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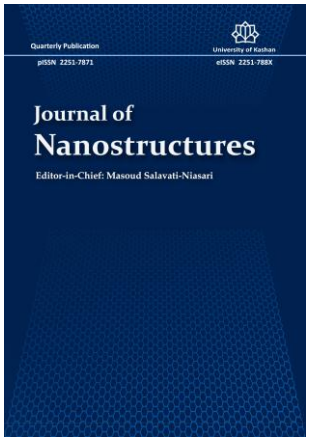

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Synthesis, characterization, and photodegradation of 2-(2-pyridal azo) 1,8–dihy droxynapthalene using ZnO nanoparticles and nanorods under visible light

Haider Abdulelah[1, *], Raed A. Dheyab[2], Fatima H. Malk[1], Ghufran Shabeeb[1], Ban Hamdan AlMulla[3], and Rafid AL-Asadi[4]

[1] Department of Material Science, Polymer Research Centre, University of Basrah, Iraq.

[2]Chemical Engineering Department, College of Engineering, University of Basrah, Iraq.

[3]School of Electrical Engineering, Faculty of Engineering, University of Technology Malaysia (UTM).

[4]Chemistry Department, College Education, University of Basrah, Iraq.

[*]Corresponding author.
E-mail address: haider.abdulelah@uobasrah.edu.iq (Haider Abdulelah)

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Abstract

Many academic researchers have focused throughout the last decades on the decomposition of the organic contaminants in wastewaters aided by oxide semiconductor nanostructures, as well as the manufacture of these nanomaterials using simple, environmentally, rapid, and cost-effective procedures. ZnO nanowires (or nanorods) have received a great deal of attention due to their unusual material features and outstanding performance in electronics, optics, and photonics. ZnO nanoparticles (NPs) are prepared as a seed layer for growth nanorods (NRs) and used to remove synthetic dyes to reduce their environmental impact. Visible light (200W) was used as a source for degradation of 2-(2-pyridal azo) 1,8– dihy droxynapthalene dye with assisted ZnO NPs and NRs. In three hours, ZnO NRs removed 50.4% of Azo dye. Photolysis has been proven to be the most effective method for removing pigments. XRD and SEM were used to describeZnO NPs and ZnO NRs.

Keywords: Azo Dye; Photocatalyst; visible light and ZnO (NRs).

Introduction

Environmental pollution has become a serious problem due to rapid industrial development, and one of the environmental pollutants in the industrial processes of textiles and tall paper from which large quantities of colored dyes are produced, in addition to the aquatic environment that pollutes non-dissolving sewagewater when it reaches natural water [1]. Organic dyes and chemicals used in different sectors (including paper, textile, cosmetics, pharmaceutical, and plastics) result in polluted wastewaters that can impact aquatic habitats and, as a result, human life. For this reason, several chemical, physical, and biological techniques have been used to remove the color of dyestuff effluents,such as thin films, chemical absorption, absorption, and others [2-10].

Natural and industrial dyes are used in industrial applications, containing dyes [11, 12], and electronic applications such as diode emitting [13] and instant markers[14], as well as liquid crystal technology [15]. Nevertheless, comparing the photocatalytic efficiency of compositions utilizing different ZnO substances is difficult since the experimental setup varies widely from work to work. Azo is used as a dye in general because of its molecular structure [16-20]. Dyes can be used in several electronic and optical applications when combined with polymers. Polymers containing dyes are used in a variety of applications, including medicine [21] and sensors [22], solar cells [23], and others, where the dye alters the optical properties of polymer films.

Azo dyes are widely utilized in a wide range of applications and industries, including photography, printing, and other sectors [24, 25], as well as cosmetics, silk,nylon, and other materials [26-40]. Azo dyes can enter the human body and causes manyside effects such as endocrine disruptions, tumor formation, and allergies [41]. ZnO is considered one of the important semiconductors with 3.3eV energy gaps and large binding energy of 60meV [42-45]. ZnO nanorods of nanoscale diameters had also gained special interest amongst ZnO nanomaterials owing to their huge particular surface area, which can improve their efficiency in a variety of uses. ZnO applications in several fieldsincluding optoelectronics, sensors, optics, thermoelectric properties [46], and photocatalysis which has aroused great interest. ZnO is considered superior in the photodegradation of organic materials [47, 48].

