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A Green and Facile Hydrothermal Synthesis of ZnO Nanorods for Photocatalytic Application

Sze-Mun Lam[1]* and Jin-Chung Sin[2]

[1]*Department of Environmental Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Malaysia*

[2]*Department of Petrochemical Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Malaysia*

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***Corresponding author:** Sze-Mun Lam, Department of Environmental Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan University, Malaysia, Tel: +60 5468 8888; Email: lamsm@utar.edu.my

Abstract

ZnO nanorods were prepared via a green and facile hydrothermal approach using ZnO powder and 30 vol% H_2O_2 aqueous solution. X-ray diffraction results revealed that the synthesized ZnO product was highly crystalline having hexagonal wurtzite structure. The band gap energy of ZnO nanorods was determined to be 3.28 eV using optical reflectance spectrum. The rod-like morphological features of ZnO nanostructures were observed from microscopy analyses. A possible formation mechanism was also proposed. The synthesized ZnO product showed an enhanced UV photocatalytic performance compared to that of commercial TiO_2 for the resorcinol degradation. There was an optimal photocatalyst amount of 1.0 g/L, at which the degradation efficiency of resorcinol was completely degraded under exposure of UV light for 120 min. The active hydroxyl ($\cdot$OH) radicals formed during the photocatalytic process were tested using a photoluminescence-terephthalic acid (PL-TA) measurement, which were validate to be significantly affected by the photocatalyst amount. Other organic pollutants including phenol, bisphenol A and methylparaben could also be photodegraded in the presence of similar conditions. These features demonstrated the ZnO nanorods practical applications in environmental remediation.

Keywords: Semiconductors; Nanocrystalline Materials; Optical Materials; Properties; Photocatalysis

Introduction

Zinc oxide, a typical kind of II-IV compound semiconductor with a wide band gap (3.37 eV) has garnered much attention due to its wide potential applications in luminescence, sensors, solar cells, surface acoustic wave filters and in gas and liquid phase pollution control [1-3]. In most of the catalytic applications, high surface area and optimum pore size are needed for interaction with active sites and diffusion of reactive species [4,5], this led to the huge interest in the development of one-dimensional (1D) ZnO nanostructures such as nanotubes, nanowires, nanobelts, nanorods and etc. In particular, the quick recombination of charge carriers resulted in waste of energy supplied by the photon can be considered as one of main factors influencing efficiency of the photocatalytic process.

Several researchers have proposed that the charge carrier recombination effect can be greatly reduced in nanorods architecture compared to nanoparticles and should be favoured in photocatalytic applications [4-6]. Moreover, the large specific surface area as well as good dispersibility in solution rate has given ZnO nanorods a superior platform. ZnO nanorods are used extensively in the research of ultraviolet photodetectors, field effect transistors, light emitting device arrays and photocatalytic applications [7,8]. In literature, rod-like ZnO nanoparticles can be synthesized using different methods such as template-assisted growth, electrodeposition, chemical vapour deposition (CVD), thermal evaporation, hydrothermal method and so on [1,8-10]. Each fabrication method has its own distinctive advantages and functional features. Hydrothermal method is of particular interest because nanorods can be produced in an unsophisticated manner at low temperatures and through simple chemical synthesis routes.

In this work, we developed a green hydrothermal method to fabricate ZnO nanorods without any organic solvent or surfactant. This method used ZnO powder and 30 vol% H_2O_2 aqueous solution as the starting materials. In addition, the synthesis method was environmental friendly since no use of toxic reactants and no release of unwanted by-products and pollution. The fabricated samples were characterized by different techniques such as such as X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and UV-vis diffuse reflectance spectroscopy (DRS) measurements. The hydroxyl ($\cdot$OH) radicals concentration for different ZnO nanorod amounts were evaluated upon the photocatalytic processes. More importantly, the prepared ZnO nanorods displayed high photocatalytic activities on the degradation of organic pollutants

such as resorcinol, phenol, bisphenol A (BPA) and methylparaben (MP) under UV light irradiation.

