SYNTHESIS OF COMPOSITE NANOPARTICLES IN THE TiO$_2$-SnO$_2$ SYSTEM UNDER HYDROTHERMAL CONDITIONS

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Keywords: Titanium oxide, Rutile, Anatase, Tin oxide, Cassiterite

1 Introduction
TiO$_2$ has been widely studied and applied for photocatalyst, pigment, wet-type solar cells, gas sensors, and so on [1,2]. SnO$_2$ is an attractive material in the field of gas sensing due to enhanced response to H$_2$ and CO [3-5], transparent conductor [6], and catalyst [7]. Titanium dioxide and tin dioxide, which are both wide band gap semiconductors: 3.06 eV for rutile TiO$_2$ and 3.60 eV for SnO$_2$ [8-10], have several similarities in structural and electronic properties. The ionic radius of Ti$^{4+}$ (0.68 Å) is similar to, but smaller than, that of Sn$^{4+}$ (0.71 Å). Since TiO$_2$ and SnO$_2$ both adopt the rutile-type structure, they form solid solutions which exist as stable phase above 1450 °C [11], though there exists a miscibility gap [12]. There are many studies relating to the synthesis and individual properties of TiO$_2$ and SnO$_2$. It is interesting and effective to form composite nanoparticles in the TiO$_2$-SnO$_2$ system to enhance the photocatalytic activity of TiO$_2$. Hydrothermal method is useful for the chemical synthesis of metal oxide, complex oxide, solid solution, and composite nanoparticles [13-16]. Aqueous solution routes for the chemical synthesis of inorganic materials are useful from the environmental point of view. Nanoparticles of anatase-type titania solid solutions [17-24] have been directly synthesized via the aqueous solution routes. There are many studies relating to the synthesis and individual properties of TiO$_2$ and SnO$_2$. However, the hydrothermal synthesis and characteristics of composite nanoparticles in the TiO$_2$-SnO$_2$ system have not been much investigated. In the present study, the formation of composite nanoparticles in the TiO$_2$-SnO$_2$ system under hydrothermal conditions in the presence of urea and their characteristics were investigated.

2 Experimental Procedure
A mixed aqueous solution of TiCl$_4$ and SnCl$_4$ in a total cation concentration (Ti + Sn) of 0.1 mol/dm$^3$ added with suitable amount of urea was prepared in a Teflon container. The vessel in which the Teflon container was placed was heated at 180 and 240 °C for 10 h. After hydrothermal treatment, the precipitates were washed, separated from the solution, and dried. Commercially available pure TiO$_2$ powder (ST-01, anatase, Ishihara Sangyo, Japan) was used as the reference. The as-prepared powders were examined using X-ray diffractometry (XRD) with Cu K$_\alpha$ radiation and observed under transmission electron microscopy (TEM). The lattice parameters were measured using silicon as the internal standard. The specific surface area of the prepared samples was calculated from the adsorption isotherm of nitrogen at 77 K based on the Brunauer-Emmett-Teller method (BET). The diffuse reflectance spectra measurements have been made. The photocatalytic activity was estimated from the change in the concentration of methylene blue (C$_{16}$H$_{18}$N$_3$S, MB) under ultraviolet ray (UV) irradiation from black light (20 W). To 250 cm$^3$ of aqueous MB solution (5.0×10$^{-5}$ mol/dm$^3$), 0.10 g of sample powders were dispersed via ultrasonic stirring for 5 min and maintained in the dark for 0-5 h with stirring in order to estimate time dependence of adsorption of MB. On the other hand, the sample in the solution was maintained for 0-5 h under irradiation of ultraviolet ray with an intensity of 1mW/cm$^2$ under stirring. The UV-light irradiation time dependence of MB concentration decomposed by the sample powders was estimated by the measurement of the concentration of MB remained in the solution based on the absorbance change using the spectrophotometer.

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3 Results and Discussion

3.1 Synthesis of Composite Nanoparticles

XRD patterns of the precipitates formed under weakly basic conditions at 240 °C are shown in Fig. 1. In the composition range Ti 0 ~ 70 mol%, all the precipitates were detected as a single-phase rutile-type structure, and no trace of diffraction peaks due to another phase was detected. Slight and gradual shifts of the XRD lines of the rutile-type phase (cassiterite phase) were observed with change in the ratio of Ti/Sn. The composite nanoparticles consisting of anatase- and rutile-type phases were formed at the composition of Ti 80 and Ti 90 mol%. In this composition range, the amount of anatase-type phase in the composite nanoparticles increased with increased Ti content.

