Journal of Thermodynamics & Catalysis

Oda et al., J Thermodyn Catal 2014, 5:1
DOI: 10.4172/2157-7544.1000127

Research Article Open Access

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

Amjed Mirza Oda[1]*, Salih Hadi Kadhum[2], Ahmed Salih Farhood[2] and Hussain Abdul alkadhum[2]

[1]*Science Department, College of Basic Education, University of Babylon, Iraq*
[2]*Chemistry 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 Ag_2O 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 process 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 TiO_2 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 semiconductive materials such as TiO_2 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 TiO_2 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 mgL^{-1}. A UV-vis spectrophotometer (uv.

***Corresponding author:** Amjed Mirza Oda, Science Department, College of Basic Education, University of Babylon, Iraq, Tel: +9647812475243; E-mail: almajid1981@yahoo.com

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

Citation: Oda AM, Kadhum SH, Farhood AS, Alkadhum HA (2014) Degradation of Congo Red Solution by Zinc Oxide/Silver Composite Preheated at Different Temperatures. J Thermodyn Catal 5: 127. doi: 10.4172/2157-7544.1000127

1650 PC, Shimadzu Co., Japan) was used to determine the absorbance of Congo red at a wavelength of 496 nm.

Result and Discussion

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 new reflections occurring at 2θ of 27.9° and 46.4° are typical peaks of Ag_2O (JCPDS 040783). 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 a and c of the ZnO was estimated using hexagonal structure formula as described in which gives values of a = 3.257Å and c = 5.257 A [13]. 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 in ZnO:Ag may exist on the substitution sites and the interstitial sites. As the radius of Ag^+ ions (1.26Å) is larger than that of Zn^{2+} (0.74Å), the formation energy is very low for ions on the substitution sites, but rather high on the interstitial sites. Thus, it is reasonable that Ag ions prefer to occupy the substitution sites [14].

a and c parameter were calculated from equation (1)

$$d=(a/\ ((3/4)\ (h^2 + k^2 + hk) + (a^2 / c)l^2))^{1/2} \ldots\ldots\ldots 1$$

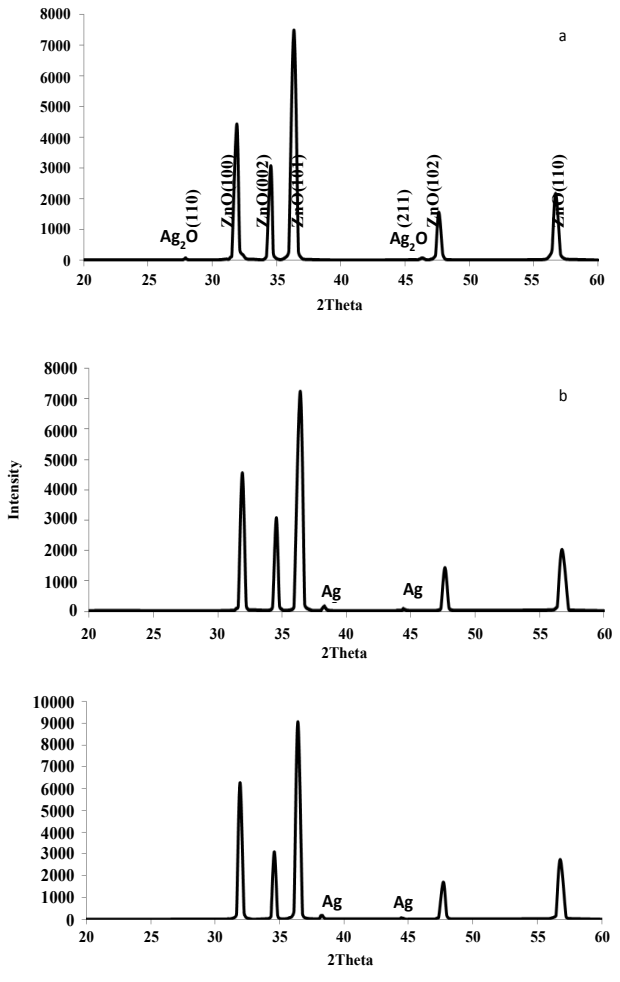

Figure 1: XRD spectrum of zinc oxide-Ag composite heated at different temperature, 373 K (a), 573 K (b) and 773 K (c).

T, K	d @100 , Å	d,@ 002 Å	a,Å	c,Å	Unit cell volume nm^3	Density gm. /cm^3
373	2.896	2.594	3.344	5.188	50	5.370
573	2.802	2.593	3.235	5.186	47	5.740
773	2.797	2.587	3.229	5.175	46	5.780

Table 1: The value of d space, crystal parameters, volume and density of unit cell of ZnO-Ag after heat treatment.
D= 0.94 λ/B Cosθequation 3, θ:diffraction angle, λ: x-ray wave length (1.154 Å), B: the angle width at half maximum height

T, K	ZnO particle size, nm	Ag particle size, nm
373	41.4	41.3*
573	43.4	38.2
773	46.5	31.7

*particle size of Ag_2O

Table 2: The particle size at different temperature (calculated at hkl= 101).

