A Surfactant-Free Synthesis Technique of Coral-Like Zno Hierarchical Structures for Photocatalytic Degradation of Resorcinol under UV Irradiation

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Abstract. Hierarchical coral-like ZnO structures were successfully prepared by a surfactant-free wet chemical method. Various characterization tests were carried out to analyze the as-prepared ZnO samples. The coral-like ZnO was used to degrade resorcinol at three different solution pH values (pH 5.0, pH 8.0 and pH 11.0). It was observed that the resorcinol adsorption onto the ZnO was strongly dependent on the electrical charge properties of both photocatalyst and resorcinol. Photocatalytic degradation of resorcinol reached the highest at pH 11.0 due to high concentration of hydroxyl ions for hydroxyl radicals generation.

1. Introduction

Advanced oxidation process using semiconductor photocatalysts has garnered much interest in recent years due to its efficiency of conversion of solar energy into chemical energy in various applications including degradation and complete elimination of environmental pollutants [1,2]. Among various oxide semiconductor photocatalysts, considerable efforts have been made to synthesize diverse nanoscale semiconductor materials (nanorods, nanoparticles, nanoneedles and nanosheets) with controlled morphologies and dimensions [3,4]. Recently, hierarchical structures combined the features of nanoscale building blocks have been found to be attractive class of materials owing to their unique properties and peculiar structure different from those of mono-morphological structures [3,5,6]. Studies have revealed that hierarchical structures were more structurally stable to hinder the aggregation of particles and offered larger number of surface activation sites for photocatalytic reaction [3,5]. Many hierarchical structures such as flower-shaped, urchin-shaped, spherical-shaped and dandelion-shaped have been synthesized via different methods [5-9]. However, most of the hierarchical structures were prepared with the aid of surfactant or template, which were difficult to obtain low-cost mass production.

ZnO is a II-IV compound semiconductor with direct wide band gap of ~3.3 eV, which has been widely used as significant photocatalytic material due to its photochemical and catalytic properties together with its low cost [10]. The present work thus focuses on the surfactant-free wet chemical method to synthesize ZnO hierarchical structures with coral-like morphology for photocatalytic

degradation of resorcinol aqueous solution. Resorcinol was chosen since it is a well-known endocrine disrupting chemical and extensively used in the dyes, adhesives and pharmaceuticals manufacturing. The resorcinol effect on rats and humans have found the disruptions of thyroid activity via the interference of triiodothyronine (T3) and thyroxine (T4) metabolism [11].

2. Experimental

All the chemical reagents were analytical-grade purity and used as purchased without further purification. The details for the synthesis of hierarchical coral-like ZnO structures were as follows: zinc nitrate hexahydrate and sodium hydrate with the molar ratios 1:6 were dissolved in 80 mL deionized water. After 3 h stirring, the resulting white precipitates were collected by filtration, washed with deionized water and followed by drying in air at 60^{o}C for 12 h. The dried precipitates were finally calcined at 650^{o}C for 2 h.

The obtained samples were characterized by field-emission scanning electron microscopy (FESEM, Quanta FEG 450), energy dispersion X-ray (EDX, Oxford X-max), X-ray diffraction (XRD, Philips PW1820 diffractometer), UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Perkin Elmer Lambda 35) and nitrogen adsorption-desorption (Micromeritics ASAP 2020).

The photocatalytic experiment was conducted in an immersion well photoreactor (height: 200 mm, outer diameter: 100 mm, inner diameter: 60 mm). A 15 W UV Pen-Ray (UVP) lamp (λ_{max} = 365 nm) as UV source was placed in the center of cylindrical photoreactor. The photon intensity was measured as 0.840 mWcm^{-2} at distance 10 mm away from the UV lamp. The experiments were conducted with the initial resorcinol concentration of 20 mg/L and 350 mg of ZnO catalysts. The ZnO catalysts were added to the photoreactor containing 350 mL of resorcinol solution. The pH adjustment was done using equimolar NaOH and HCl solutions. Before the photocatalytic reaction, the mixture was equilibrated under darkness for 60 min to reach adsorption-desorption equilibrium. Then, the suspension was exposed to UV irradiation. 5 mL suspensions were collected after every 30 min irradiation and then centrifuged to remove the solid particles. The concentrations of resorcinol were monitored using a high performance liquid chromatography (HPLC, Perkin Elmer Series 200). The HPLC separation was carried out using a mobile phase composed of acetonitrile-water mixtures at wavelength of 238 nm. In order to determine the reproducibility of all the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within ±4%.