3.2 Characteristics of Composite Nanoparticles

TEM images of composite nanoparticles consisting of anatase and rutile phases are shown in Fig. 2. The particle size of the precipitates increased with increased Ti content in the sample. The ratio of the existence of large particle in the sample also tended to increase with increased Ti content in the sample. It is considered that the small particle and large particle may correspond to rutile-type and anatase-type phases, respectively. This result is supported from the crystallite size and the line broadening of diffraction lines as shown in Fig. 1, i.e. broad diffraction peaks of rutile-type (Ti, Sn)O₂ and sharp diffraction peaks of anatase-type TiO₂. The particle size of the samples observed in the TEM micrographs relatively well corresponded to the increase in the crystallite size of rutile-type precipitates estimated from the XRD line broadening. Although the specific surface areas of the samples gradually decreased from approximately 140 to 90 m²/g with increased Ti content, the values of the specific surface areas of the composite samples containing Ti 80–90 % were approximately 100 m²/g. The change in the specific surface area of the samples was in good accordance with the data of the crystallite size and particle size of the precipitates. The optical band gap values of the composite nanoparticles estimated from the diffuse reflectance spectra of the as-prepared samples in the composition range of Ti 80–90 mol% showed slightly smaller band gap values than that of anatase-type pure TiO₂.

3.3 Photoactivity of Composite Nanoparticles

The effect of the composition and constitution of crystalline phase on the photocatalytic activity of the samples in the TiO₂-SnO₂ system was estimated. The adsorptivity and photocatalytic activity of the samples were evaluated separately by the measurement of the concentration of MB remaining in the solution after maintenance in the dark and under UV-light irradiation, respectively. The decrease in MB concentration, i.e. the adsorption of MB is shown for the sample (0.10 g) dispersed in 250 cm³ of aqueous MB solution (5.0×10⁻⁵ mol/dm³) after maintenance in the dark for 5 h with stirring showed that the adsorption of MB depended on the composition of the samples. It increased with the decrease in Ti content in the precipitates. The samples which have Ti content below 50 mol% showed high adsorption of MB, though the samples Ti 90 and 100 mol% scarcely showed the adsorption of MB.

The changes in the photodegradation amount of MB with time under UV-light irradiation for the samples are shown in Fig. 3. The sample Ti 0 showed low-level catalytic activity. The composite nanoparticles containing 10 and 20 mol% SnO₂, consisting of anatase and rutile phases showed better photocatalytic activity in comparison with anatase-type pure TiO₂ (Ti 100 mol%) and reference sample ST-01. The rate constants of the samples Ti 80 and 90 mol%, which are composite nanoparticles consisting of anatase- and rutile-type phases, are approximately 2 times larger than that of the anatase-type pure TiO₂ (Ti 100 mol%). It is known that the coupling of two semiconductors, possessing different energy levels for their corresponding conduction and valence bonds, provides an approach to achieve a more charge separation, an increased lifetime of the charge carriers and an enhanced interfacial charge transfer to absorbed substrates [1]. The photocatalytic activity of anatase was improved by the formation of composite nanoparticles with SnO₂, which was due to the achievement of a more charge separation, an increased lifetime of the charge carriers and an enhanced interfacial charge transfer to absorbed substrates [1].
4 Summary

The hydrothermal treatment of the precursor solution of TiCl\textsubscript{4} and SnCl\textsubscript{4} was carried out under weakly basic conditions in the presence of urea at 180 and 240 °C. The composite nanoparticles consisting of anatase and rutile phases were formed at 180 ~ 240 °C at the composition Ti 80 and Ti 90 mol%. The amount of anatase-type phase in the composite nanoparticles increased with increased Ti content. The rutile-type solid solutions between TiO\textsubscript{2} and SnO\textsubscript{2} were hydrothermally synthesized as nanoparticles in the composition range Ti 0 to Ti 70 mol%. The specific surface areas of the samples gradually decreased from approximately 140 to 90 m\textsuperscript{2}/g with increased Ti content. The particle size of the composite nanoparticles was in the range of 5 to 15 nm. The composite nanoparticles consisting of anatase and rutile phases with composition Ti\textsubscript{0.90}Sn\textsubscript{0.10}O\textsubscript{2} and Ti\textsubscript{0.80}Sn\textsubscript{0.20}O\textsubscript{2} showed improved photocatalytic activity.

Fig. 1. XRD patterns of precipitates formed from the mixed solution of TiCl\textsubscript{4} and SnCl\textsubscript{4} under hydrothermal conditions at 240 °C for 10 h.

Fig. 2. TEM images of precipitates formed at the composition (a) Ti 80 mol% and (b) Ti 90 mol%.

Fig. 3. Photocatalytic degradation of methylene blue as a function of UV irradiation time for samples.

References