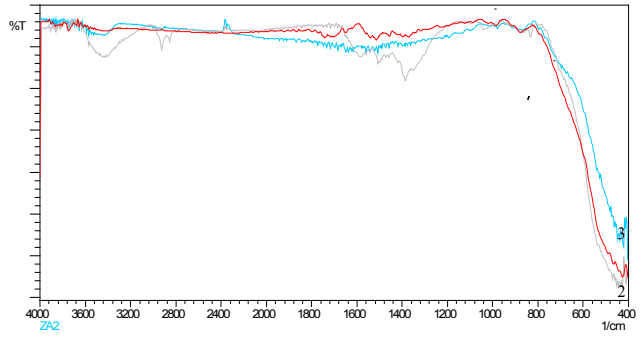

Figure 2: FTIR spectra of zinc oxide composite treated with different temperature (1- ZnO-Ag 373, 2- ZnO-Ag 573, 3- ZnO-Ag 773).

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):

$$d_{th} = M_w * z * 1.66 / Vo \ldots\ldots\ldots 2$$

d_{th} is the density of unit cell, Mw is the molecular weight, z is the No. of atom in the unit cell and Vo is the volume of unit cell [15]. The particle size calculated by using Scherrer's equation which is take the formula (Table 2):

FTIR analysis of ZnO-Ag copmosites 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} attribute 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

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 CO_2 and H_2O 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 373 the 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 short 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 Ag_2O to Ag particle which expose to poisoning by dye and dye intermediate during the decolorization.

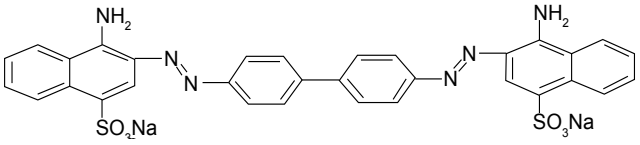

Figure 3: The structural formula of Congo red.

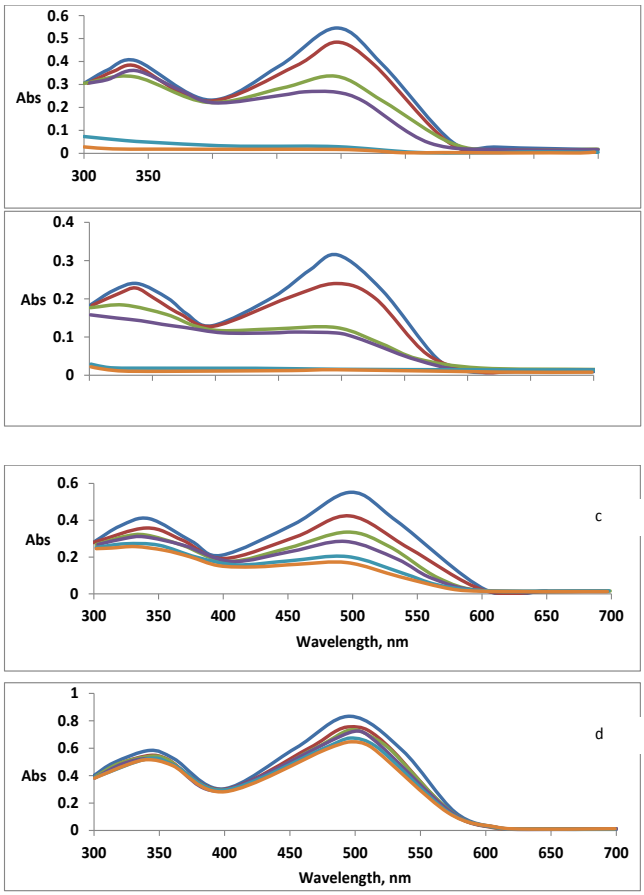

Figure 4: The uv. vis spectra of photodegradation of 25 ppm of Congo red solution with catalysts and sunlight. (a: ZnO, b: ZnO-Ag 373 K, c: ZnO-Ag 573 K, d:ZnO-Ag 773 K).

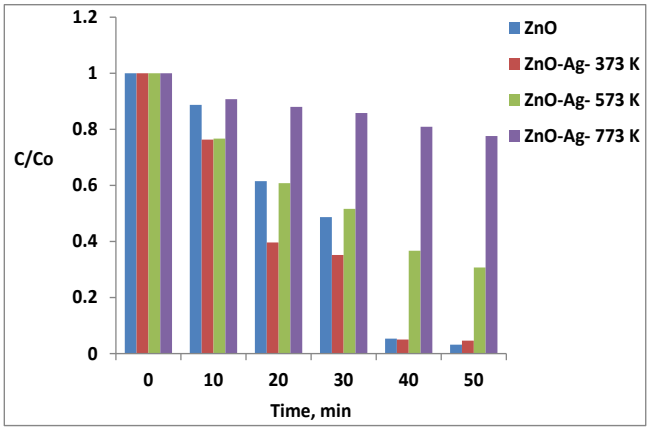

Figure 5: The decolorization efficiency of ZnO, ZnO-Ag 373 K, ZnO-Ag 573 K and ZnO-Ag 773 K.

