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RESEARCH ARTICLE

Facile and fast preparation of Nano-rod ZnO for photocatalytic application under low intensity of UV light irradiation

Mac Van Hung[1], Vu Anh Tuan[1]*

1 School of Chemical Engineering, Hanoi University of Science and Technology, Vietnam. Tel.: (+84) 912.911.902

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***Corresponding author**.

Tel: (+84) 912.911.902
tuan.vuanh@hust.edu.vn

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Abstract

Objective: This study aims to degrade the organic dyes in aqueous medium and low UV intensity by nano-rod ZnO. **Methodology:** The ZnO was prepared by a facile and fast method, as-synthesized ZnO was characterized by SEM, XRD, N_2 adsorption/desorption isotherm, and diffuse reflectance UV-vis. The composition of samples before and after calcination steps was analyzed by XRD. The catalytic performance of ZnO was evaluated by the degradation of dyes in aqueous solution under a low UV light irradiation. **Finding:** the precursor was completely transformed to ZnO at 400 °C. The ZnO was nano-rod structure with the crystalline phase of hexagonal wurtzite. The degradation efficiency of ZnO for Janus Green B in 10 min was 96.8%, it was 95.8% in 40 min for Congo Red. The reaction kinetic of photodegradation of dyes was followed by the first-order kinetic model and the photodegradation mechanism of ZnO for dyes was proposed. **Application/Improvement:** The facile and fast method was developed for the synthesis of nano-rod ZnO, it could be applied for practical application in wastewater treatment.

Keywords: ZnO; dyes; photocatalyst; first-order kinetic; Nano-rod

1 Introduction

Today, the rapid development of industry leads to the release of large amounts of pollutants into the environment. Particularly, industrial wastewater contains a lot of toxic organic substances, it affects the ecosystem and human health if they are not treated before being discharged into the environment. Therefore, industries need to apply a suitable method for the treatment of wastewater to that it can be accepted within the permissible standards.

The UN World Water Development Report, in many developing countries, more than 70 percent of unprocessed industrial waste is discharged into water sources and contaminated water [(1)]. The largest sources of hazardous industrial wastewater come from mining, pulp mill, textiles, tanning, sugar mills, and pharmaceutical manufacturing [(2)]. In many cases, industrial wastewater not

only discharges directly but also infiltrates the ground causing groundwater contamination and underground wells.

Zinc oxide (ZnO) has been known to oxidize harmful organic substances in wastewater effectively under the UV light irradiation. It was reported that the photocatalytic ability of ZnO was strongly depended on the morphology and surface area in which the synthesis method played an important role $[3–5] Nanosize ZnO synthesized by facile and fast method showed the highly effective degradation of tartrazine under UV light[6]. The hierarchical flower-like ZnO could degrade caffeine under UV light irradiation, showing up to 97.6% degradation within 120 min for caffeine solution of 5 mg/L[7]. The nanowires ZnO was synthesized by the co-precipitation, when calcination temperature was varied, the grain size was changed, leading the variation of catalytic performance. The degradation efficiency of acid red 57 was 90.03% within 200 min at a calcination temperature of 400 °C and catalyst dosage of 2.5 g/L[8] . ZnO nanorods with an average length and diameter of 186 and 20 nm, respectively, prepared by hydrothermal method could degrade orange II at 10 mg/L, the catalyst dosage of 1 g/L and the degradation efficiency of 100% in 150 min[9].

To improve the catalytic performance of the catalyst, ZnO composites were developed by different methods. ZnO nanorod arrays on the surface of BiOI nanosheets were prepared by the two-step method with using PVP as the stability agent, the degradation efficiency of methyl orange increased from 18 to 37%[10]. CdS-ZnO@ZnS nanorods grown on reductive graphene oxide prepared via combining a hydrothermal growth and liquid-phase chemical conversion to improve the performance in H_2 production, the highest photocatalytic hydrogen production rate was 1865 μmol $h^{-1}.g^{-1}$[11] . RGO/ZnO/$ZnFe_2O_4$ composite prepared by a two-step method could degrade methylene blue at degradation efficiency was 100% in 60 min[12] . ZnO/RGO nanocomposites synthesized by the hydrothermal method exhibited the degradation efficiency of RhB of 100% at the concentration of 5 mg/L[13] . In the practical application in water treatment by photocatalytic catalyst, not only degradation efficiency but the cost of material related the synthesis method and the energy consumption play an important role for each type of catalyst.

