A facile synthesis of hierarchical Sn$_3$O$_4$ nanostructure in an acidic aqueous solution and their strong visible light-driven photocatalytic activity

Hui Song$^1$, Su-Young Son$^{1,2}$, Seul Ki Kim$^1$, and Gun Young Jung$^1$ (✉)

Nano Res., Just Accepted Manuscript • DOI 10.1007/s12274-015-0855-2
http://www.thenanoresearch.com on July 9, 2015

© Tsinghua University Press 2015

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.
Hierarchical Sn$_3$O$_4$ Nanosphere covered with single crystalline nanoplates can absorb intense energy at visible wavelengths from the Sun. The generated holes react with the hydroxyl groups in aqueous solution to form hydroxyl radicals, which can effectively attack and decompose the organic pollutants.
A Facile Synthesis of Hierarchical Sn₃O₄ Nanostructure in an Acidic Aqueous Solution and Their Strong Visible Light-Driven Photocatalytic Activity

Hui Song, Su-Young Son, Seul Ki Kim, and Gun Young Jung (*)

School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Carbon Covergence Materials Research Center, Institute of Advanced Composite Materials Korea Institute of Science and Technology (KIST), Jeollabuk-do, South Korea.

Received: day month year / Revised: day month year / Accepted: day month year (automatically inserted by the publisher)
© Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2011

ABSTRACT
Hierarchical Sn₃O₄ nanospheres were synthesized via hydrothermal reaction under strongly acidic ambient conditions. The morphology of Sn₃O₄ was varied with decreasing values of pH; the prickly Sn₃O₄ nanosphere was changed into a Sn₃O₄ nanosphere covered with single crystalline nanoplates with a high surface-to-volume of ca. 55.05 m²g⁻¹ and a band gap of ca. 2.25 eV. A small amount (0.05 g) of the hierarchical Sn₃O₄ nanostructures completely decomposed a 30 % methyl orange (MO) solution in 100 ml deionized water in 15 min under one-Sun condition (UV + Vis. light). The Sn₃O₄ photocatalyst exhibited a fast decomposition rate of 1.73 x 10⁻¹ min⁻¹, which is a 90.86 % enhancement relative to that of the commercially available P25 photocatalyst. The high photocatalytic activity of the hierarchical Sn₃O₄ nanostructure is attributed to its ability to absorb visible light and its high surface-to-volume area.

KEYWORDS
Sn₃O₄, Hierarchical structure, Hydrothermal, Morphology engineering, Photocatalyst

1. Introduction
Tin oxide has several advantages of controllable size or shape via the simple hydrothermal method,[1] excellent optical and electrical properties (transparency at wavelengths of 300 ~ 800 nm and a low electronic resistivity of 8.6 x 10⁻⁵ Ωcm⁻¹), its non-toxicity[2] and so on. With these merits, it has been utilized in various fields such as gas sensors,[3,4] lithium ion batteries,[5] dye-sensitized solar cells[6] and photocatalysts.[7-9] Regarding its use as a photocatalyst, tin oxide has a strong resistance against acidic/alkali solutions and exhibits a good photocatalytic activity without generating secondary pollutions under irradiation with ultraviolet (UV) light.[8,9] However, there are few works on solely using the tin oxides under irradiation with visible light because of its wide band gap. Therefore, co-catalysts with a narrow
energy band gap, such as CdS[10], Ru(bpy)₃²⁺[11] and Pt[12], have been introduced to enhance the photocatalytic activity of tin oxide under irradiation with visible light. However, because the cost of co-catalysts is expensive, the development of photo-catalytic materials for generating electron-hole pairs under visible light is necessary to effectively utilize sun light.

Unlike SnOs as a photocatalyst, SnOs has been used as a visible light-driven photocatalyst because it has experimentally shown to absorb light at visible wavelengths.[13-15] Therefore, the pollution decomposition efficiency of SnO₄ photocatalysts is higher than that of SnO₂ under the Sun.[13] However, studies on the SnO₄ have just begun, including investigations into its growth mechanism,[16-18] crystal structure and theoretical properties.[19,20]

SnO₄ was formed as one of intermediate tin oxides (i.e., SnO₄, SnO₃, and SnO₂) during the disproportionation reaction of Tin(II) oxide (SnO).[21] SnO₄ was mainly generated by dry chemical methods including carbothermal evaporation,[15] thermal decomposition of SnO₂,[22] carbothermal reduction,[23] Vilasi et al. reported that SnO₄ coexisted as a transition form at the process temperature range of 400-500 °C during the phase transformation from SnO to SnO₂.[24] However, only a small quantity of SnO₄ was obtained. Indeed, SnO₂ was the major product in the reaction, which was thermodynamically more stable than SnO₄ during the oxidation of Sn⁺² at high temperatures.

For this reason, hydrothermal methods were used to generate SnO₄ at temperatures below 200 °C without the production of unwanted SnO₂.[25-29] Li et al. synthesized hierarchical SnO₄ structures (diameter: ~ 1 μm) at 180 °C hydrothermally at pH 3 in an autoclave Teflon vessel, which made it difficult to adjust the pH during the hydrothermal process for controlling the morphology. They showed that the hierarchical SnO₄ structure had the highest pollution decomposition rate among other photocatalysts such as SnO, SnO₂ and N-doped TiO₂.[13] However, only 10 ppm concentration of methyl orange (MO) in 80 ml solution was decomposed in 20 min by the photocatalytic reaction of 0.04 g SnO₄.

