element since it can effectively trap the photo-excited electrons from the semiconductor to liberate the holes [9,11]. Congo red an anionic dye has been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen [12].

Experimental

Materials

ZnO powder (Fluka Co.) and congo red dye powder (BDH) were used without any further purification. Silver nitrate (BDH) and methanol (GCC Co) used for photo deposition.

Preparation of ZnO/Ag*

A Beaker of 1 liter was filled with a solution of 50% of methanol. 5 g of ZnO powder was added with silver nitrate which gives 1% in weight of Ag ion. The slurry stirred for 1h then irradiated with high pressure mercury lamp (125 W) for 2h. The mixture appear dark violet converts to pale yellow to gray color is appeared when the solution is halved. ZnO-Ag composites were collected by evaporation of solvent and dried at 100°C for 2 hours. The powder ZnO-Ag annealed for 2 h at 573 and 773 K then characterized by XRD and FTIR analysis.

Photoactivity of catalyst

ZnO, annealed powders and congo red dye powder (BDH) were used without any further treatment. Experiments were carried out in Pyrex beaker of 500 ml volume. The working volume was 100 ml at 316 K and the concentration of dye was 25 ppm. The slurry magnetically stirred in a dark condition for 2 hours to disperse fully and establish an adsorption/desorption equilibrium. Photodegradation was initiated after it exposed to sun light without focusing. The samples were collected with drawing syringe and centrifuged doubly (recommended). The loading of catalysts was 1000 mg/L. A UV-vis spectrophotometer (uv.

*Corresponding author: Amjed Mirza Oda, Science Department, College of Basic Education, University of Babylon, Iraq, Tel: +9647812475243; E-mail: alnajid1981@yahoo.com

Received February 05, 2014; Accepted February 23, 2014; Published March 19, 2014


Copyright: © 2014 Oda AM, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
As the radius of Ag⁺ ions (1.26 Å) is larger than that of Zn²⁺ (0.74 Å), in ZnO:Ag may exist on the substitution sites and the interstitial sites. After heat treatment a typical peaks appeared at 2θ=37 and 44 belong to Ag metal. XRD data also show that no traces of impurities are detected in the preparation step. The lattice parameters of this work were obtained by using hexagonal structure formula as described in which gives values of a = 3.257 Å and c = 5.257 Å [13]. The a and c of the ZnO was estimated using hexagonal structure formula as

\[ d = \left( \frac{a^2}{2} \right) \left( \frac{h^2 + k^2 + l^2}{4} \right) + \left( \frac{a^2}{c} \right) l^2 \]  

The corresponding XRD patterns appear in Figure 1 of the as-photo deposited sample. The reflection peaks after the drying match well with the XRD pattern of hexagonal wurtzite ZnO (JCPDS 361451). The lattice parameters of this work area=3.344 Å and c=5.188 Å. The lattice parameters a and c of the ZnO was estimated using hexagonal structure formula as

\[ a = \frac{2}{\sqrt{3}} \left( \frac{a^2}{2} \right) \left( \frac{h^2 + k^2 + l^2}{4} \right) + \left( \frac{a^2}{c} \right) l^2 \]  

\[ c = \frac{4}{\sqrt{3}} \left( \frac{a^2}{2} \right) \left( \frac{h^2 + k^2 + l^2}{4} \right) + \left( \frac{a^2}{c} \right) l^2 \]  

No. of atom in the unit cell and V is the volume of unit cell [15]. The lattice parameters of this work area=3.344 Å and c=5.188 Å. The lattice parameter of ZnO was increased in the c-axis with Ag dopant. Ag ions prefer to occupy the substitution sites [14].

\[ d_{th} = \frac{M_w z * 1.66}{V_o} \]  

Where d is space between crystal levels, (h, k, l) Miller indices and a=b, c are crystal parameters. Table 1 shows the d space and crystal parameters (a and c) and these results showed a shrinkage process in the d space and as well as a and c parameter after heat treatment of ZnO-Ag. Thus the volume of unit cell decreases and the density increases and the later calculated by equation (2):

\[ \rho = \frac{M_w z}{V_o} \]  

\[ \rho = \frac{M_w z}{V_o} \]  