Materials and Methods

Synthesis of ZnO Nanorods

All the chemical reagents used in our experiments are analytically pure and purchased from Acros Organics. In a typical procedure, 2.0 g of ZnO powder was weighted into a Teflon-lined stainless steel autoclave of 200 mL capacity, to which 150 mL of 30 vol% H_2O_2 aqueous solution was added under ultrasonic condition. The autoclave was sealed and maintained at 180°C for 24 h and then allowed to cool to room temperature naturally. The as-formed precipitates were filtered, washed with distilled water and dried at 60°C for 12 h.

Analytical Techniques

The obtained samples were characterized using X-ray diffraction (XRD) pattern using a Philips PW1820 diffractometer with Cu Kα radiation at a scanning rate of 2° min-1 in the range of 20°-80°. Transmission electron microscopy (TEM) image was analyzed using a Philips CM-12 operated at 120 keV. High resolution transmission electron microscopy (HRTEM) image was taken on a Fei Tecnai 20. UV-vis diffuse 9reflectance spectrum (DRS) was measured using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. The spectra were recorded timely in the range of 200-800 nm using $BaSO_4$ as the reference standard.

Photocatalytic Test

All experiments were carried out in a batch-mode immersion well photoreactor. The photoreactor was made of Pyrex glass with dimensions of 200 × 100 × 60mm (height × outer diameter × inner diameter). In the center of the cylindrical photoreactor, a 15 W UV Pen-ray (UVP, Inc.) lamp with a maximum emission at about 365 nm was applied as the UV source. The average UV output intensity at 10 mm away from UV light, measured by radiometer (Cole Parmer, Series 9811) was 1.060 mW/cm^2. The temperature of the system was maintained at 26 ±2°C by cooling the water jacket. In a typical experiment, the catalyst (100 mg) was added in 100 mL resorcinol solution (10 mg/L) in a beaker. The mixture was subjected to magnetic stirring for 1 h in the dark prior to the exposure of light irradiation. At specific time intervals, 2 mL of the sample was removed from the system, centrifuged and the resorcinol concentration at different time intervals was evaluated by a high performance liquid chromatography (HPLC) (Perkin Elmer Series 200). The HPLC unit consisted of isocratic pumps from Varian with a UV-vis detector. C_{18} column (150 mm-length x 4.6 mm-ID x 5 µm particle size) was used in sample analysis at a flow rate of 1 mL/min. The photodegradation of other organic pollutants including phenol, BPA and MP in the presence of prepared samples were monitored based on our previous report [1].

Results and Discussion

Characterization of photocatalyst

Figure 1a presents the XRD pattern of the ZnO samples. As can be seen, the sample was identified as ZnO hexagonal wurtzite structure with the main diffraction peaks at 2θ = 31.8°(100), 34.4°(002), 36.2°(101), 47.5°(102), 56.6°(110), 62.8°(103), 66.4°(200), 67.9°(112) and 69.1°(201) (JCPDS file No. 36 -1451) [4,11]. No peaks belonging to any other phase were detected, indicating the high purity of the products. The UV-vis DRS spectrum of the ZnO samples (Figure 1b) depicted a steep absorption edge which lay between 370 and 390 nm without any other absorption peak. The observed region was a characteristic region for the absorption band of the wurtzite hexagonal phase of ZnO [12]. The band gap energy of the ZnO products can be obtained from the plot of $(F(R)hv)^{0.5}$ versus photon energy (E_{phot}). The band gap energy was determined to be 3.28 eV (inset of Figure 1b), which was consistent with that reported for ZnO nanorods [4,12-19].

