Controlled-Synthesis and Photocatalytic Properties of h-In₂O₃ and c-In₂O₃

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Indium oxide (In₂O₃) is an important semiconductor with a wide band-gap of 3.6 eV that has been widely used in solar cells, gas sensors, optoelectronics, and photocatalysis.¹⁻⁷ Many efforts have been devoted to the synthesis of In₂O₃ with various morphologies, such as nanocubes, nanotubes, nanotowers, nanorods, and hollow spheres.⁸⁻¹³ In₂O₃ has two phases of hexagonal In₂O₃ (h-In₂O₃) and cubic In₂O₃ (c-In₂O₃).^{14,15} Most of the synthetic methods have focused on preparing one of the two In₂O₃ phases. However, relatively little is known about the controlled synthetic method for the two specific phases of In₂O₃ that is carried out by adjusting the synthetic conditions. In this study, simple methods were reported for the production of InOOH and In(OH)₃ using hydrothermal reactions in aqueous solutions containing InCl₃, ethylenediamine (EDA), and *N,N,N',N'*-tetraethylethylenediamine (TEEDA). The selective formation of InOOH or In(OH)₃ was controlled by varying the amount of water. h-In₂O₃ and c-In₂O₃ were also selectively synthesized through the thermal oxidation of the InOOH and In(OH)₃ products, respectively as precursors. The photocatalytic properties of the h-In₂O₃ and c-In₂O₃ products that were fabricated this work were also examined.

Experimental Section

InCl₃ (98%, Aldrich), TEEDA (98%, Aldrich), EDA (99%, Aldrich), and Rhodamine B (RhB, 90%, Aldrich) were used as received. TEEDA was used as a ligand for the indium ions. EDA was also used for the solvent. For the preparation of InOOH, 2.4 mL of TEEDA and 5 mL of distilled water were added to 45 mL EDA solution of 0.11 M InCl₃ with stirring for 10 min. The reaction solution was transferred into a Teflon-lined autoclave with a capacity of 100 mL and heated at 180 °C for 10 h. The autoclave was naturally cooled down to room temperature. InOOH was obtained through filtration, several washing steps with ethanol, and drying at 60 °C for 12 h. The synthesized InOOH sample was used as a precursor for the preparation of h-In₂O₃ through a simple thermal oxidation at 500 °C in air for 2 h. For the preparation of In(OH)₃, the amount of distilled water was changed to 15 mL while the other conditions were the same as the preparation of InOOH. The synthesized In(OH)₃ sample was also used as a precursor for the preparation of c-In₂O₃ through a simple thermal oxidation at 500 °C for 2 h.

The photocatalytic activities of the In₂O₃ samples were evaluated through the photodegradation of RhB under a halogen lamp irradiation of 50 W. In a typical procedure, 200 mg In₂O₃ powder was added to 50 mL of a 2.5×10^{-4} M RhB aqueous

solution in a 100 mL round bottom flask. Before the illumination, the solution was stirred for 15 min in the dark in order to reach uniformity and the absorption equilibrium. During the photodegradation process, 3 mL of the RhB solution was sampled every hour, and the RhB concentration was monitored using a UV-vis spectrophotometer.

The structures of InOOH, In(OH)₃, h-In₂O₃, and c-In₂O₃ were analyzed using X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) with Cu K α radiation. The morphologies of the products were characterized using scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010). The UV-vis absorption spectra were measured using a Perkin-Elmer Lambda 25 spectrophotometer.

