Photocatalytic Activities of Hydrothermally Synthesized \( \text{Zn}_2\text{SnO}_4 \)

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Received January 10, 2011, Accepted March 22, 2011

**Key Words**: \( \text{Zn}_2\text{SnO}_4 \), Hydrothermal synthesis, Photocatalytic activities

Zinc stannate (\( \text{Zn}_2\text{SnO}_4 \)) is a transparent conducting oxide with high electron mobility, high electrical conductivity and low visible absorption, and is used widely as gas sensors, electrode materials, and photoluminescence materials.\(^ {1-3} \) \( \text{Zn}_2\text{SnO}_4 \) has also attracted considerable interest for its high photocatalytic activity. The decomposition reactions of benzene and water-soluble dyes using \( \text{Zn}_2\text{SnO}_4 \) as a photocatalyst were reported.\(^ {4,7} \) \( \text{Zn}_2\text{SnO}_4 \) is normally synthesized by solid state reactions with \( \text{ZnO} \) and \( \text{SnO}_2 \) at high temperatures.\(^ {8,9} \) The high temperature calcination of coprecipitated \( \text{Zn} \) and \( \text{Sn} \) hydroxides with the alkali from an aqueous solution were also used to prepare \( \text{Zn}_2\text{SnO}_4 \).\(^ {10} \) Recently, the hydrothermal synthesis of \( \text{Zn}_2\text{SnO}_4 \) was reported.\(^ {11-13} \) Hydrothermal methods have advantages over the solid state reactions and high temperature calcinations methods, such as a lower reaction temperature and simpler method for producing nano-sized particles. Therefore, hydrothermal methods should be used to prepare \( \text{Zn}_2\text{SnO}_4 \) nanoparticles to improve the photocatalytic activity. However, relatively little is known regarding the relationship between the photocatalytic activity and synthetic conditions of hydrothermal methods of \( \text{Zn}_2\text{SnO}_4 \).

This paper reports the photocatalytic activity of \( \text{Zn}_2\text{SnO}_4 \) nanoparticles prepared by a simple hydrothermal method from \( \text{Zn}(\text{CH}_3\text{COO})_2 \) and \( \text{SnCl}_4 \) with different amounts of \( \text{NH}_3\text{OH} \) to control the pH from 8 to 11. The photocatalytic activity of \( \text{Zn}_2\text{SnO}_4 \) nanoparticles prepared by hydrothermal synthesis from \( \text{Zn}(\text{CH}_3\text{COO})_2 \) and \( \text{SnCl}_4 \) with different types of hydroxylation agents at pH 9 was also examined.

Figure 1 shows XRD patterns of the as-prepared samples obtained by hydrothermal methods from \( \text{Zn}(\text{CH}_3\text{COO})_2 \) and \( \text{SnCl}_4 \) in the presence of different amounts of \( \text{NH}_3\text{OH} \) to control the pH from 8 to 11. At pH 8 and 9, aggregated forms of \( \text{Zn}_2\text{SnO}_4 \) nanoparticles were observed, as shown in Figures 2(a) and 2(b). However, micron-sized, cubic-shaped \( \text{ZnSn(OH)}_6 \) products were observed at pH 11, as shown in Figure 2(d). This suggests that \( \text{ZnSn(OH)}_6 \) has a characteristic cubic-shaped morphology. On the other hand, \( \text{Zn}_2\text{SnO}_4 \) nanoparticles do not have a unique morphology. The coexistence of \( \text{Zn}_2\text{SnO}_4 \) and \( \text{ZnSn(OH)}_6 \) was observed at pH 10. Figure 2(c) shows \( \text{Zn}_2\text{SnO}_4 \) nanoparticles attached to the outer surface of the micron-sized cubic \( \text{ZnSn(OH)}_6 \) crystals. Figure 3 shows high-resolution TEM (HRTEM) image of the \( \text{Zn}_2\text{SnO}_4 \) nanoparticles obtained at pH 9. The size of the individual nanoparticle was approximately 10 nm. The observed lattice spacing of 0.49 nm corresponded to the (111) plane of cubic \( \text{Zn}_2\text{SnO}_4 \) crystals. The fast Fourier transform (FFT) pattern corresponds to the lattice fringe, as shown in the inset of Figure 3.