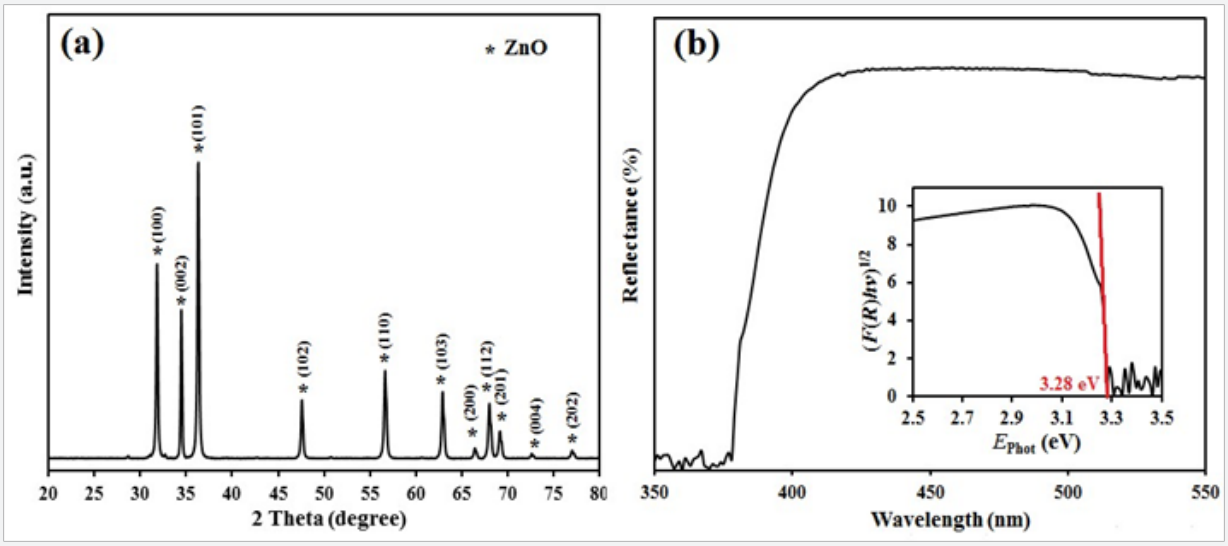

Figure 1: XRD pattern (a) and UV–vis DRS spectrum (b) and plot of $(F(R)hv)^{0.5}$ vs E_{phot} (hv) of (inset of b) of rod-like ZnO nanostructures.

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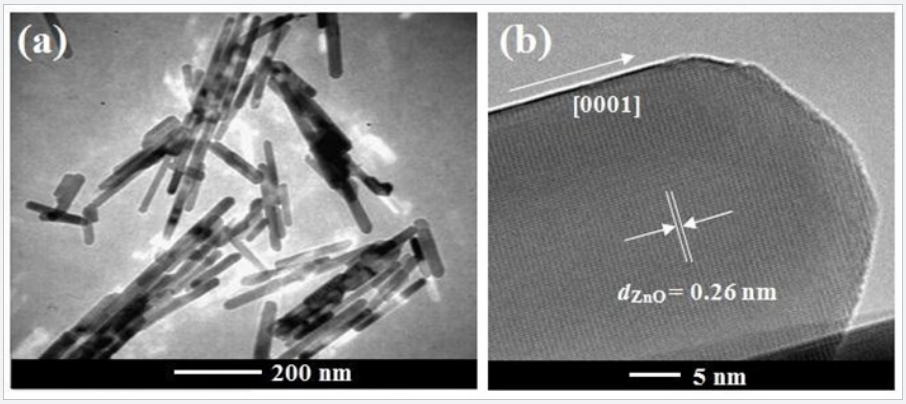

Figure 2: TEM (a) and HRTEM (b) images of rod-like ZnO nanostructures.

