An Illustration of Photocatalytic Properties of ZnOnanorods array Films

A. Nekoubin[1♣], H. Ghayour Najafabadi[2], M. Nasr Esfahani[2]
1- Young Researchers Club, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran
2- Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, P.O.Box 517, Iran

ARTICLE INFO

Article history:

Received: 16 Aug. 2011
Accepted:19 May2012
Published online:14 Dec. 2012

Keywords:

Photocatalytic
Degradation
Zinc Oxide
Nanorods
UV Light

ABSTRACT

ZnO nanorods array films were coated on a glass template through a two-step chemical process. First, a sol-gel spin coating method was used to produce a ZnO seed layer and after that, the ZnO nanorods arrays were grown on it through a low temperature aqueous method. Synthesized films were studied by scanning electron microscope (SEM) and X-ray diffractometer (XRD). X-ray diffraction results showed single crystalline wurtzite with a c-axis preferential (002) orientation. The deposited ZnO layers had c-axis orientation, and showed a sharp X-ray diffraction peak at 2θ=34.40 degrees, corresponding to the (002) of hexagonal ZnO crystal. The SEM images showed vertical orientation of rods, and the diameters of rods were under 100nm. The photocatalytic degradation of XG6 azo dye in aqueous solutions was examined with a combination of ZnO nanorods array film as a photocatalyst and UV light. Results showed that the films are effective in decolorization of dye.

Introduction

Nowadays, most industrial countries around the world face the environmental problems of dangerous wastes processing, pollution of underground water resources and poisoning with polluted air. It is estimated that about 1.1 billion people are at the risk of using polluted water. Due to this, the water day in the year 2010 attracted attentions in the field of water quality with the motto "clean water for the healthy world"[1-3].

During the times, soils and water resources are polluted with the hazardous chemical materials such as poisonous substances. Materials like heavy metals (mercury, lead and cadmium), air planes' fuel, vehicles' fuel, destructive materials, solutions and byproducts of industries and manufactures are among the most important pollutants. Combinations such as eternal organic and aromatic compounds, PVC's, chlorine eternal organic compounds, pesticides and Arsenic compositions are some of the related general combinations [4].

Toxic waste is one of the most important problems in controlling the contaminations. Abandoning wastes which contain high amounts of polluting materials like reactive dyes is an old problem. To eliminate this contamination, some methods like adsorption on activated carbon, reverse osmoses, biological methods etc. are applicable, but these specified methods are not effective for the completed ecomposition of dyes [5].

♣Corresponding author: A. Nekoubin, nekoubin@gmail.com, 09138328130

Textile and other industrial dyes are the greatest category of chemical productions in the globe. Among them, azo dyes are the most important with the major applications in the industry and play an outstanding role in all the fields. Furthermore, they impose the greatest loss on the environment [9,10]. All contaminators of water could be eliminated via regular chemical and physical techniques. On the contrary, it is impossible to remove dyes through a separate method [6]. Lately, attentions have been focused on the advanced oxidation process (AOP) for decomposition of organic materials of the polluted water, and photocatalytic decomposition may be an economical method to solve this problem. The use of photocatalyst semiconductor as a complementary or modifier to methods like burning of dangerous chemical wastes in high temperatures, non-air fermentation and physicochemical methods is one possibility [7].

Semiconductors are not only useful in the production of chemical materials, but also functional for the conversion of contaminant in the wastewater to the harmless substances. For example, n-type heterogeneous semiconductors like zinc oxide are well known for the elimination of contamination in aqueous environments via advance oxidation process. In the presence of zinc oxide, under the emission of near UV light, many organic compositions in the aqueous solutions are degraded to simple compounds like CO_2 and H_2O.This process is one of the remarkable procedures in water purification. Zinc oxide is considered as one of the best photocatalysts, because it has high oxidizing potential, and it is also harmless, inexpensive and resistant against radiation. Initially, the semiconductors were used in the form of powder, but recently, due to some reasons like saving time and costs, uncomplicated recovery of catalysts, high effectiveness and great specific surface area, they have been replaced by films[8].