The object of this study is a synthesis of nano-rod ZnO by facile and fast precipitation method for degradation of dyes under UV light irradiation with a low intensity of 15W. Physical properties of ZnO were characterized by XRD, SEM, FT-IR, UV-vis diffuse reflectance, and N_2 adsorption/desorption isotherm. The photocatalytic performance of as-prepared samples was evaluated for degrading Janus Green B, Methylene Blue, Tartrazine, Congo Red, and Nile Blue.

2 Experimental

2.1 Materials

Janus Green B (JGB, 99%), Methylene Blue (MB, 99%), Tartrazine (TA, 99%), Congo Red (CR, 99%), and Nile Blue (NB, 99%) were purchased from Sigma-Aldrich Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99.5%) and hexamethylene tetramine (HMTA) (99%) were purchased from China. All chemicals were used without any further purification and distilled water was used in all the experiments.

2.2 Synthesis of Nano-rod ZnO

In a typical procedure for the synthesis of ZnO nanoparticles, 0.1 mol $Zn(NO_3)_2.6H_2O$ and 0.1 mol Hexamethylene tetramine were dissolved in a beaker with 100 mL distilled water to form a clear solution. The solution result was stirred in 20 min, and then heated up to 90 °C and kept at this condition for 1 h. The precipitate was filtered and washed several times with distilled water, and then dried at 80°C overnight, the white solid was denoted as ZHC. Finally, ZHC was calcined at 400°C for 2h with heating rate 1°C/min, the pure ZnO nanoparticles were obtained.

2.3 Characterization

The crystalline phase of sample was investigated by X-ray power diffraction. XRD pattern was obtained by using Bruker D8 Ax XRD-diffractometer (Germany) with Cu Kα irradiation (40kV, 40 mA). The 2θ ranging from 10° to 80° was selected to analyze the crystal structure. The morphology of the sample was observed by field

emission scanning electron microscopy (FE-SEM, JEOL-7600F). The textural properties were measured via N_2 adsorption/desorption isotherms using a Micro metrics (Gemini VII analyzer). The specific surface area, pore volume and pore diameter were obtained by using the Brunauer-Emmett-Teller (BET) method. Diffuse reflectance UV-vis spectra of the as-synthesized sample were measured on a UV-vis-NIR spectrometer (Cary 500).

2.4 Photodegradation of dyes by nano-rod ZnO

The photodegradation of dyes on the catalyst was carried out by batch test. Typically, 50 mg of catalyst was added into a 250 mL glass beaker containing 100 mL of a dye 10 mg/L. At given time intervals of 10 min, 2 mL of samples were withdrawn from the suspension and then filtered by a syringe filter (0.45 μm PTFE membrane) to remove the catalyst. The dye concentration of the filtrate was analyzed by a UV-Vis spectrophotometer (Agilent 8453) at the maximum absorbance wavelength of dye.

$$Degradation\ efficiency\ (\%) = \frac{C_{0-}C_t}{C_o} \times 100\ \% \tag{1}$$

The photodegradation rate of dye on catalysts can be evaluated by using the pseudo-first-order model as follow:

$$\ln \frac{C_0}{C_t} = kt \tag{2}$$

Where C_0 and C_t are the concentration of JGB at initial (t =0) and time t (min), respectively. k is the pseudo first-order rate constant. The k value was calculated from the slope of the ln (C_0/C_t) – t plots.