Figure 2a shows the TEM image of the as-prepared ZnO products. It was clear that the products were rod shaped and have a smooth surface. The nanorods exhibited diameters of around 10 nm and lengths of up to 200 nm. The clear lattice fringes in the HRTEM image (Figure 2b) revealed that the as- prepared ZnO nanorods were well-crystallized. The measured interplanar spacing of about 0.26 nm corresponded to the d-spacing of the (002) crystal plane of wurtzite structured ZnO, which inferred that the nanorod grew along the [0001] direction.

Formation of Rod-Like ZnO Nanoparticles

To understand the formation process of nanorods, temperature-dependent morphology evolution experiments were carried out. Figure 3a displays the TEM images of the microstructural characteristic of the products as a function of hydrothermal temperature. After the heat treatment at 60°C, the ZnO nanoparticles turn into small spherical shaped ZnO_2 (Figure 3a). These particles were interconnected and formed into agglomerated granules. Hydrothermal treating of ZnO at 100°C allowed the samples to slowly convert the composition of the ZnO_2 to ZnO. Figure 3b shows the TEM image of that few nanorods were produced and interconnected compactly in the granules of ZnO_2. The complete transformation of the ZnO_2 to ZnO was achieved by hydrothermal treatment after 140°C. Figure 3c presents a large number of rod-like ZnO nanoparticles. Further increasing the temperature to 180°C, ZnO rod-like structures with the longer lengths ranging from several hundred nanometers to several micrometers were obtained (Figure 3d).

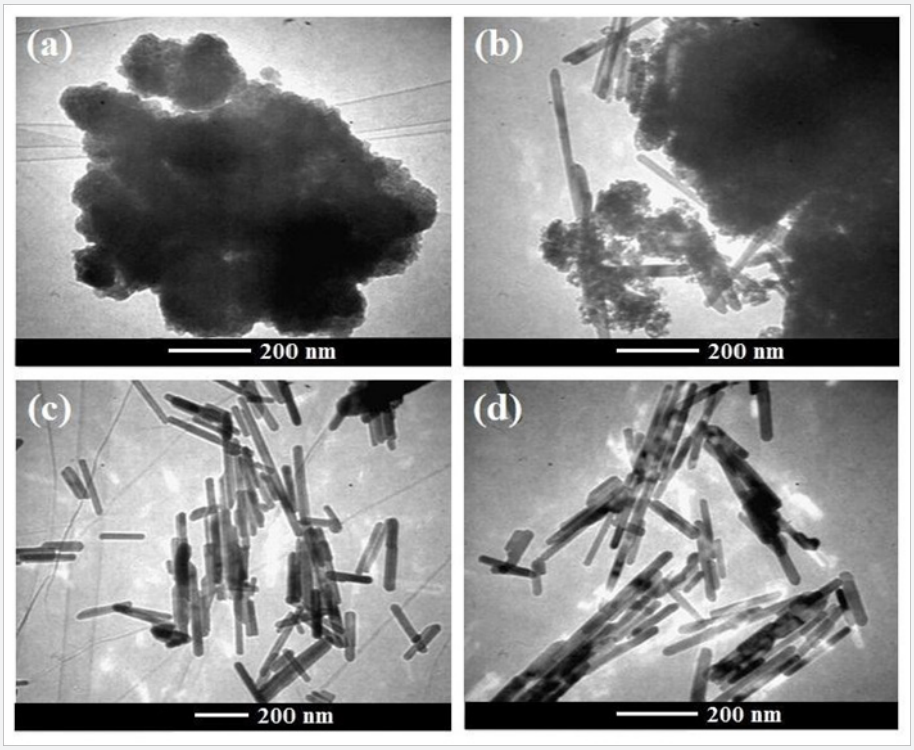

Figure 3: TEM images of the samples treated at different growth stages: (a) 60°C; (b) 100°C, (c) 140°C and (d) 180°C.