FTIR analysis of ZnO-Ag coposites shows in Figure 2, where ZnO absorbs in the range of 400-600 cm⁻¹ attributed to the Zn-O bonds and weak absorption at 1650 cm⁻¹ and 3400 cm⁻¹ due to O-H water bending and stretching respectively [16]. There is a little shifting in case of ZnO-Ag (373 K) to the high energy absorption may be due to the distortion of the surface of oxide particles by silver oxide photodeposited and then shifted to low energy absorption due to silver oxide transforms to silver metal as heat treatment. There is additional absorption at 1400 cm⁻¹ attributed to C-H bending, 2925 cm⁻¹ and 3034 cm⁻¹ belong to C-H stretching and 3400 cm⁻¹ for O-H stretching as result of methanol adsorption on catalyst (the solvent).

Photodegradation of 25 ppm of Congo red solution was carried out at summer day by using zinc oxide and the as-prepared zinc oxide/Ag composites as catalysts and sunlight as light source. First, this mixture was stirred in the dark, which leads to a total adsorption of Congo red on zinc oxide particles; this mixture was stirred for 50 min under direct sun light. Then the mixture was transferred to a dark room and kept for different times, after which samples were taken and analyzed for absorbance of remaining Congo red.
sunlight. The experiment was conducted between 11:30 and 12:30 a.m. The temperature under sunlight was 316 K. With reaction time running, the red color intensity of Congo red decreases until disappearance. This indicates decomposition of Congo red on zinc oxide particles' surface. This decolorization was more in the presence of ZnO-Ag in the same condition of experiments (Figure 2).

Degradation of CR may occur via the following steps, (i) cleavage of benzene ring (specifically, benzene rings on the sides decompose), (ii) cleavage of C-S bond between the aromatic ring and the sulfonate groups by OH• radicals attack, (iii) cleavage of various C–N and C–C bonds of the chromophore group and (iv) N–N double bond cleavage. The dye mineralized to give CO2 and H2O during the irradiation (Figure 3) [3].

All the spectra in Figure 4 show the decolorization of congo red in aqueous solution and the process is very fast in the presence of ZnO and ZnO-Ag at 373 K as-prepared catalyst. According to Figure 4a the adsorption at dark reaction is more after ZnO doping by silver comparing in Figure 4b, where the adsorption was more. The deposited silver particles increase the surface area and made a new active site changed pathway of decolorization to be a shorter time life. In contrast with the ZnO treated thermally at 573 and 773 K, that both of them were inhibited in surface area (the adsorption is less) and the decolorization. This may be due to heat treatment made a less number of active sites and the conversion of Ag2O to Ag particle which expose to poisoning by dye and dye intermediate during the decolorization.

The Photocatalytic decolorization action was developed by Ag ion sensitization. The bleaching was more and reached colorless in 50 min. Ag ion made modification on ZnO surface to create new active sites making ZnO-Ag ion more active than ZnO alone in the same illumination conditions. That is clear because of doping process overcame the limitation of the rate of photocatalytic degradation that decreased with recombination of photogenerated electron-hole (e−–h+) pairs [9,10]. Ag is considered to be an interesting doping element since it can effectively trap the photo-excited electrons from the semiconductor to liberate the holes [11]. We can see the efficiency of decolorization was developed by Ag ion and modification be more suitable in case of Ag ion, air presence, uv illumination and just drying at 373 K. This procedures are important that efficiency was ZnO/Ag 373 K > ZnO/Ag 573 K > ZnO/Ag 773 K and Figure 5 showed that. In the previous study Congo red degraded in 240 min by using sun light and used mixed cerium – iron oxide [17], also Congo red was degraded in 120 min using anatase TiO2 and last 80 min [18]. Also in this research we found the degradation is not slow as found in nanosized TiO2 [19] where reaction last in this study is 50 min only.

**Conclusion**

Congo red dye was degraded with high photodegradation efficiency by sun light. The reaction done without focusing sun radiant and the catalyst work properly. The photooxidation of methanol in the photodeposition making Ag ion converts to Ag2O system making a good doping on the ZnO surface.

**References**


