Fabrication of Samarium-doped ZnO Hierarchical Micro/nanospheres with Enhanced Fluorescent Light-Driven Photocatalytic Activity

Jin-Chung Sin1, Sze-Mun Lam1, Keat-Teong Lee1 and Abdul Rahman Mohamed1

1School of Chemical Engineering
Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia
Email: sinjinchung@gmail.com

Abstract—Samarium-doped ZnO hierarchical micro/nanospheres (Sm/ZnO) were synthesized via a facile and surfactant-free chemical solution route. The obtained products were characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX), UV–visible diffuse reflectance spectroscopy (UV-vis DRS) and photoluminescence spectroscopy (PL). Photocatalytic test showed that the Sm/ZnO exhibited higher activity for phenol degradation compared to pure ZnO. The photocatalytic enhancement of Sm/ZnO was attributed to factors such as improved optical absorption property and improved lifetime of the charge carriers.

Keywords-ZnO; Samarium; Photocatalysis; Phenol

I. INTRODUCTION

Nowadays, “green life” has been inspiring people to pay more and more attention to the removal of hazardous organic pollutants in the wastewater. One of the best ways to eliminate the organic pollutants is by ZnO mediated photocatalytic treatment. Assemblage of ZnO nanoscaled building blocks including nanorods, nanowires and nanosheets into three-dimensional (3D) hierarchical architectures have been a research hotspot [1,2]. What is more, there are many reports of ZnO hierarchical architectures exhibiting better activity than mono-morphological ZnO nanostructures [3–5]. For example, Lu et al. [3] reported that flowerlike hierarchical ZnO microarchitectures synthesized via a citrate-mediated hydrothermal route showed an enhanced photocatalytic performance compared with the ZnO nanoparticles, nanorods and nanosheets. Thus, in this study, we synthesized the ZnO hierarchical micro/nanospheres using a facile chemical solution route without any organic solvent or surfactant. The photocatalytic activity of synthesized products was evaluated by phenol degradation. To improve the photocatalytic properties of ZnO, Sm were doped into ZnO through a simple and rapid approach. Sm is one of the rare earth metals has the ability to shift the band gap of ZnO into visible region and to control electron-hole recombination via the electrons trap effect supplied by the alterable chemical valence (Sm3+ and Sm5+) sites [6,7], thereby showing the potential for good photoactivity in the degradation of phenol. To the best of our knowledge, this is the first work reporting the photocatalytic degradation of phenol with Sm/ZnO.

II. EXPERIMENTALS

In a typical experiment, 5.0 mmol Zn(NO3)2•6H2O was dissolved in 80 mL of deionized water. Then 30 mmol NaOH was added into the above solution and stirred for 3 h. After stirring, the resulting white precipitates were filtered, washed with deionized water for several times, dried at 60°C for 12 h and finally calcined at 450°C for 2 h. Sm doping solution was prepared exactly like the pure one by dissolving 0.05 mmol Sm(NO3)3•6H2O into the solution of Zn(NO3)2•6H2O at the first step.

The synthesized products were characterized by FESEM (Quanta FEG 450) together with EDX analysis, TEM (Philips CM 12), XRD (Philips PW 1820), UV-vis DRS (Perkin Elmer Lambda 35 UV-vis) and PL (Perkin Elmer Lambda S55).

The photocatalytic activities of synthesized products were evaluated by phenol degradation. A 55 W compact fluorescent lamp placed about 12 cm above the reaction solution was used to produce light irradiation. The UV leakage of the compact fluorescent lamp was measured, which was 0.101 mW/cm² as determined by UVA and UVC radiometers (Series 9811, Cole Parmer, USA). Since the intensity of UV light was very low, it can be assumed that the photodegradation was mainly due to the action of visible light. It is also worth noting that the contribution of UV light was much lower than in case of solar light, which typically contained UV flux in the range of 2–3 mW/cm² [8]. Batch tests were performed by adding 100 mg catalyst to 100 mL 20 mg/L phenol solution. The concentration of phenol was determined using high performance liquid chromatography (HPLC) with a mobile phase mixture of acetonitrile and water in the ratio of 30:70 at wavelength of 254 nm.

III. RESULTS AND DISCUSSIONS

The FESEM images of the samples are shown in Fig. 1. From Fig. 1(a1), it can be seen that the synthesized products were spherical-shaped and grown in large quantity.
diameters of micro/nanospheres varied from 870 nm to 2.80 μm, which has a relatively narrow size distribution. From Fig. 1(a2), it was found that the microsphere presented a hierarchical structure. The microsphere was accumulated by lots of interleaving 2D nanosheets with average thickness of ~17 nm, forming an open porous structure through oriented aggregation. The TEM observations of the products in Fig. 1(a3) further confirmed the FESEM results. Furthermore, the growth of ZnO was not influenced by the doping of Sm atoms as the Sm(NO$_3$)$_3$•6H$_2$O was used for providing Sm$^{3+}$ ions to be doped, and the molar content of the dopant agent in comparison with ZnO source was too small to alter the morphology (Fig. 1b).