To examine the photocatalytic activity of \( \text{Zn}_2\text{SnO}_4 \) and \( \text{ZnSn(OH)}_6 \) products obtained by hydrothermal methods, Rh6G was chosen as the pollutant model molecule. The photodegradation of Rh6G under UV lamp irradiation after the addition of \( \text{Zn}_2\text{SnO}_4 \) and \( \text{ZnSn(OH)}_6 \) as photocatalysts was evaluated. Figure 4(a) shows the temporal evolution of the UV-vis spectra of Rh6G in the absence of a catalyst. The absorption peaks of Rh6G decreased slightly with the irradiation time. The concentrations of Rh6G species were calculated simply from the maximum absorption intensities at 527 nm using the Beer-Lambert law. The photodegradation...
efficiency was only 2.2% for 90 min, which demonstrated that the photodegradation of Rh6G was extremely low in the absence of a catalyst. Figures 4(b), 4(c), 4(d) and 4(e) show the temporal evolution of the UV-vis spectra of Rh6G in the absence of a catalyst. We will plan to prepare the ZnSn(OH)$_6$ product obtained by a hydrothermal method at pH 9 using NH$_4$OH. The BET surface area of ZnSn(OH)$_6$, prepared at pH 9 when rate constants are normalized to surface area. This suggests that ZnSn(OH)$_6$ with larger BET surface area can be an excellent photocatalyst. We will plan to prepare the ZnSn(OH)$_6$ with larger BET surface area to enhance the photocatalytic activity of ZnSn(OH)$_6$ later.

Most of photodegradation reactions of dyes obey first-order reaction kinetics.\textsuperscript{14,15} The reaction rate constant can be obtained simply from the integrated form of first-order reaction kinetics according to equation (1).

$$\ln\left(\frac{C}{C_0}\right) = -kt$$  

where $C_0$ is the initial concentration, $C$ is the concentration of Rh6G after a set UV irradiation time. Figure 5 shows the first-order reaction kinetic plots of the photodegradation of Rh6G in the absence of a catalyst and in the presence of the as-prepared samples prepared at four different pH values. As shown in Figure 5, straight lines were observed. This suggests that the photodegradation of Rh6G obeys first-order reaction kinetics. The rate constant for the photodegradation of Rh6G in the presence of Zn$_2$SnO$_4$ and ZnSn(OH)$_6$ products prepared at pH 8, 9, 10 and 11 were $2.0 \times 10^{-2}$, $2.0 \times 10^{-2}$, $2.5 \times 10^{-2}$, $1.4 \times 10^{-2}$, and $3.8 \times 10^{-3}$ min$^{-1}$, respectively. Therefore, the photocatalytic activity of Zn$_2$SnO$_4$ is better than that of ZnSn(OH)$_6$. The BET surface areas of Zn$_2$SnO$_4$ and ZnSn(OH)$_6$ prepared at pH 8, 9, 10 and 11 were 82.5, 94.8, 15.4, and 13.5 m$^2$/g, respectively. The photocatalytic activity of Zn$_2$SnO$_4$ depends strongly on the BET surface areas of Zn$_2$SnO$_4$. The rate constant for the photodegradation of Rh6G in the presence of TiO$_2$ powder was $3.1 \times 10^{-2}$ min$^{-1}$. Based on the rate constant of photodegradation of Rh6G, the photocatalytic activity of Zn$_2$SnO$_4$ prepared at pH 9 using NH$_4$OH is approximately 81% that of the TiO$_2$ powder. ZnSn(OH)$_6$ with BET surface areas of 48 m$^2$/g was used as a photocatalyst for the decomposition reactions of benzene.\textsuperscript{16} Even though overall photocatalytic activity of Zn$_2$SnO$_4$ is superior to that of ZnSn(OH)$_6$, in this work, the photocatalytic activity of ZnSn(OH)$_6$ prepared at pH 11 was slightly better than that of Zn$_2$SnO$_4$ prepared at pH 9 when rate constants are normalized to surface area. This suggest that ZnSn(OH)$_6$ with larger BET surface area can be an excellent photocatalyst.