In the oxidation and reduction systems, charge separation leaves behind pairsof electron holes, which can form free radicals. Hydroxyl (.OH), one of the most efficient oxidants of organic materials that can degrade contaminants, is one of the free radicals created and active [49]. A

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photocatalyst with potential energy levels, strong absorption qualities in the visible region, and an appropriate energy gap, and creates electron-hole pairs and a negative red. ox potential for excited electrons is required for successful dyebreakdown [50-53]. figure (1) depicted the process of photocatalysis.

In this work, the catalytic activity of the ZnONPs and ZnONRs was determined by measuring the PAD dye degradation when exposed to visible light.

Experimental details

ZnO nanoparticles and nanorods were synthesized by using sol-gel and hydrothermal methods, respectively. In short, 3g of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was dissolved in 100ml of pure ethanol (C_2H_5OH) under vigorously stirring for 15 minutes. Then, add 1.5ml of diethanolamine ($C_4H_{11}NO_2$) to increase viscosity. 2ml of the solution was deposited onto (2cm×2cm) glass by using the spin coating method. The sample was placed on a hotplate at 250 ^{0}C to form ZnO nanoparticles.

ZnO nanoparticles sample was used as a seed layer growth ZnO nanorods byusing the hydrothermal method. The seed layer was placed in an autoclave containing a solution of 0.5M of Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamine ($C_6H_{12}N_4$) under 150 ^{0}C for 12h to form ZnO nanorods. Samples were immersed in 10ml of Azo dye for 12 hours to form a semiconductor/dye hybrid junction.

The azo dye PAD was made using a chemical method [36]. The structure of the dye molecule is depicted in figure (1). The dye powder was dissolved in ethanolsolvent and stirred for 3-4 hours at room temperature. To achieve a uniform thickness, the stirred solution was cast horizontally on the substrates. Allow the solution to slowly evaporate at room temperature before vacuum drying. The structure of the dye molecule is presented in Figure (2).

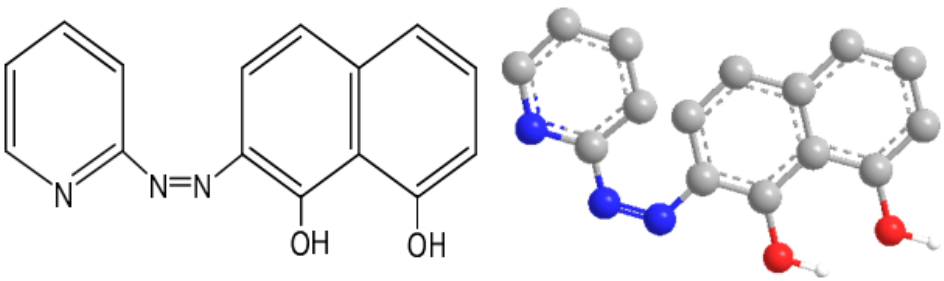

Fig.(2): The structure of PAD dye

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Results and Discussion

Morphology: Synthesized ZnO NPs and ZnO NRs were examined by FE-SEM image for morphological features. Figure 3(a) shows ZnO NPs and (b) shows a vertically aligned ZnO NRs with an average diameter of 99nm.