Zinc oxide (ZnO) could be a future material in the scientific community. ZnO has been widely studied since 1935. The new trend for this material is due to the development of crystal technology, epitaxial growth, and alloying of this material for optoelectronic and photonic devices which are based on ZnO. Nowadays, ZnO could be fined in many different forms such as single crystal powder, thick and thin films as well as nanostructures. Each of these forms has extended and variable applications. Zinc oxide is usually observed with the chemical formula of ZnO, in the form of white powder, and is almost insolvable in water [9-11].

In the current research, firstly, a ZnO nanorods array film with high surface area was synthesized through a low temperature aqueous method in different conditions and after that, the effect of different catalysts wasinvestigated on the decomposition of X6G dye (light yellow).

Experimental procedure

Materials and Equipment

All used chemicals were prepared from Merck Company, Germany, as shown in the **Table 1**. All materials were in 99.9% purification. Apparatus and study equipment are shown in **Table2**.

Preparation of zinc oxide catalyst

Well aligned ZnO nanorods were grown via a low temperature aqueous technique under different conditions. ZnO nanorods were grown-up on a ZnO seed layer fabricated via sol-gel spin coating process. In this research, the effect of growth time, morphology, length and aspect ratio of ZnO nanorods was studied. Studies have revealed that many different

Table 1. Chemicals used in this research.

No.	Material	Chemical formula
1	Zinc acetate dihydrate	$Zn(CH_3COO)_2.(H_2O)_2$
2	2-Methoxyethanol	$C_3H_8O_2$
3	Monoethanolamine	C_2H_7NO
4	Zinc nitrate tetrahydrate	$Zn(NO_3)_2.(H_2O)_4$
5	Methenamine	$(CH_2)_6N_4$

Table 2. Equipment used in this research.

No.	Instrument	Model
1	Spectrophotometer Uv-Vis	Shimadzo/JASCO Corp. V-750
2	Spin coater	Hettich
3	XRD	X'pert Philips
4	SEM	LEO VP. 435

parameters like precursor concentration, growth time and seed layer can have a significant effect on the morphology, size and orientation of the rods.

Synthesis of ZnO seed layer via sol-gel method

In the present work, ZnO crystals as a seed layer were deposited on the glass substrate via sol-gel spin coating process. For preparation of precursor solution, Zinc acetate dihydrate (ZnA) was solved in the mixture of Monoethanolamine (MEA) and 2-methoxyethanol. The molar ratio of MEA to ZnA was kept equal (1:1), and ZnA concentration was 0.75 molar. The prepared solution was stirred magnetically at 60 °C for 30 min with the velocity of 400 rpm. Consequently, a clear and homogenous solution was acquired. The pre-cleaned glass substrates were coated via spin coater. After coating process, the annealing procedure was performed on the samples for 1 hat 300°C with the heating ratio of 5°C/min.

Synthesis of ZnO nanostructures

A solution containing Zinc nitrate tetrahydrate and Methenamine with the concentration of 0.1M was prepared. Double distilled water was used in the solution preparation. The final product was stirred magnetically at room temperature with the ratio of 1000rpm for 30min.The achieved product was nearly clear and had a milky color. The solution was sealed in the autoclave and the process was completed for 2hat 95°C. After the process, it was observed that the glasses were covered by a nearly white layer. The schematic of procedure is shown in **Fig. 1**. Moreover, the experiment was done for 4 and 8 h under similar conditions.

Photocatalytic degradation experiments

For the investigation on degradation of zinc oxide films, an azo dye type X6G (light yellow) was used, and its chemical structure is shown in **Fig. 2**. The pH and concentration of dye solution were fixed at 6.5 and 5, respectively. 10 ml of dye solution was transferred in the petridish and a sample of catalysts was placed in it. After that, it was radiated with the UV light (4 lamps 365nm, 8W) in the degradation chamber shown in **Fig. 3**.

Characterization of catalyst

In order to investigate the morphology, diameter and length of rods, all prepared films were studied by scanning electron microscope (SEM). Also, for the phase study of prepared films and orientation of rods, the films were studied by X-ray diffractometry method (XRD).