3. Results and discussion

The as-prepared ZnO samples were morphologically characterized by the FESEM. The highly dense coral-shaped structures were observed in Figure 1(a). The magnified image in Figure 1(b) clearly displayed that the structure of the coral-like ZnO was accumulated by lot of nanosheets and the thickness of the nanosheets ranged from 50-132 nm. In addition, the nanosheets interlaced with each other and formed porous hierarchical coral-like ZnO structures through oriented aggregation. Figure 1(c) depicts the EDX spectrum of as-prepared ZnO samples. The Zn and O peaks were observed, revealing the as-prepared samples were pure ZnO. A signal of C was attributed to the adhesive carbon tape used in the EDX analysis. In support, XRD analysis of the as-prepared ZnO samples was also conducted to investigate the crystalline phases as shown in Figure 1(d). The diffraction peaks in the XRD pattern can be indexed to a hexagonal wurtzite structure. The sharp diffraction peaks and no impurity phases were detected in the XRD pattern, which confirmed the well-crystallinity and purity of the as-prepared ZnO samples.

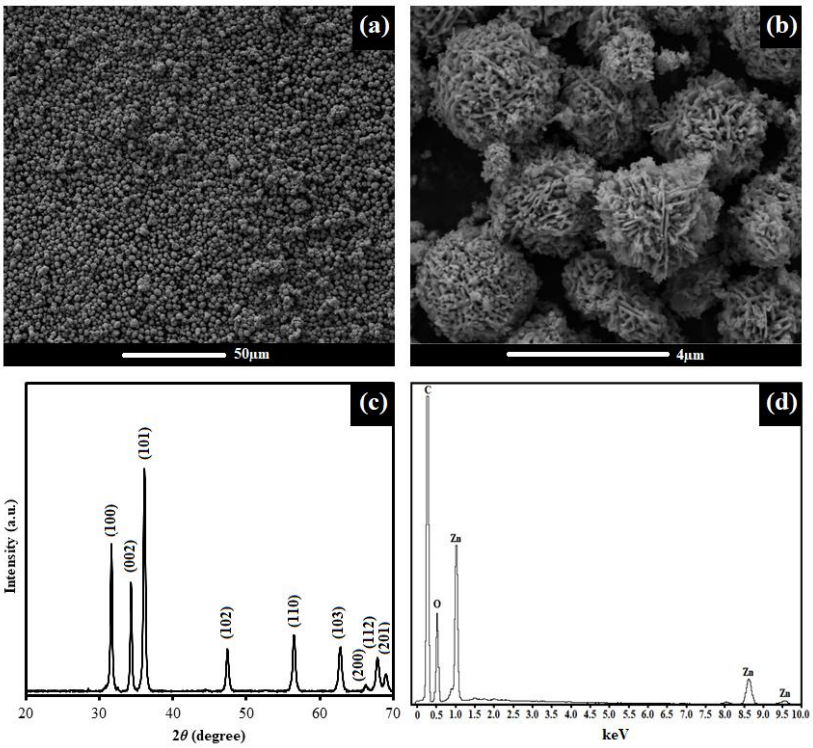

Figure 1. (a) Low-magnification and (b) high-magnification FESEM images, (c) EDX spectrum and (d) XRD pattern of as-prepared hierarchical coral-like ZnO structures.