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> ZnO> ZnO/Ag 573 > ZnO/Ag 773 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 TiO_2 and last 80 min [18]. Also in this research we found the degradation is not slow as found in nanosized TiO_2 [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 Ag_2O system making a good doping on the ZnO surface.

References

1. Zhang S, Chen Z, Li Y, Wang Q, Wan L (2008) Photocatalytic degradation of methylene blue in a sparged tube reactor with TiO2 fibers prepared by a properly two-step method. Catalysis Communications 9: 1178-1183.

2. Yang Y, Luan J (2012) Synthesis, property characterization and photocatalytic activity of the novel composite polymer polyaniline/Bi2SnTiO7. Molecules 17: 2752-2772.
3. Erdemoğlu S, Aksu SK, Sayilkan F, Izgi B, Asiltürk M, et al. (2008) Photocatalytic degradation of Congo Red by hydrothermally synthesized nanocrystalline TiO2 and identification of degradation products by LC-MS. J Hazard Mater 155: 469-476.
4. Talebian N, Nilforoushan MR (2010) Comparative study of the structural, optical and photocatalytic properties of semiconductor metal oxides toward degradation of methylene blue. Thin Solid Films 518: 2210-2215.
5. Chong MN, Jin B, Chow CW, Saint C (2010) Recent developments in photocatalytic water treatment technology: a review. Water Res 44: 2997-3027.
6. Ahmed S, Rasul MG, Brown R, Hashib MA (2011) Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. J Environ Manage 92: 311-330.
7. Mekasuwandumronga O, Pawinratb P, Praserthdamb P, Panpranot J (2010) Effects of synthesis conditions and annealing post-treatment on the photocatalytic activities of ZnO nanoparticles in the degradation of methylene blue dye. Chemical Engineering J 164: 77-84.
8. Whang TJ, Hsieh MT, Chen HH (2012) Visible-light photocatalytic degradation of methylene blue with laser-induced Ag/ZnO nanoparticles. Applied Surface Science 258: 2796-2801.
9. Sakthivel S, Shankar MV, Palanichamy M, Arabindoo B, Bahnemann DW, et al. (2004) Enhancement of photocatalytic activity by metal deposition: characterisation and photonic efficiency of Pt, Au and Pd deposited on TiO2 catalyst. Water Res 38: 3001-3008.
10. Subba Rao KV, Lavédrine B, Boule P (2003) Influence of metallic species on TiO2 for the photocatalytic degradation of dyes and dye intermediates. J Photochem Photobiol A 154: 189-193.
11. Wang R, Guo J, Chen D, Miao YE, Pan J, et al. (2011) ‘‘Tube brush’’ like ZnO/SiO2 hybrid to construct a flexible membrane with enhanced photocatalytic properties and recycling ability. J Mater Chem 21: 19375-19380.
12. Chatterjee S, Chatterjee BP, Guha AK (2007) Adsorptive removal of Congo red, a carcinogenic textile dye by ash and activated carbon: kinetic study and equilibrium isotherm analysis. Chemosphere 61.
13. Dorset DL (1998) X-ray Diffraction: A Practical Approach. Microsc Microanal 4: 513-515.
14. Kaipeng Liu, Beifang Yang, Hong wei Yan, Zheng ping Fu, Mei wangWen, et al. (2009) Effect of Ag doping on the photoluminescence properties of ZnO films. J Luminescence 129: 969-972.
15. Richard Tilley JD (2006) Crystals and Crystal Structure. John Wiley & sons Ltd, England.
16. Saleh TA, Gondal MA, Drmosh QA, Yamani ZH, AL-yamani A (2011) ZnOnano particles on multiwall carbon nanotubes. Chemical Engin J 166: 407-412.
17. Pradhan GK, Parida KM (2010) Fabrication of iron-cerium mixed oxide: an efficient photocatalyst for dye degradation. International Journal of Engineering, Science and Technology 2: 53-65.
18. Rajeev Jain, Shalini Sikarwar (2006)Photocatalytic and adsorption studies on the removal of dye Congo red from wastewater. Int J Environment and Pollution 27: 159-178.
19. Rajeev KW, William W, Liu Y, Michelle LM, Joshua CF, et al. (2005) Photodegradation of Congo Red catalyzed by nanosized TiO2. Journal of Molecular Catalysis A: Chemical 242: 48-56.