Results and Discussion

Scaninig electron microscope studies (SEM)

In order to observe the grown rods, the films were studied by SEM. Imaging was done both from side-view to study length of rods, and from top-view to study their diameters and changes during the time. Top-view of rods is shown in **Fig.4a**, and its cross-section view is shown in **Fig. 4b**. Infact, these images had an important effect on the study of the quality and quantity of grown rods. A coated substrate and its SEM image are shown in **Fig. 5**.

Fig.1. Schematic process of synthesis of ZnO nanorods on template.

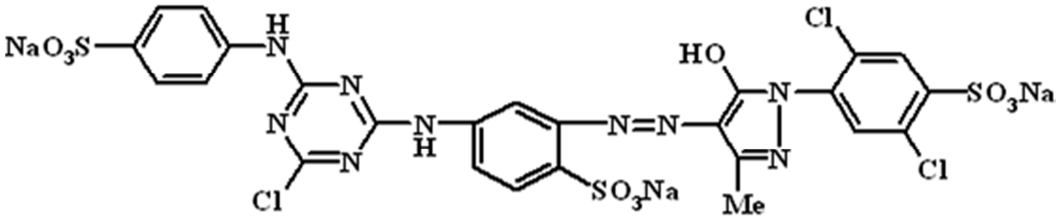

Fig.2. Chemical structure of commercial diazo dye, light Yellow X6G.

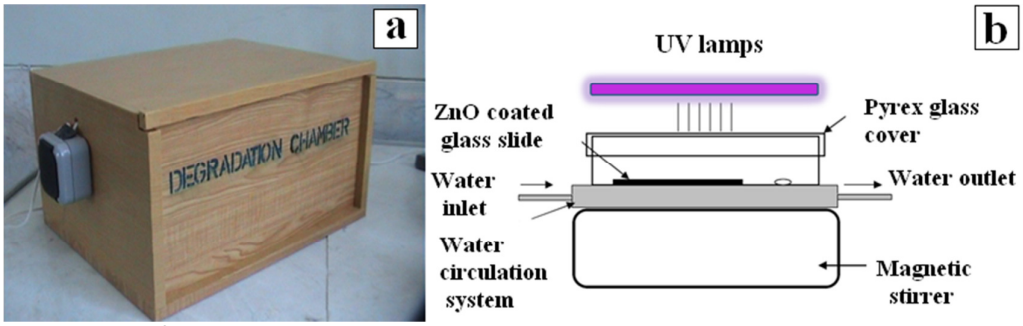

Fig.3. (a) Schematic diagram of photoreactor for degradation (b) Its inner part.

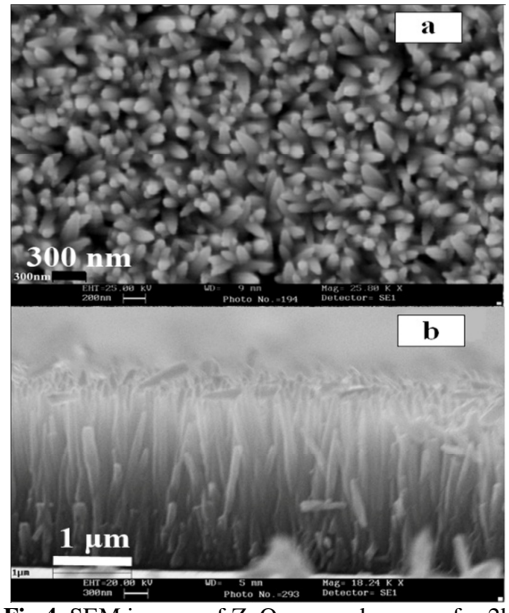

Fig.4. SEM images of ZnO nanorods grown for 2h and in the concentration of 0.05M (a) top view (b) cross section view.

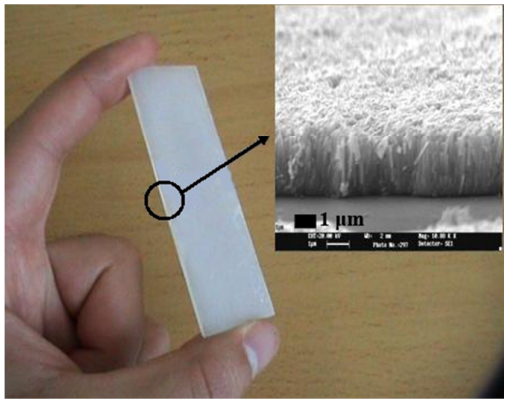

Fig. 5. A sample of coated glass accompanied with its SEM image.