UV-vis DRS analysis was conducted to elucidate the optical properties of as-prepared samples. From Figure 2(a), a strong absorption in the UV region which lay between 370 and 390 nm was observed. This was a characteristic and significant region of the absorption band of the hexagonal wurtzite structure of ZnO [12]. The band gap energy was determined using E_g (eV) = 1240/λ (nm), where E_g is the band gap energy and λ is the wavelength (nm) of absorption onset. The E_g of the samples was measured to be 3.22 eV, which was close to the values reported in literatures [4,12]. Full nitrogen sorption isotherms were also determined to obtain the specific surface area and the pore size of the as-prepared ZnO samples as shown in Figure 2(b). The obtained isotherms were identified as type IV, showing the existence of abundant mesopores in the ZnO samples. From the corresponding pore size distribution curve in the inset of Figure 2(b), the mesoporous with peaks at maximum points of 2 nm and 29 nm were indicated. The specific surface area was evaluated to be 6.5 m^2/g from data point by the Brunauer–Emmett–Teller (BET) method.

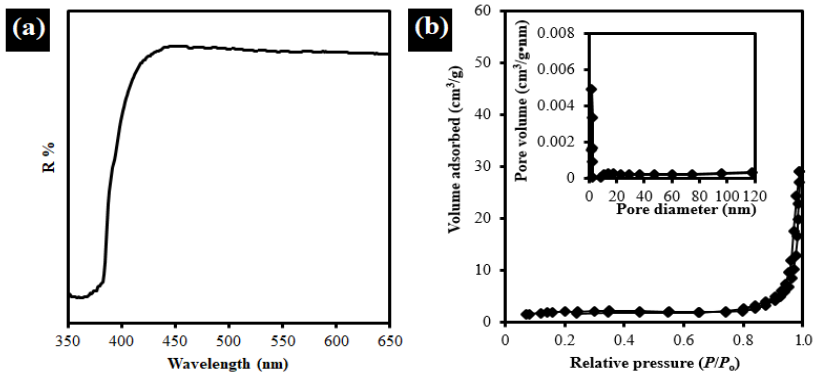

Figure 2. (a) UV-vis DRS spectrum and (b) N_2 adsorption–desorption isotherms of the as-prepared hierarchical coral-like ZnO structures. Inset of (b) is the pore size distribution.

Photogeneration of electron-hole pairs is generally played pivotal role in the photocatalytic degradation of organic pollutants. The photogenerated hole (h^+) in the valence band can trap on the ZnO surface and reacted with either surface bound hydroxide species or adsorbed water molecules through the following reactions [13]:

$$h^+ + OH^- \rightarrow \bullet OH \quad (1)$$

$$h^+ + H_2O \rightarrow \bullet OH + H^+ \quad (2)$$

At the same time, the photogenerated electron (e^-) in the conduction band of ZnO reacted with adsorbed oxygen on the ZnO surface to promote the superoxide anion radical ($O_2\bullet^-$) formation and then converted to active hydroxyl radical (•OH). The •OH, $O_2\bullet^-$ and h^+ formed by ZnO via e^-- h^+ generation under light irradiation, which are highly active species to break the organic pollutants into CO_2 and H_2O [13,14].

$$e^- + O_2 \rightarrow O_2\bullet^- \quad (3)$$

$$O_2\bullet^- + H^+ \rightarrow \bullet OOH \quad (4)$$

$$\bullet OOH + H^+ + e^- \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \quad (6)$$

$$\text{Organic Pollutants} + (\bullet OH, O_2\bullet^- \text{ and } h^+) \rightarrow \text{degradation intermediates} \rightarrow CO_2 \text{ and } H_2O \quad (7)$$

Figure 3(a) shows the resorcinol degradation over hierarchical coral-like ZnO structures schematically. Figure 3(b) depicts the adsorption of resorcinol onto the surface of as-prepared ZnO samples at different solution pH values. It was observed that increase in solution pH from 5.0 to 11.0 decreased the adsorption efficiency of resorcinol. Since the zero potential point of ZnO was 9.3 [11], the ZnO surface was positively charged at pH 5.0 and an electrostatic attraction between positively charged ZnO with molecular form of resorcinol molecule led to maximum resorcinol adsorption efficiency. In contrast, the ZnO surface deprotonated at higher pH and formed repulsive forces with the negatively charged resorcinol. The degradation process mainly happened at the interface between the catalyst surfaces and organic pollutants, thus the adsorption of resorcinol is an important step in photocatalysis. Even though the organic pollutants with high adsorption efficiency degraded faster, the effect sites for UV light absorption decreased with increasing the adsorption. It should also be noted that higher pH value can provide large amount of OH^- ions on the ZnO surface and favoured the formation of •OH, which then led to photocatalytic enhancement of resorcinol. Figure 3(c) shows the degradation percentage of resorcinol at each irradiation time for different solution pH values. It can be observed that the concentration of resorcinol gradually decreased with increasing the irradiation time at all investigated pH values. The kinetic studies of resorcinol degradation over the as-prepared ZnO samples are shown in Figure 3(d). The photocatalytic reactions of resorcinol were in agreement with the first-order kinetic behaviour according to the Langmuir-Hinshelwood model and can be stated as [11]:

$$\ln(C_o/C) = kt \quad (8)$$

where k is the observed rate constant, C_o is the equilibrium concentration of resorcinol and C is the concentration at time t. The k values for the photocatalytic reactions at pH 5.0, pH 8.0 and pH 11.0 were measured to be 0.0074, 0.0136 and 0.0271 min^{-1}, respectively. The k value of photocatalytic reactions over coral-like ZnO at pH 11.0 was 3.7-fold and 2.0-fold higher than those of photocatalytic reactions at pH 5.0 and pH 8.0, respectively. Therefore, even though the adsorption of resorcinol was low at alkaline pH, the explanation for this behaviour was the presence of higher concentration of OH^- ions or higher fraction of hydrolyzed forms of resorcinol, which can lead to higher concentration of •OH radicals to enhance the photodegradation rate.

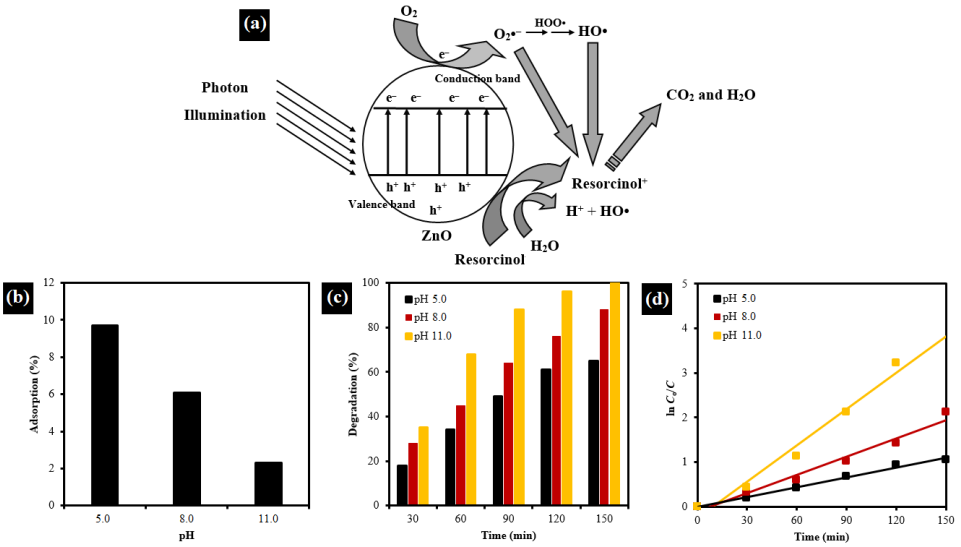

Figure 3. (a) Schematic illustration of resorcinol degradation over hierarchical coral-like ZnO structures, (b) Adsorption of resorcinol onto ZnO at different pH values, (c) Degradation percentage of resorcinol as a function of irradiation time and (d) First-order linear plots of ln(C_o/C) versus irradiation time.

4. Conclusions

Hierarchical coral-like ZnO structures were successfully synthesized via a surfactant-free wet chemical method. The as-prepared ZnO samples were characterized using FESEM, EDX, XRD, UV-vis DRS and nitrogen adsorption-desorption measurements. The photocatalytic degradation of resorcinol over as-prepared ZnO samples was carried out at three solution pH values (pH 5.0, pH 8.0 and pH 11.0). The results showed that the extent of resorcinol adsorption onto the ZnO strongly dependent on the electrical charge properties of both photocatalyst and resorcinol. High photodegradation of resorcinol was obtained at pH 11.0 with the high concentration of OH^- ions for •OH radicals generation.

Acknowledgments

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