NaOH, NH$_3$OH, DMEDA, and TMEDA were used as a ligand and hydroxylating agent to examine the effect of the ligand on photocatalytic activity of Zn$_2$SnO$_4$ obtained using hydrothermal methods at pH 9. XRD patterns of four products matched the reported data for single Zn$_2$SnO$_4$ crystals (JCPDS 24-1470, a = 0.8657 nm) without impurities. Figure 6(a), 6(b), 6(c) and 6(d) show the UV-vis spectral changes in Rh6G in the presence of the four Zn$_2$SnO$_4$ products prepared using NaOH, NH$_3$OH, DMEDA, and TMEDA, respectively. The photocatalytic efficiencies of Rh6G in the presence of Zn$_2$SnO$_4$ prepared using NaOH, NH$_3$OH, DMEDA, and TMEDA were 74.4%, 90.5%, 95.5%, and 84.2% for 90 min, respectively. The rate constant for the photodegradation of Rh6G in the presence of Zn$_2$SnO$_4$ prepared using NaOH, NH$_3$OH, DMEDA, and TMEDA was $1.5 \times 10^{-2}$, $2.5 \times 10^{-2}$, $3.2 \times 10^{-2}$ and $2.0 \times 10^{-2}$ min$^{-1}$, respectively. The BET surface areas of Zn$_2$SnO$_4$...
products prepared at pH 9 using NaOH, NH₄OH, DMEDA, and TMEDA were 57.2, 94.8, 86.6, and 61.9 m²/g, respectively. Therefore, the photocatalytic activities of Zn₂SnO₄ products prepared at pH 9 using the different hydroxylation agents were in the following order: DMEDA > NH₄OH > TMEDA > NaOH. The photocatalytic activity of Zn₂SnO₄ prepared at pH 9 using DMEDA was approximately 103% that of the well-known TiO₂ photocatalyst.

In conclusion, Zn₂SnO₄ and ZnSn(OH)₆ were synthesized using a hydrothermal reaction from Zn(CH₃COO)₂ and SnCl₄ with different amounts of NH₄OH. A single phase of Zn₂SnO₄ and ZnSn(OH)₆ were formed at pH 8, 9, and pH 11, respectively. At pH 10, Zn₂SnO₄ and ZnSn(OH)₆ coexisted. The photocatalytic activity of Zn₂SnO₄ prepared at pH 9 was better than that of ZnSn(OH)₆ prepared at pH 11 by factor of 6.6. The photocatalytic activity of Zn₂SnO₄ nanoparticles prepared using the different hydroxylation agents were in the following order: DMEDA > NH₄OH > TMEDA > NaOH. The photocatalytic activity of Zn₂SnO₄ prepared at pH 9 using DMEDA was almost equal to that of the well-known TiO₂ photocatalyst.

**Experimental Section**

Zn(CH₃COO)₂ (98%, Aldrich), SnCl₄ (98%, Aldrich), NaOH (97%, Aldrich), NH₄OH (28%, Aldrich), N,N-dimethyl ethylenediamine (DMEDA, 95%, Aldrich), N,N,N',N'-tetramethyl ethylenediamine (TMEDA, 99%, TCI), Rhodamine 6G (Rh6G, 99%, Aldrich), and TiO₂ powder (Degussa, P-25) were used.
as received. In a typical experiment, 20 mL of a 0.10 M Zn(CH₃COO)₂ solution was added to 20 mL of a 0.05 M SnCl₄ solution. Different amounts of a NH₄OH solution was added to the mixed solution to obtain the various pH values (pH 8, 9, 10, and 11). A 60 mL sample of the final solution was transferred to a 100 mL Teflon-lined autoclave and heated to 140 °C for 16 h. The product was filtered, washed several times with ethanol and water, and dried at 80 °C for 12 h.

The photocatalytic activity of the ZnSnO₄ and ZnSn(OH)₄ samples was evaluated by the photodegradation of Rh6G under a 12 W UV lamp (λ = 254 nm). In a typical procedure, 10 mg ZnSnO₄ (or ZnSn(OH)₄) powder was added to 100 mL of 1.04 × 10⁻⁵ M Rh6G aqueous solutions in a 100 mL round bottom flask. The suspensions were then irradiated under a UV lamp at a 3 cm separation distance in dark condition. Every 15 minutes during the photodegradation process, 3 mL of the Rh6G solution was sampled and separated by centrifugation. The concentrations of the supernatants were monitored using a UV-vis spectrophotometer. To compare the photocatalytic activity of TiO₂ with that of ZnSnO₄, 10 mg of TiO₂ was used with the other conditions kept the same as those used for the photodegradation of Rh6G by adding ZnSnO₄.

The structures of the ZnSnO₄ and ZnSn(OH)₄ products were characterized by powder X-ray diffraction (XRD, PANalytical, Xpert-pro MPD) using Cu Kα radiation. The morphology of the products was observed by scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL JEM-3010). The Brunauer-Emmett-Teller (BET) surface areas of the sample were calculated from the N₂ adsorption/desorption isotherms determined at liquid nitrogen temperature using an automatic analyzer (Micrometric, Tristar 3202). Prior to adsorption, the samples were outgassed for 8 h under a vacuum at 120 °C.

Acknowledgments. This study was supported by Basic Science Research Program through National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2010-0007492).

References