X-ray Diffractometry (XRD) studies

The XRD tests were done on Synthesized nanorods films samples which had been grown at three different growth times of 2(B1), 4(B2) and 8(B3). The results are

shown in **Fig. 6**. Based on the obtained data from XRD tests, two points are perceived; firstly, in all concentrations, the sharpest peak is for (002) planes that shows well c-axis orientation of rods, and other peaks are scarce. Secondly, the growth time has noeffect on rods orientation.

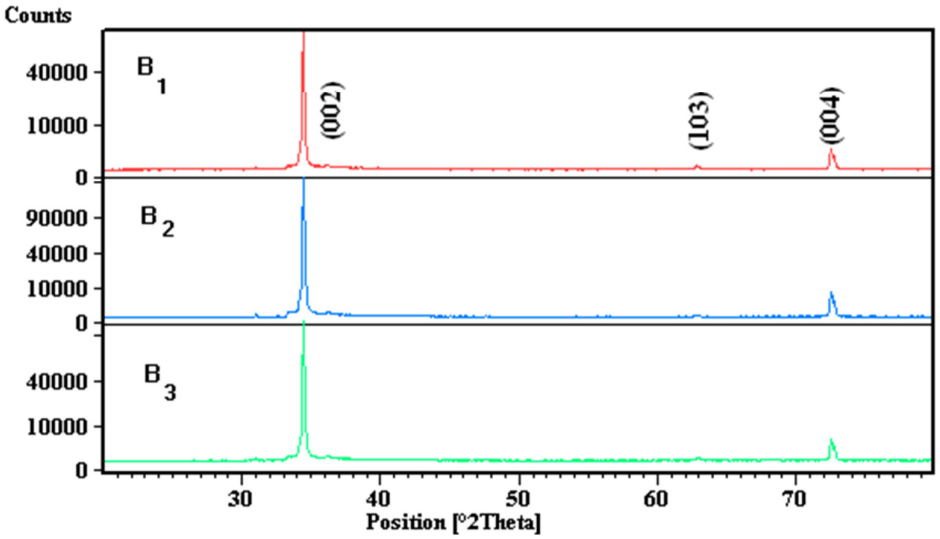

Fig. 6. XRD patterns for micro/nanorods grown in 0.05 M concentration of precursor and 2(B1), 4(B2), and 8(B3) h hydrothermal growth time.

in the range of visible as shown in **Fig. 7**. The film has shown a powerful absorption about 380nm, which is in accordance with theinherent band gap of zinc oxide (Eg=3.37 eV).

Photocatalytic performance of ZnO nanorods

Decolorization (decomposition) rate of zinc oxide films

Decomposition efficiency of X6G dye was calculated by **Eq. 1** as follows:

$$(Efficiency\ \%) = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

C and C_0 are the equilibrium concentrations of dye before and after radiation of UV light. The decomposition efficiency of X6G is shown in **Fig. 8**. The curve of dye decomposition versus decomposition time was plotted using data obtained from experiments on a catalyst sample, and all experiments were performed in a constant condition: temperature of 25°C, pressure of 1atm and 5ppm of dye concentration.

The sample was in the absence of zinc oxide catalyst, but under the UV light radiation for 100min, it showed that less than 10% of dye is decomposed (curve(♦) in **Fig. 8**).In the presence of catalysts and UV light radiation

Optical characterization of catalysts

The optical properties of well aligned ZnO nanorods were studied by the measurement of absorption spectrum of UV-visible. ZnO nanorods films showed a robust absorption intherange of ultraviolet and a wide absorption

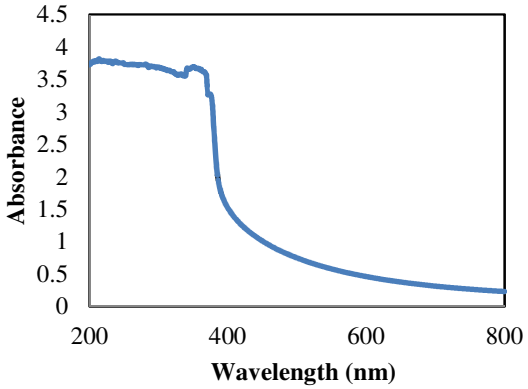

Fig.7. The absorption curve of ZnO nanorods array film.