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On the basis of studies mentioned above, it can be concluded that the formation of such rod-like structure was achieved via a nucleation-growth process. In hydrothermal synthesis, the starting materials used were only ZnO powder and 30 vol.% H_2O_2 aqueous solution and ZnO_2 was the sole resulting solid. Thus, it was believed that the formation of ZnO_2 may be formed as shown in Eq. (1). Due to no valence change of Zn and O occurred, the formation of ZnO_2 was just through a precipitation conversion reaction [13]. That was ZnO powder increasingly dissolved in the H_2O_2 aqueous solution under the relatively high temperature and high pressure hydrothermal environment, resulting in the formation of Zn^{2+} ions. At the same time, peroxide anions (O_2^{2-}) would be produced from the dissociation of H_2O_2 in water according to Eq. (2).

$$ZnO + H_2O_2 \rightarrow ZnO_2 + H_2O \quad \text{(nucleation)} \quad (1)$$

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \leftrightarrow 2H^+ + O_2^{2-} \quad (2)$$

When the concentration of Zn^{2+} and O_2^{2-} reached the saturation level, ZnO nuclei were formed. It was considered that the as-fabricated ZnO_2 nuclei may serve as building blocks for the formation of single crystal growth of ZnO_2 [4,12,13]. With reaction time under proper heating conditions, the ZnO_2 nuclei concentration increased which led the growing of ZnO_2 nanocrystals into rod-like structures. Nevertheless, the as-fabricated ZnO_2 nanorods were thermally unstable and would thoroughly decompose into ZnO and O_2 when hydrothermally treated at ≥ 140°C as shown in Eq. (3).

$$2ZnO_2 \rightarrow 2ZnO + O_2 \quad (3)$$

Photodegradation of Resorcinol via ZnO nanorods

To evaluate the photoactivity of the products, the photodegradation of resorcinol was carried out under UV light irradiation. Resorcinol was chosen as the model substrate since it is a well-known endocrine disrupting chemical (EDC) widely used in the manufacture of adhesives, dyes, in food processing, pharmaceuticals, etc [14]. Exposure of resorcinol can occur at its production sites, in effluent streams, through its use in pharmaceutical applications and in cigarettes [15]. The results in Figure 4a showed that the resorcinol in aqueous solution was completely degraded by ZnO nanorods after 120 min irradiation. For comparison, direct photolysis of resorcinol and resorcinol degradation over commercial TiO_2 were also conducted under the similar conditions. It was clear that the decrease in the resorcinol concentration without photocatalyst was negligible and about 92.5% resorcinol was degraded in the presence of commercial TiO_2. It implied that the as-prepared ZnO nanorods were active photocatalysts.

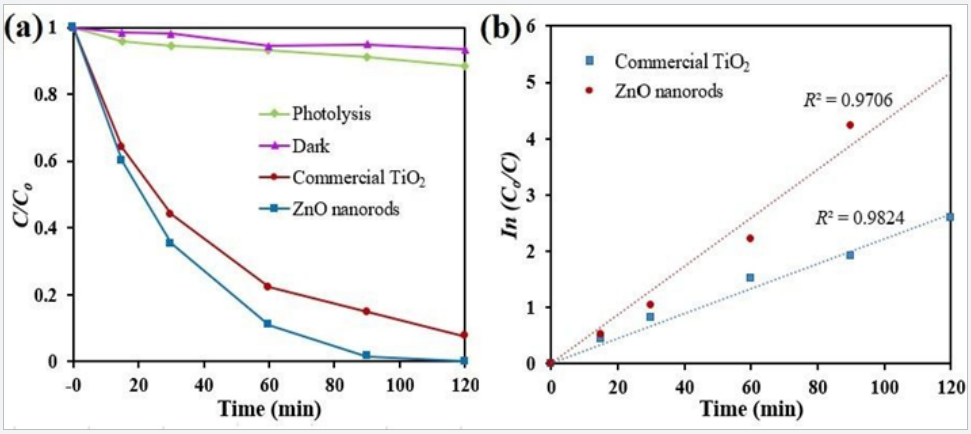

Figure 4: (a) C/C_o versus time curves of photodegradation of 10 mg/L resorcinol under various experimental conditions and (d) kinetic studies of the resorcinol degradation at different time intervals.