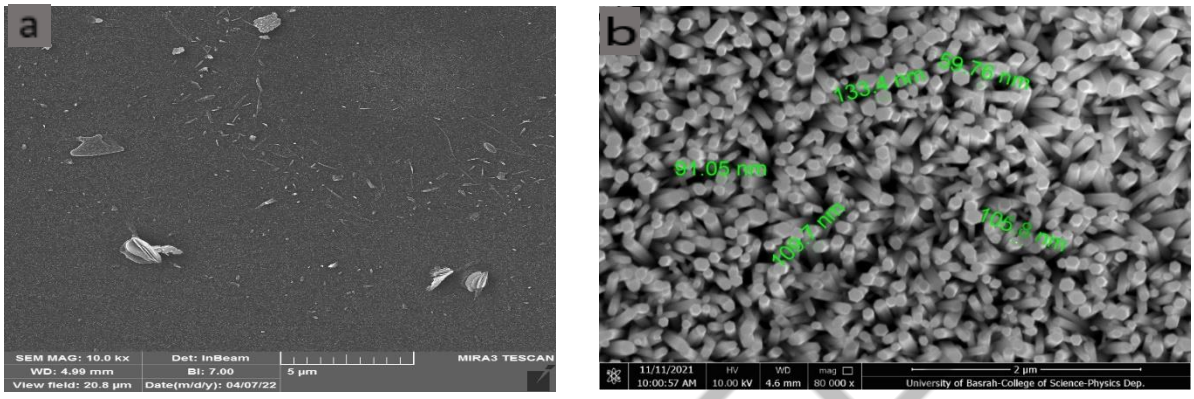

Fig.(3): FE-SEM of ZnO NPs (a), and ZnO NRs (b).

X-Ray Diffraction (XRD): Figure (4) shows the XRD pattern of ZnO NPs and ZnO NRs growth on a glasssubstrate (2cm×2cm). XRD results of ZnO NPs were observed that weak peaks located at (100), (002), and (101) planes, while A dominant diffraction peak for (002)of ZnO NRs indicates a vertical growth in c-axis orientation[54]. ZnO was formedin a hexagonal wurtzite structure [55].

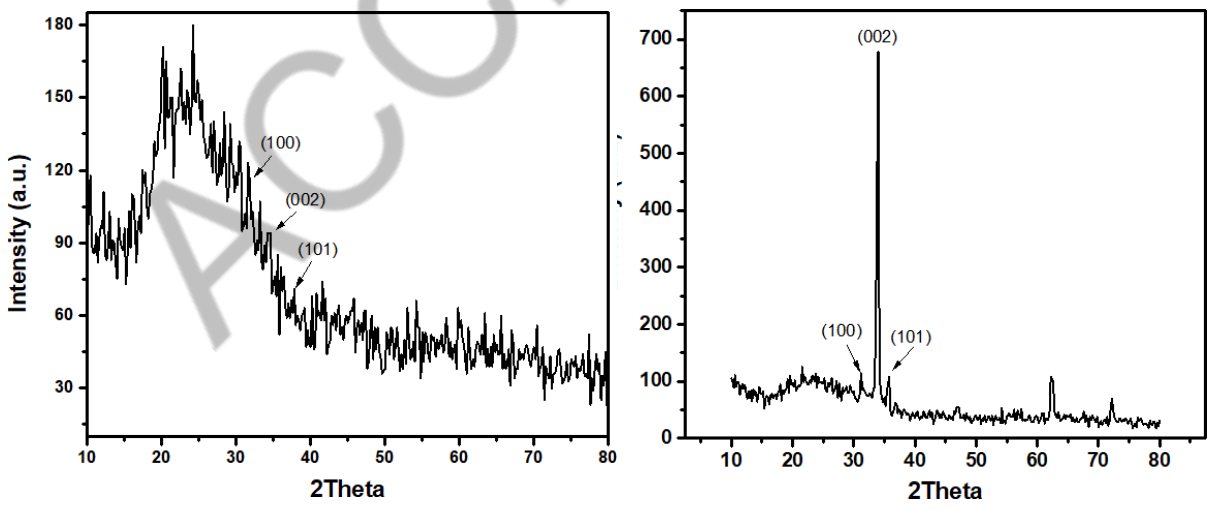

Fig.(4): X-ray diffraction of ZnO NPs, and ZnO NRs

Catalyst's characterization: All experiments were carried out in visible light (200W, Xenon) under fan cooling. Figure 5(a) shows clear peaks at 420nm and 580nm attributed to the ZnO nanoparticles/Azo dye. Figure 5(b) observed weak peaks spectra absorbance at the same positions

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of the ZnO nanorods/Azo dye sample. The degradation rate (D) wasestimated according to the following equation [56]:

$$D(\%) = \frac{A_0 - A}{A_0} 100\%$$

Where A_0 is the absorbance at 0 minutes and A is the absorbance at t minute.