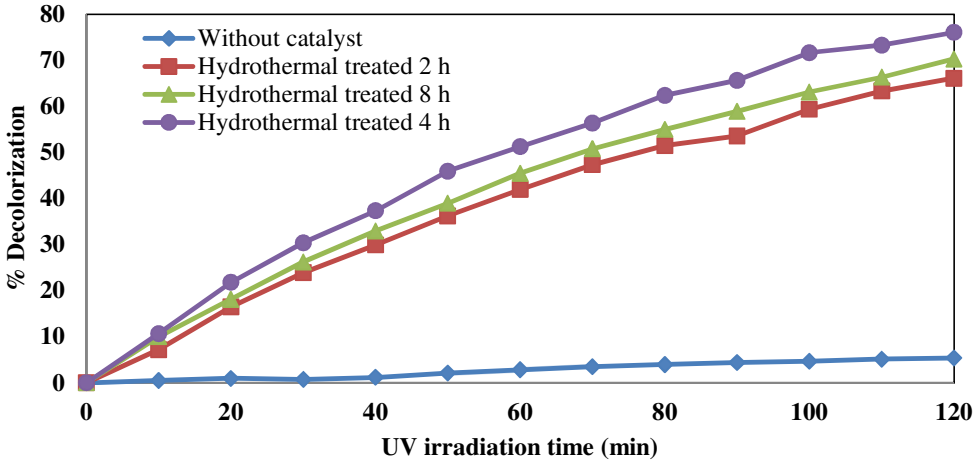

Fig.8. Decomposition of X6G (5 ppm) dye solution without photocatalyst (♦) and in the presence of ZnO nanorods film with hydrothermal treated for 2 (■), 4 (●) and 8 h (▲).

for 100min, about 65% of sample B1, and about 75% of B3 are decomposed.

Generally, photocatalytic development of catalyst for decomposition of contaminants depends on the band gap of material, nanometric structure and high surface area. It should be mentioned that in this research, high surface area of well aligned ZnO nanostructures results in high photocatalytic activation of that. Furthermore, the structuresof well aligned ZnO nanostructure accelerates the transportation of electrons and holes in the crystal, bringing about the modification of photocatalytic properties of this structure.

Degradation rate of dye with ZnO nanostructures films

Plotting $Ln(C/C_0)$ versus degradation time, gives the rate constant (k) (**Fig. 9**). While the degradation efficiency is considered with k constant, the amount of k for the B1, B2 and B3 samples is 0.009,0.012 and 0.01 min^{-1}, respectively. The results show that the lowest degradation rate is related to grown rods in 2 h(sample B2) while sample with 4 h growth time (sample B2) has a higher rate in comparison to the sample with 8h growth time. The reason can be found in the high amount of aspect ratio in 4h growth time, though the more of aspect ratio it has, the more surface is in contact with the dye.

Conclusions

Well-aligned ZnO nanorods with hexagonal structure were synthesized through a low-cost and environmentally friendly method. The ZnO seed layer was synthesized via sol-gel spin coating process. The rods were grown at three different growth times and the length, diameter and aspect ratio changes of rods were studied. The changes in growth time showed that with the rising of growth time, the diameter and length of rods were raised until rods tended to coalescence to each other and produce a monolithic surface which lowered the aspect ratio. The degradation of azo dye X6G (light yellow) in the presence of UV-visible ray produced from four 8W lamps with 365nm wavelength with ZnO nanorods film was done for the first time.

To investigate the reaction progress, a UV-visible spectroscopy was used. This was done through comparison of adsorbtion spectrum of the samples before and after of degradation at various times. The results showed that the sample with 4h growth time had the best degradation efficiency and the highest contact surface with the solution due to its high surface area.