Results and Discussion

Figure 1 shows the XRD patterns and the Miller indices of the InOOH, In(OH)₃, h-In₂O₃, and c-In₂O₃ products that were obtained using the hydrothermal method and thermal oxidation. The InOOH products were obtained using the hydrothermal method at 180 °C for 10 h with 0.11 M InCl₃, 45 mL EDA, 2.4 mL TEEDA, and 5 mL of distilled water. All of the peaks in Figure 1a corresponded to orthorhombic InOOH and were in good agreement for the reported data for this system (JCPDS 17-0549, *a* = 0.526 nm, *b* = 0.456 nm, *c* = 0.327 nm). The In(OH)₃ products were obtained using the same hydrothermal conditions

Figure 1. XRD patterns of the (a) InOOH, (b) In(OH)₃, (c) h-In₂O₃, and (d) c-In₂O₃ products that were obtained using the hydrothermal method and thermal oxidation.

Figure 2. (a) SEM, (b, c) TEM, and (d) HRTEM images of the InOOH products that were obtained using the hydrothermal method with a low amount of water.

Figure 3. (a) SEM, (b, c) TEM, and (d) HRTEM images of the h-In₂O₃ products that were obtained through the thermal oxidation of InOOH.

Figure 4. (a) SEM and (b) TEM images of the In(OH)₃ products that were obtained using the hydrothermal method with a high amount of water.

Figure 5. (a) SEM, (b, c) TEM, and (d) HRTEM images of the c-In₂O₃ products that were obtained through the thermal oxidation of In(OH)₃.

for InOOH, except that 15 mL of distilled water was used. All of the peaks in Figure 1b were also in good agreement with cubic In(OH)₃ (JCPDS 06-0202, $a = 0.790$ nm). The h-In₂O₃ and c-In₂O₃ products were obtained through the thermal oxidation of the InOOH and In(OH)₃ precursors, respectively, at 500 °C for 2 h. All of the peaks in Figures 1c and 1d were indexed to h-In₂O₃ (JCPDS 22-0336, $a = 0.5487$ nm, $c = 1.451$ nm) and the c-In₂O₃ (JCPDS 44-1087, $a = 1.012$ nm), respectively.

Figure 2 shows the SEM and TEM images of the InOOH products that were obtained using the hydrothermal method. In these SEM images, InOOH exhibited a spherical structure with a diameter of 300 - 500 nm (Figure 2a). Additionally, every sphere was composed of many small spheres with an average diameter of 10 - 20 nm (Figures 2b and 2c). The observed lattice spacing of 0.275 nm corresponded to the (110) plane of the InOOH crystals, in Figure 2d. Figure 3 shows the SEM and TEM images of the h-In₂O₃ products that were prepared by oxidizing InOOH at 500 °C for 2 h. The SEM and TEM images of the h-In₂O₃ resembled InOOH. Therefore, the morphology of the InOOH did not change during the oxidation. The fringe pattern indicated a spacing of 0.270 nm, which corresponded to the (110) plane of h-In₂O₃ (Figure 3d). Figure 4 shows the SEM and TEM images of the In(OH)₃ products that were obtained using the hydrothermal method. A cubic structure with an average length of 20 - 30 nm was observed (Figure 4b). The SEM and TEM images of the c-In₂O₃ products that were prepared by oxidizing In(OH)₃ are shown in Figure 5. The cubic shape of In(OH)₃ with a sharp edge changed to a particle shape with a dull edge for c-In₂O₃. The fringe pattern of the (222) plane of c-In₂O₃ was also observed (Figure 5d).

The amount of water in this simple hydrothermal reaction system played an important role in the selective formation of the InOOH and In(OH)₃ products. In(OH)₃ was formed when larger amounts of water were used, while InOOH was produced using a small amount of water. The dehydration process

Scheme 1. Schematic reaction paths that were involved in the formation of h-In₂O₃ and c-In₂O₃

Figure 6. The UV-vis spectra of the (a) h-In₂O₃ and (b) c-In₂O₃.