3 Results and discussion

3.1 SEM analysis

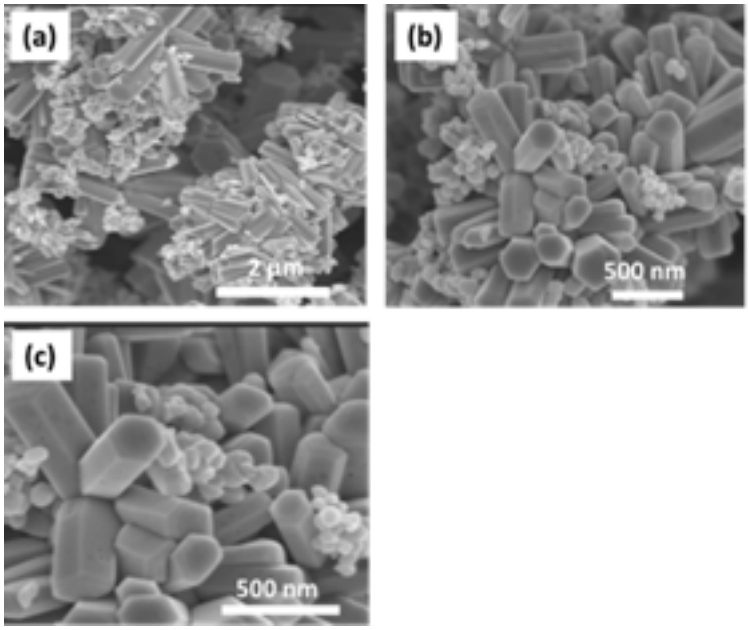

Fig 1. (a-c) SEM images of nano-rods ZnO with the different scale bars.

The SEM images of as-synthesized ZnO are depicted in Figure 1 . ZnO was observed as a spherical aggregation with 2-3 μm in size (Figure 1(a) and (b)), it was assembled from many hexagonal rods, approximately width of

100-150 nm and length of 400 nm in Figure 1(c). Thus, exception of the ZnO particles are shaped like nanoneedles, nanowires, nanobelts, nanosheet, nano flower, etc., the nanorods ZnO is expected as a great morphology for the photocatalytic application process.

3.2 XRD analysis

Figure 2 shows the XRD patterns for the ZHC and ZnO samples. The peaks at 2θ = 14.5 of ZHC was associated with the (200) plan, which was consistent with the hydroxide carbonate $[Zn_5(CO_3)_2(OH)_6]$ (JCPDS 19–1458)[14,15]. Themain peaks of ZnO were identified at 2θ = 31.7, 34.4, 36.2, 47.5, 56.6, 62.8 and 67.9 ° revealed the diffraction of hexagonal wurtzite phase[16]. It indicated that the precursor was completely transformed to ZnO at 400 °C. Based on the XRD results, the formation of $[Zn_5(CO_3)_2(OH)_6]$ and ZnO can be an be expressed by the following equations:

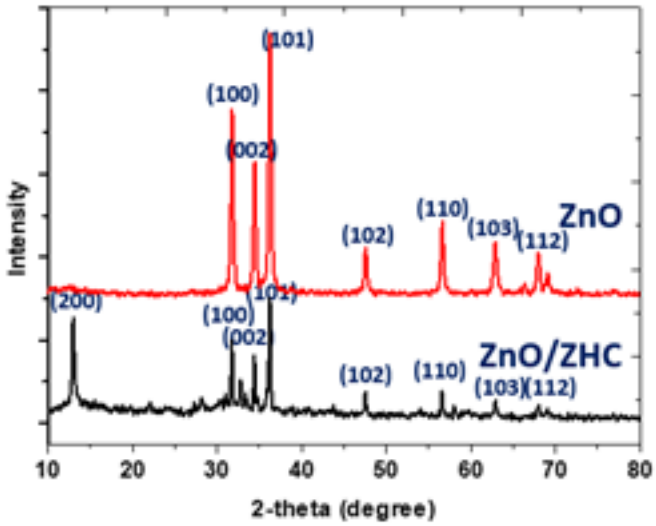

Fig 2. XRD patterns of ZHC and AC.

$$(CH_2)_6N_4 + H_2O = 6HCHO + 4NH_3 \quad (3)$$

$$NH_3 + H_2O = NH_4^+ + OH^- \quad (4)$$

$$Zn^{2+} + 2OH^- = Zn(OH)_2 \quad (5)$$

$$Zn(OH)_2 + 2OH^- = Zn(OH)_4^{2-} \quad (6)$$

$$Zn(OH)_4^{2-} = ZnO + 2OH^- + H_2O \quad (7)$$

$$Zn^{2+} + 10OH^- + 2CO_2 = Zn_2(CO_3)_2(OH)_6 + 2H_2O \quad (8)$$

3.3 N_2 adsorption/desorption isotherm analysis

The N_2 adsorption/desorption isotherm was conducted to investigate the porosity of the material, including its specific surface area and pore sizes. The isotherm and pore size distribution curves nano-rod ZnO sample are presented in Figure 3. The isotherm curve was identified as type IV. When the relative pressure (P/P_o) increased from