The kinetics of resorcinol degradation reactions are presented in Figure 4b, which followed pseudo- first-order kinetics in agreement with the literature [2,3,8]. For a first-order reaction, $-dC/dt = kt$, or $\ln (C_o/C) = kt$, where C_o is the equilibrium concentration of resorcinol after 1 h dark adsorption, C is the concentration of resorcinol remaining in the solution at irradiation time t and k is the observed rate constant. A plot of $\ln(C_o/C)$ versus t generated a straight line and the slope was the k. As shown in Figure 4b, the linear relationship was achieved with more than 97% linear fit (R^2), revealing an excellent concurrence with the given model. The k values for the ZnO nanorods and commercial TiO_2 were calculated to be 0.043 and 0.022 min^{-1}, respectively.

Influence of Photocatalyst Amount

The influence of the photocatalyst amount on the degradation of resorcinol was investigated at different ZnO nanorods under UV light irradiation (as recorded in Figure 5a). When the amount of photocatalyst at 1.0 g/L, a complete degradation of resorcinol was achieved, which was higher than that at 0.25, 0.5 and 2.0 g/L. Higher amount of photocatalyst indicated more availability of total active sites or surface area of the photocatalyst. A decline in degradation efficiency was typically found at photocatalyst overloading because of optical opaque and agglomeration of the excess photocatalysts in the solution. This indicated that an optimal photocatalyst amount was 1.0 g/L. The kinetic results

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are illustrated in Figure 5b. The results clearly comfirmed the optimal photocatalyst amounts 1.0 g/L with the maximal degradation rate as compared to those of other photocatalyst amounts.

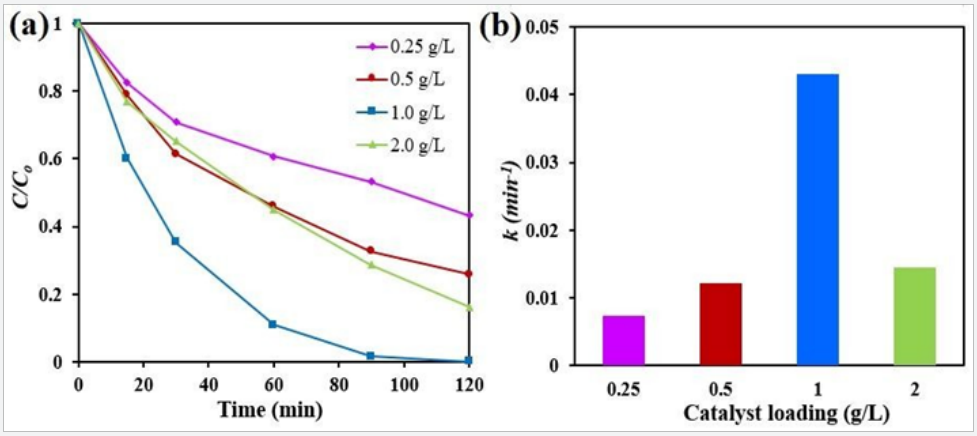

Figure 5: (a) Photodegradation of 10 mg/L resorcinol at different photocatalyst amounts and (b) kinetic contants for photodegradation of resorcinol under UV light irradiation.