Figure 7. The absorption spectral changes of RhB (a) in the absence of the catalyst and in the presence of the (b) commercial In₂O₃, (c) h-In₂O₃, and (d) c-In₂O₃ samples that were prepared using the methods that were described in this work.

of In(OH)₃ to InOOH might have occurred when a small amount of water was used. Furthermore, the phenomenon of the controlled synthesis of h-In₂O₃ and c-In₂O₃ was also observed for the simple oxidation of InOOH and In(OH)₃, respectively. Therefore, the selective synthesis of h-In₂O₃ and c-In₂O₃ was simply controlled by the amount of water in the hydrothermal reaction system. The schematic reaction paths that were involved in formation of h-In₂O₃ and c-In₂O₃ are presented in Scheme 1.

Figure 6 shows the absorption spectra of the h-In₂O₃ and c-In₂O₃ samples in ethanol solution. The absorption shoulders located at 310 nm for the h-In₂O₃ and c-In₂O₃ corresponding to a bandgap of *ca.* 4.0 eV, which is larger than that of bulk In₂O₃ of 3.6 eV. There is also weak absorption in the blue visible region, which is adequate for the photocatalysis experiment using a halogen lamp. RhB was chosen as the pollutant model molecule in order to investigate the photocatalytic activities of the

Figure 8. The normalized photodegradation curves of the RhB concentrations with respect to the halogen lamp irradiation time.

h-In₂O₃ and c-In₂O₃ samples. The photocatalytic activities of the h-In₂O₃ and c-In₂O₃ were evaluated for degradation of RhB under halogen lamp irradiation. Figure 7 demonstrates the absorption spectral changes of RhB in the absence of the catalyst and in the presence of the commercial In₂O₃, h-In₂O₃, and c-In₂O₃ samples that were prepared using the methods that were described in this work. Figure 7a shows the UV-vis spectra of RhB in the absence of the catalyst. The absorption peaks of RhB slightly decreased with the irradiation time. A very small shift in the $\lambda_{\max}$ (554 nm) of RhB was observed, indicating the facile cleavage of the whole conjugated chromophore structure. The photodegradation efficiency was only 10.1% after 4 h, which demonstrated that the photodegradation of RhB was extremely low without a catalyst. Figures 7b, 7c, and 7d show that the absorption peaks of RhB gradually decreased with the irradiation time in the presence of the commercial In₂O₃, h-In₂O₃, and c-In₂O₃ samples, with photodegradation efficiencies of 30.1%, 80.3%, and 84.0%, respectively. Therefore, the photocatalytic properties of the h-In₂O₃ and c-In₂O₃ products that were prepared in this study were superior to the commercial In₂O₃. The dependence of the detailed photocatalytic properties of h-In₂O₃ and c-In₂O₃ on the shape and size will be intensively examined later.

The $\lambda_{\max}$ of the absorption spectra of RhB shifted to shorter wavelength with respect to the irradiation time in the presence of the commercial In₂O₃, h-In₂O₃, and c-In₂O₃. These results suggested that the RhB degradation processes in the presence of the indium oxides were different from the degradation in the absence of the indium oxides. During the photocatalysis, the blue shift of RhB was derived from the formation of *N*-deethylation, which preferentially occurred before the destruction of

the chromophore structure of RhB.¹⁶⁻¹⁸ Therefore, the blue shift in the $\lambda_{\max}$ of RhB was observed by the decreasing length of the conjugated chromophore structure because of the deethylation during the photodegradation of RhB in the presence of the indium oxides. The normalized photodegradation curves describing the changes in the RhB concentration with respect to the halogen lamp irradiation time are shown in Figure 8.

Conclusion

The InOOH and In(OH)₃ products were selectively synthesized through a hydrothermal reaction while adjusting the amount of water. h-In₂O₃ and c-In₂O₃ products were selectively prepared through the thermal oxidation of the InOOH and In(OH)₃ products, respectively, as precursors. The morphology of the InOOH, In(OH)₃, h-In₂O₃, and c-In₂O₃ products were examined. The photocatalytic activities of h-In₂O₃ and c-In₂O₃ were better than commercial In₂O₃. Deethylation was observed during the photodegradation of RhB in the presence of h-In₂O₃ or c-In₂O₃.

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