0.91 to 0.98, a sharp hysteresis loop was observed, indicating the presence of mesoporous material. Besides, when the relative pressure was higher than 0.98, an abrupt increase in the amount of adsorbed nitrogen was observed. The pore size distribution was relatively wide and most of the pores in a range from 15 to 100 nm. As a result, the ability to diffuse and efficiently transport hydroxyl radicals in photochemical reactions enhances the catalytic activity of the ZnO material[17,18]. Thesurface area and average pore size of as-prepared ZnO were 24.4 m^2/g and 0.280 cm^3/g, respectively.

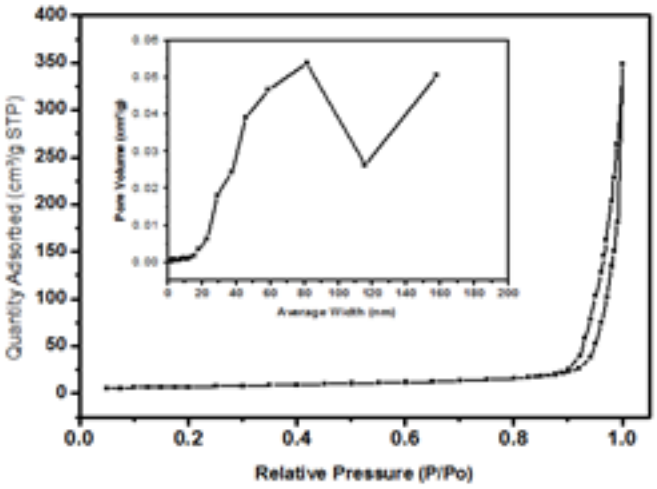

Fig 3. N_2 adsorption/desorption isotherm (inset:pore size distribution) of as-synthesized ZnO.

3.4 UV-vis diffuse reflectance

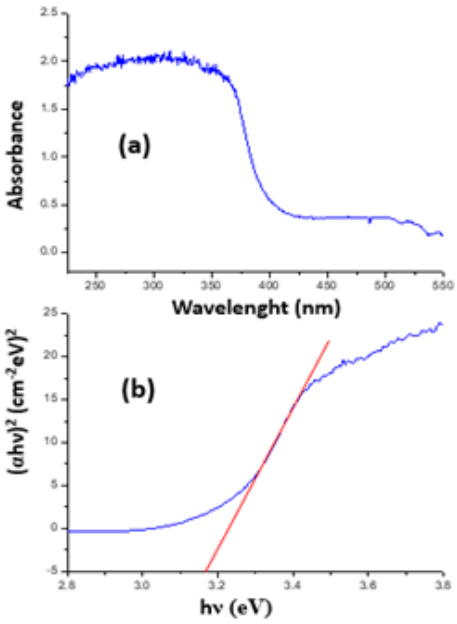

Fig 4. (a) UV-vis diffuse reflectance spectra and (b)Tauc's plot of the ZnO.

Figure 4 shows the UV-vis diffuse reflectance spectra and Tauc's plot of the ZnO sample. ZnO showed a relatively high absorption at wavelength from 230-350 nm, then it significantly decreased at a wavelength from 350-400 nm and showed a stability at above 400 nm, in Figure 4(a). The hν values were plotted against $(\alpha h\nu)^2$ and extended to calculate the band gap energy of the as-prepared ZnO by the Tauc's method[19] , the results are presented in Figure 4(b). The band gap energy of ZnO was 3.16 eV, showing a low value as compared to the literature value (3.37 eV) in the previous report[20] . The lower band gap value can facilitate the transfer of electrons from the valence band to the conduction band, leading to speed up the photocatalytic process.