Hydroxyl radicals as Active Species

Photocatalyst-based catalytic mechanism included a portion of photogenerated charge carriers reacted with adsorbed O_2 and H_2O to form active species such as •OH radicals that further partook in the degradation of organic pollutant [16-19]. The generated •OH radicals over ZnO nanorods in the photocatalytic reaction can be evaluated by PL technique with terephthalic acid (TA) as a probe molecule. The generated •OH radicals in the photocatalytic reaction could readily react with TA and produce the highly fluorescent compound, 2-hydroxyterephthalic acid (2HTA) as shown in Eq. (4) [1].

$$\bullet OH + TA \rightarrow HO-TA(2HTA) \quad (4)$$

Figure 6 displays the PL spectra changed observed during the irradiation of the as-prepared ZnO nanorods in the aqueous basic solution of TA. Generally, PL intensity at about 425 nm was accordance to the amount of generated •OH radicals. It can be clearly seen that the amount of generated •OH radicals on 1.0 g/L ZnO nanorods were larger than those of other samples. This result was also consistent with the results of photocatalytic test in Figure 5.

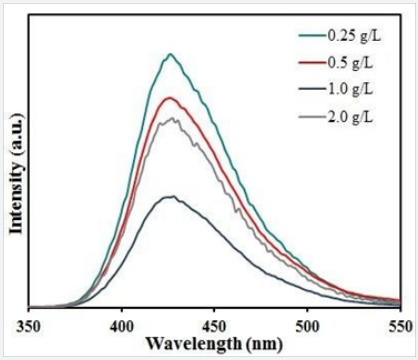

Figure 6: PL spectra of ZnO nanorods at different photocatalyst amounts in basic TA solution for 60 min of irradiation.

Photodegradation of Various Pollutants

In addition to resorcinol degradation, the ZnO nanorods could be utilized in photodegradation of other organic pollutants as shown in Figure 7. Phenol and bisphenol A (BPA) were effectively degarded under the same experimental conditions as those in the degradation of resorcinol. The results indicated that the ZnO nanorods not only can degrade the resorcinol but also can degrade the other non-absorbing visible organic compounds. When ZnO nanorods were added into the phenol and BPA solutions, the degradation efficiencies were found to be 81.4% and 87.2%, respectively. For methylparaben (MP), the ZnO nanorods increased the degradation efficiency from 4.5% (for photolysis alone) to 62.8% in 120 min. Obviously, ZnO nanorods indicated different photoactivities in degradation of various organic pollutants and however, it could improve the degradations of all pollutants aforementioned owing to their photocatalytic ability.

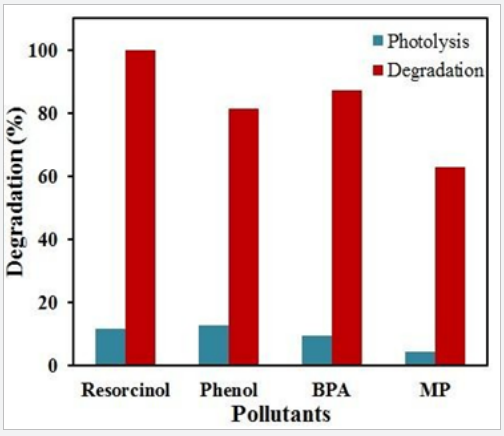

Figure 7: Photodegradation of (a) resorcinol, (b) phenol, (c) BPA and (d) MP under UV light irradiation (photocatalyt amount: 1.0 g/L; volume of pollutant: 100 mL; concentration of pollutant: 10 mg/L; treatment time: 120 min).

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Conclusion

ZnO nanorods were successfully synthesized via a facile and green hydrothermal method using ZnO powder in 30 vol% H_2O_2 aqueous solution. The as-synthesized samples have been analyzed in details which indicated well crystalline, good optical property and special morphologies. The possible reaction and growth mechanism was also discussed based on microscopic results. It displayed superior photocatalytic activity compared to the commercial TiO_2 for the resorcinol degradation. The amount of ZnO nanorods of about 1.0 g/L has resulted in the superior degradation rate of resorcinol solution at which the generated ·OH radicals showed their maximum as shown in the PL-TA test. These nanorods could be utilized in photodegradation of organic pollutants such as resorcinol, phenol, BPA and MP. These provide the photocatalytic system practicality in degrading various organic pollutants.

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