Figures 5(a) and (b) depicted the rate of degradation of the ZnO NPs sample was 40% after exposure three hours to the visible light, while 50.4% degradation ofZnO NRs since the surface area of ZnO NRs is greater than ZnO NPs means more harvesting of light.

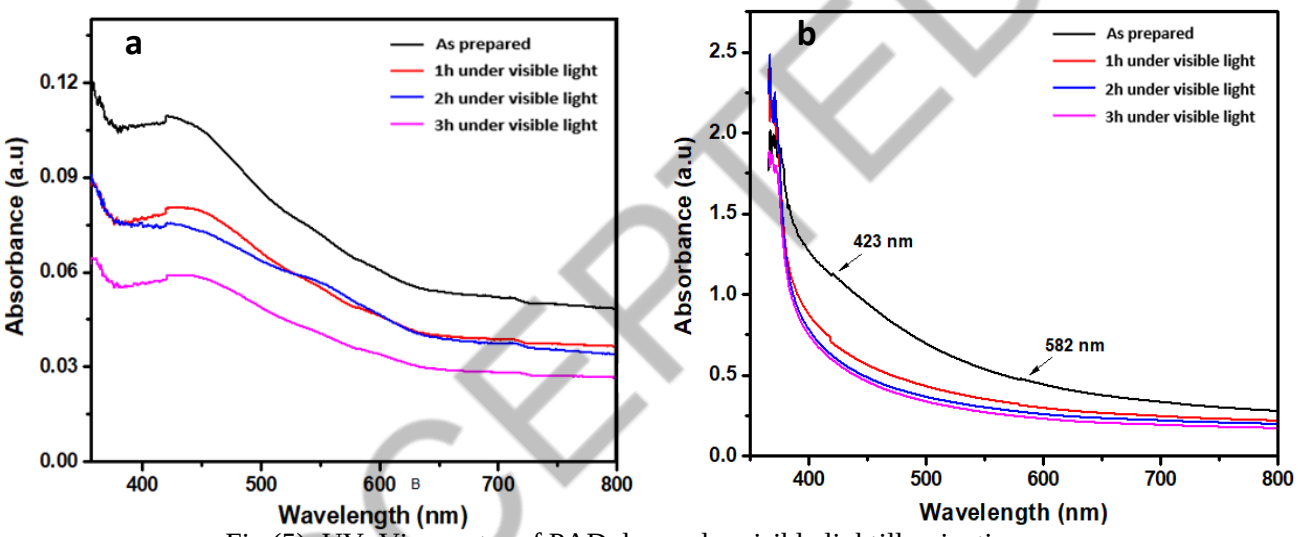

Fig.(5): UV–Vis spectra of PAD dye under visible lightillumination

(a) ZnO NPs and (b) ZnO NRs.

Conclusions: This research showed a simple way for creating highly efficient visible-light photocatalytic materials. Sol-gel and hydrothermal techniques were used to make ZnONPS and ZnONRs, respectively. Under visible light irradiation, physical combinations of ZnONPS and ZnONRs were used to photocatalytically degrade (2-(2-pyridal azo) 1,8-dihy droxynapthalene). ZnO NRS, with an average diameter of 99 nm showed high activity and removing 50.4 % of the azo dye. The first-order kinetics was used to model the breakdown of azo dyes on ZnO NRs. Furthermore, cycle experiments and radical scavenging tests on the degradation revealed that ZnO NRs has excellent photocatalytic performance and durability for an extended period, and superoxide ions are the major chemically reactive, indicating that azo dyes share a similar breakdown process.

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