3.5 Photocatalytic degradation mechanism of dyes on ZnO

The photocatalytic activity of the as-prepared ZnO sample was evaluated by degrading some of organic dyes such as Methylene Orange, Tartrazine, Nile Blue, Janus Green B, and Congo Red under a low UV irradiation. The reaction conditions were fixed, the catalyst dosage of 0.5 g/L, dye concentration of 10 mg/L, pH=6.5, the results are presented in Figure 5 and Table 1 . Congo Red was rapidly degraded in 10 min and Janus Green B was almost removed in 40 min, the degradation efficiencies of Congo Red and Janus Green B were 96.8 and 95.8%, respectively. And, the reaction rates of Congo Red and Janus Green B were 0.306 and 0.48 min^{-1}, respectively. While, the degradations of Nile Blue, Tartrazine, and Methylene Blue were slow, the degradation efficiencies and reaction rates were lower than those of Congo Red and Janus Green B, as seen in Table 1.

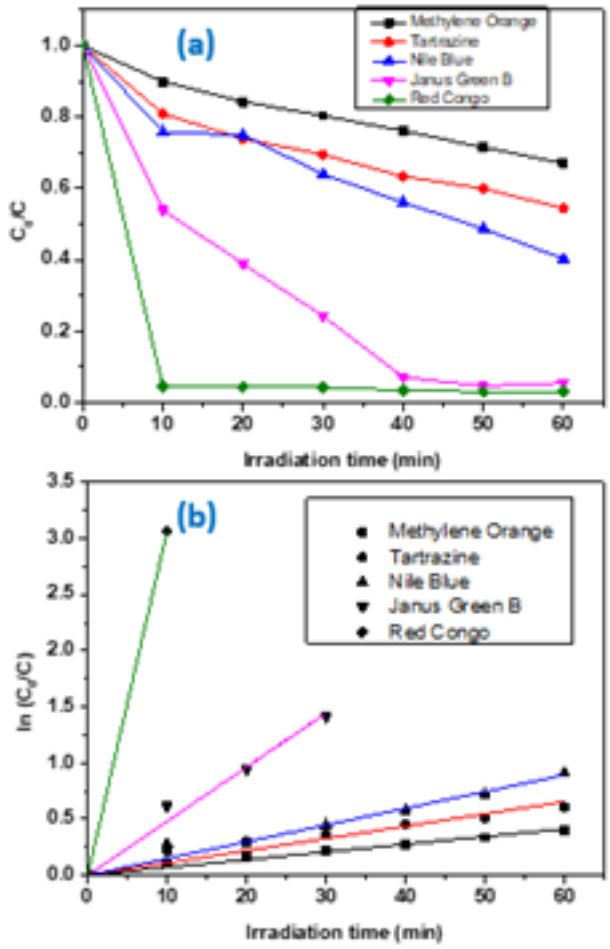

Fig 5. (a).Degradation of some organic dyes on ZnO: [catalyst] = 0.5 g/L, [dye]= 10 mg/L,and (b) the kinetic curves.

Table 1. Kinetic parameters and degradation percentage of some synthetic dyes.

Organic dyes	K (min^{-1})	R2	Degradation efficiency (%)
Methylene Orange	0.007	0.992	32.9
Tartrazine	0.011	0.976	45.6
Nile Blue	0.015	0.990	59.7
Janus Green B	0.048	0.992	95.8
Congo Red	0.306	1	96.8

3.6 Comparison of degradation of dyes by as-prepared ZnO with other catalysts

Since ZnO have been prepared by different methods for many applications such as cosmetic, paint, sensor, adsorption, and photocatalyst. Besides, the performance of a photocatalyst depends not only on morphology, surface area, capillary structure, and defect content but also on the reaction conditions. Hence, the absolute comparison of the performance of as-synthesized ZnO with other materials in previous reports is challenging. In this study, the nano-rod ZnO has a relatively large surface area and pore volume, the ZnO exhibits the spherical ZnO nanoparticles in the structure as presented in Figure 1. These may result in higher degradation efficiency and reaction rate as compared to other morphologies[21–25], as seen Table 2.

Table 2. Comparison as-prepared ZnO with other samples.