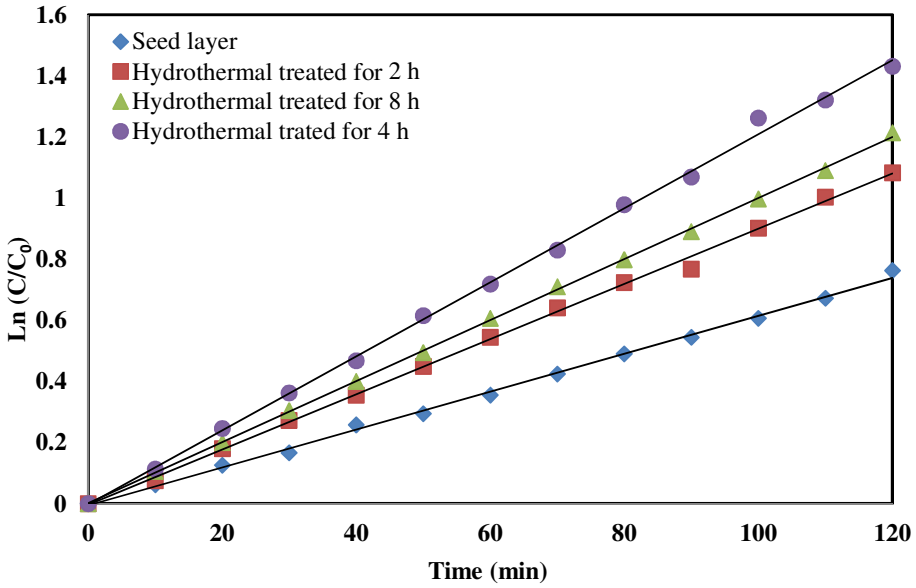

Fig.9. The kinetic of photocatalytic degradation of X6G in the presence of ZnO seed layer (♦) and in the presence of ZnO nanorods film with hydrothermal treated for 2 (■), 4 (●) and 8 h. (▲)

Acknowledgment

The authors are thankful to the Young Researchers Club of Islamic Azad University-Najafabad Branch for the financial support of this research.

References

[1] Water, a Shared Responsibility: the United Nations World Water Development Report 2. Paris: Unesco, 2006. Print.

[2] Water in a Changing World: The United Nations World Water Development Report 3. Paris: Unesco, 2010. Print.

[3] "Water Quality: Theme of World Water Day 2010 - World Water Day." Home - World Water Day. Web. 06 June 2010. <http://www.worldwaterday.org/page/2641>.

[4] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, "Heterogeneous photocatalytic decomposition of phenol over TiO_2 powder", Chem. Soc. Jpn., Vol. 58, 1985,pp. 2015.

[5] V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero, E. Pelizzetti, "Photocatalytic degradation of phenol in aqueous titanium dioxide dispersion", Toxical. Environ. Chem., Vol. 16, 1988, pp.89–96.

[6] H. Al-Ekabi, N. Serpone, "Kinetic studies in heterogeneous photocatalysis, photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO_2 supported on glass matrix",J. Phys. Chem., Vol. 92, 1988, pp. 5726–5735.

[7] M. Barbeni, E. Pramauro, E. Pelzzetti, E. Borgarell, M. Gratzel, N. Serpon, "Photodegradation of pentachloro phenol catalyzed by titanium dioxide particles", Chemisorpe,Vol. 14, 1985,pp. 195–207.

[8] C. Hsiao, C. Lee, D.F. Ollis, "Heterogeneous photocatalysis, degradation of dilute solutions of dichloromethane, chloroform, and carbon tetrachloride with illuminated TiO2 photocatalysis", J. Catal., Vol. 82, 1983, pp. 418–423.

[9] M.M. Masis, "Fabrication and study of ZnO micro and nanostructures", M.Sc. Thesis, Wright State University, Dayton-Ohio,USA, 2007.

[10] A.J. Kulkarni,"Atomistic characterization and continuum modeling of novel thermomechanical behaviors of zinc oxide nanostructures" Ph.D Dissertation, Georgia Institute of Technology,USA,2007.

[11] K.J. Lee, "Study of stability of ZnO nanoparticles and growth mechanisms of colloidal ZnO nanorods", M.Sc. Thesis, Texas A&M University, USA, 2005.