![Figure 1(a) FESEM and TEM images of pure ZnO; (b) FESEM and TEM images Sm/ZnO.](image)

Fig. 2(a) shows the XRD patterns of the as-synthesized products. All the products had typical hexagonal wurtzite structures and no peaks were detected from any other impurities. The sharp and narrow peaks showed that the products obtained to be well in a crystallized form. Moreover, the diffraction peaks of Sm/ZnO shifted slightly toward the lower angle with respect to that of pure ZnO (inset of Fig. 2(a)), indicating the substitution of Sm$^{3+}$ ions into the Zn$^{2+}$ sites in the lattices of ZnO because the ionic radius of Sm was much larger than that of Zn. Fig. 2(b) is an EDX pattern of the Sm/ZnO indicating the products were made up of Zn, O and Sm ions which showed that the Sm dopant was successfully incorporated into the ZnO. Furthermore, the EDX mapping of Sm/ZnO in Figs. 2(c)–(e) demonstrated that Zn, O and Sm ions were distributed homogeneously throughout the products.

![Figure 2 (a) XRD spectra of pure and Sm/ZnO; (b) EDX spectrum of Sm/ZnO; (c)–(e) The elemental mapping images of Sm/ZnO.](image)

Fig. 3(a) shows that the light absorption of Sm/ZnO in the visible region was higher than that of pure ZnO. Moreover, a red shift for Sm/ZnO appeared when compared to pure ZnO. This result can be attributed to the charge transfer between the ZnO valence or conduction band and the Sm ion 4f level [9]. From Fig. 3(b), the Sm/ZnO showed much lower PL intensity than pure ZnO. Generally, a weaker PL intensity implies lower electron-hole recombination rate and corresponds to higher photocatalytic activity [7]. The Sm ion incorporated with ZnO can act as an electron-trapped agent and thus promote electron-hole pairs separation.

The photocatalytic activities of the as-synthesized ZnO products were evaluated by the degradation of phenol aqueous solution. Phenol is an endocrine disrupting chemical which produced worldwide in millions of tons each year and widely used in the manufacture of resins, insulation panels, pesticides, paints and lubricants. The extensive use and poor biodegradability of phenol have resulted in its ubiquitous presence in the environment and have led to contamination of water. Indeed, dose-dependent chromosomal aberrations have been reported in spermatogonia and primary spermatocytes of mice treated with solution of phenol in water [10,11]. Therefore, phenol was chosen as the model substrate to evaluate the photocatalytic activities of the as-synthesized ZnO products in this work. The blank test showed that the concentration of phenol decreased only about 6.3% after 300 min irradiated in the absence of catalysts, indicating that the photoinduced self-decomposition can be neglected in comparison with the photocatalysis caused by various catalysts. The degradation of phenol for Sm/ZnO in the dark condition can also be neglected under the experimental condition. As shown in Fig. 3(c), the photocatalytic activity of Sm/ZnO improved remarkably compared to pure ZnO, indicating the promoting effect of the Sm modification. During photocatalysis, Sm$^{3+}$ ions can act as electron scavengers and suppressed electron-hole recombination. The reduced state of Sm$^{2+}$ ions, with 6f electrons, is very instable so that the e$^{-}$ can be easily detrapped and transferred to the O$_2$ molecules promoting the O$_2$ formation and then converted to active •OH. Meanwhile, the reactive h$^+$ at the valence band can trap on the
catalyst surface undergoing charge transfer with adsorbed water molecules or with surface-bound hydroxide species to generate active •OH. Through this way, the photogenerated charge carriers can be separated efficiently and led to the production of more active •OH, which are responsible for the enhancement of the photocatalytic activity. The degradation mechanism for the Sm/ZnO can be given as [6,7,12]:

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\begin{align*}
\text{Sm}^{3+} + e^- & \rightarrow \text{Sm}^{2+} \quad (1) \\
\text{Sm}^{2+} + \text{O}_2 & \rightarrow \text{Sm}^{3+} + \text{O}_2^- \quad (2) \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{OOH} \quad (3) \\
\text{•OOH} + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 \quad (4) \\
\text{H}_2\text{O}_2 + e^- & \rightarrow \text{•OH} + \text{OH} \quad (5) \\
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{•OH} \quad (6) \\
\text{h}^+ + \text{OH}^- & \rightarrow \text{•OH} \quad (7)
\end{align*}
\]

Thus, the separation of the charge carriers was attributed to such trapping by Sm dopant in ZnO. Subsequently, enhanced the yield of •OH quantities in the degradation of phenol, which further improved the photocatalytic activity of Sm/ZnO. Moreover, the Sm/ZnO showed red shift in the absorption wavelength range compared to pure ZnO. The red shift in the absorption band indicated that the Sm/ZnO can absorb more photons and was also favourable for photocatalytic reaction. On the basis of the above analysis, it was suggested that the enhanced photocatalytic activity of Sm/ZnO was attributed to factors such as improved optical absorption property and improved lifetime of the charge carriers.

Figure 3 (a) UV-vis DRS spectra; (b) PL spectra; (c) The degradation percent versus time curves of photodegradation of phenol.

CONCLUSIONS

In summary, by means of a facile chemical solution route, Sm/ZnO was successfully synthesized in the absence of any surfactants or structure directing reagents and confirmed by FESEM, TEM, XRD, EDX, UV-vis DRS and PL measurements. UV-vis DRS spectra revealed that Sm doping increased the visible light absorption ability of Sm/ZnO and a red shift for Sm/ZnO appeared when compared to pure ZnO. Analysis of the PL spectra indicated that the Sm/ZnO have a better electron-hole separation than the pure ZnO. The photocatalytic tests showed that doping of Sm into ZnO can significantly improve the photocatalytic efficiency of ZnO under irradiation of a compact fluorescent lamp. The enhanced photocatalytic activity of Sm/ZnO was attributed to factors such as improved optical absorption property and improved lifetime of the charge carriers.

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