ZnO samples	Particles Size	Application	Performance	Ref.
Flower	1 μm	-	-	[21]
Flower	1-2 μm	Bromop-enol dye removal	96% within 120 min, concentration of 10 ppm	[22]
Rod	80-100 nm	RhB removal	97 % within 120 min, concentration of 10 ppm	[23]
Nano-spheres	15-60 nm	RR141 removal	78% within 240 min, concentration of 10 mg/L	[24]
Nano disks	~ 200 nm	RhB removal	90 % within 90 min, concentration of 10 ppm.	[25]
Nano-Rods	width: 100-150 nm, length: 400 nm	Congo Red Janus Green B	96.8 %, within 10 min, for Congo Red 95.8%, within 40 min, for Janus Green B	This study

3.7 The mechanism of photocatalyst for degradation of dyes

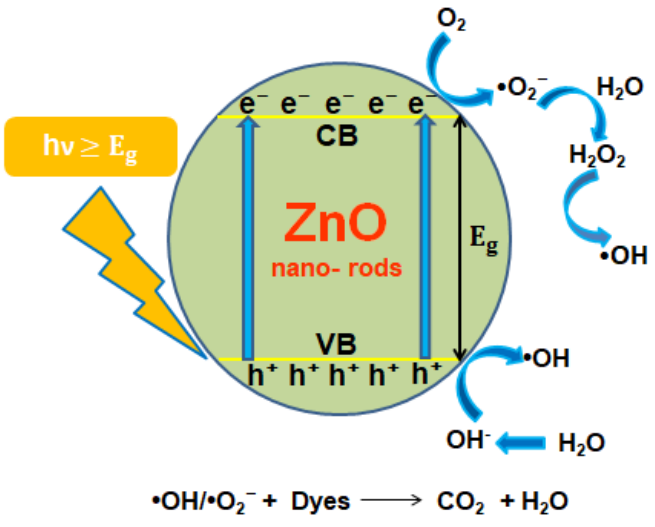

Fig 6. Mechanism of photodegradation of dyes by nano-rods ZnO under UV light

Since band gap energy (3.16 eV), the nano-rod ZnO show high reaction rate and degradation efficiency with dyes, as present in Figures 4 and 5. The mechanism for the photocatalyst activity of flower-like was proposed, as shown in Figure 6.

Upon the UV light irradiation, the electrons in the valence band of ZnO can be excited to the conduct band, leaving holes in the valence band. The electrons can active molecular oxygen to form superoxide ion (O_2^-) and the photogenerated holes react with either water (H_2O) or hydroxyl ions (OH^-). The formation of $^\bullet OH$, $^\bullet O_2^-$ radicals water have created hydroxylation, oxidation and mineralization processes, as described by equations 9-14[26–29]. Which can degrade dyes to intermediated products, CO_2 and H_2O.

Water is dissociated into ions

$$H_2O \rightarrow H^+ + OH^- \tag{9}$$

ZnO can absorb UV light (or solar light) and generate electron-hole pairs (Figure 6)

$$ZnO + hv \rightarrow e^- + h^+ \tag{10}$$

The electrons move to the surface of the catalyst and adsorbed O_2 on the surface to form $\bullet O_2^-$

$$e^- + O_2 \rightarrow {}^\bullet O_2^- \tag{11}$$

The $^\bullet O_2^-$ can react with surface adsorbed H_2O to form H_2O_2:

$$e^- + {}^\bullet O_2^- + 2H_2O \rightarrow 2H_2O_2 \tag{12}$$

Photoconversion of H_2O_2 gives $^\bullet OH$ radicals:

$$H_2O_2 + hv \rightarrow 2\,{}^\bullet OH \tag{13}$$

The holes react with OH^- ions in the water form OH radicals:

$$h^+ + OH^- \rightarrow {}^\bullet OH \tag{14}$$

4 Conclusion

Nano-rod ZnO was successfully prepared by the facile and fast method. ZnO had a hexagonal rod structure, approximately a width of 100-150 nm and a length of 400 nm. The surface area and pore volume were 24.4 m^2/g and 0.280 cm^3/g, respectively. Band gap energy of ZnO was 3.16 eV. Nano-rod ZnO had a high reaction rate and degradation efficiency for dyes, showing the degradation efficiency for Janus Green B in 10 min of 96.8% and Congo Red in 40 min of 95.8% in 40 min. These were compared to other morphologies of ZnO in literatures. In addition, the photodegradation of dyes by nano-rod ZnO was proposed.

Acknowledgments

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