Herein, we proposed a facile hydrothermal method in a 3-neck round flask to fabricate hierarchical SnO₄ nanospheres covered with single-crystalline nanoplates at a temperature below 100 °C. By adjusting the pH of the nutrient solution during the process, the morphology and phase transformation of SnO into the SnO₄ nanostructure can be controlled. The photocatalytic activity of the generated hierarchical SnO₄ nanostructure was investigated and compared with that of the commercially available TiO₂ (Degussa, P25) under one-Sun condition (i.e., Air Mass 1.5, 100 mWcm⁻²).

2. Experimental Section
2.1 Synthesis of hierarchical SnO₄ nanostructure

1.23 g of tin oxalate (Sn(C₂O₄), M = 206.78 gmol⁻¹) was dissolved in 250 ml deionized (DI) water with stirring for 30 min at room temperature. When the temperature reached 70 °C, black precipitates of SnO appeared. Then, the pH value (pH = 2, 3, 4 and 5) of the nutrient solution was adjusted by slowly adding 0.5 M hydrochloric acid (HCl, M = 40.06 gmol⁻¹, 37 %) to the solution having the black precipitate while continuously stirring for 3 hrs at 95 °C. The color of precipitate was changed from black to yellow. After completing the hydrothermal reaction, the precipitate was collected by centrifugation and then washed with DI water. Finally, the product was dried inside a common laboratory oven at 35 °C for 1 day.
2.2 Characterization of properties

The crystallographic information of hierarchical Sn₃O₄ nanostructure was analyzed by X-ray diffraction (XRD) using Cu K-alpha X-ray radiation (40 kV, 100 mA, Rigaku D/max-2400) and Raman spectroscopy with 514 nm laser beam (Horiba). The morphology of sample was observed by scanning electron microscopy (SEM, FE-SEM, JEOL 2010 F) and high resolution transmission electron microscopy (HRTEM, JEM-2100), operated at an accelerating voltage of 200 kV. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using a nanoporosity surface area analyzer (nanoPOROSITY-XQ, Mirae Scientific Instruments Inc.). A UV-Vis. spectrometer (AvaSpec-ULS2048L-USB2 Spectrometer, Jinyoung tech Inc.) was used to analyze the absorbance of the hierarchical Sn₃O₄ nanostructure and the decomposition of the MO solution. Photocatalytic activity was characterized under illumination of an AM 1.5 simulated sunlight source (SANEI solar simulator, Class A) with a power density of 100 ± 2.5 mW cm⁻².

2.3 Photocatalytic activity

0.05 g of as-produced catalysts of SnO, Sn₃O₄ and commercially available P25 (TiO₂, Degusa) were added into a 30 vol. % MO solution in 100 ml DI water. Prior to irradiation, the suspension was violently stirred in the dark for 30 min to saturate the solution with O₂. The suspension was irradiated with the light (UV + visible) from a solar simulator. At given time intervals (15, 30, 45 and 60 min), a 3 ml aliquot was extracted and filtered to remove the photocatalytic powder. The filtered solution was analyzed by the UV-Vis. spectrometer to measure the MO contents (Maximum absorption band, λ = 485 nm).

3. Results and discussion

3.1. The effect of pH on the formation of hierarchical Sn₃O₄ nanostructure

The hierarchical Sn₃O₄ nanostructures were synthesized by hydrothermal reaction at 95 °C. Tin oxalate, Sn(C₂O₄), was used as the tin ions source. Unlike the most commonly used tin salts such as tin dichloride (SnCl₂) and tin tetrachloride (SnCl₄), the Sn(C₂O₄) can easily offer abundant tin(II) ions (Sn²⁺) in the nutrient solution because it can be dissociated easily at a low temperature due to the relatively weak electro-static attraction between the pure metal ion (Sn²⁺) and the organic chelating reagent (C₂O₄⁻).[6] Thus, SnO was easily synthesized at first by using the Sn(C₂O₄) as a starting material at a low temperature. Then, in an acidic conditions the SnO was easily dissolved and changed into a tin complex ion (Sn(OH)₂²⁺). Finally, the Sn₃O₄ nanostructures were formed by dehydration of the Sn₃(OH)₂²⁺.[30]

When the temperature of nutrient solution reached 70 °C, the color of the precipitate was changed from white to black, indicating the formation of SnO, and remained black until 95 °C. However, the color of the precipitate became yellow after adding a hydrochloric acid solution at 95 °C, indicating that some changes to the SnO occurred. The morphology and phase transformation of the products were examined at different pH values of
the solution, which was controlled by varying the amount of added hydrochloric acid. After completing the hydrothermal reaction, the precipitate was collected by centrifugation and then dried to analyze the structure and determine its photocatalytic ability.

The crystallographic structures of the hierarchical SnO$_3$O$_4$ nanostructure at various pH values was characterized by X-ray diffraction (XRD) as shown in Figure 1. Figure 1a indicates the XRD peaks of a tetragonal SnO marked with the ● symbols at (001), (101) and (002), which are well matched with the standard XRD data file (JCPDS-06-0395). The phase transformation from SnO to SnO$_3$O$_4$ occurred with decreasing pH, and the XRD patterns indicated the coexistence of SnO and SnO$_3$O$_4$ at pH 5 (Fig. 1b). Only SnO$_3$O$_4$ diffraction peaks existed at pH of less than 3, as shown in Figure 1d and e, where the ■ symbols are assigned to (111), (-210), (-121), and (311) of a triclinic SnO$_3$O$_4$ (JCPDS-20-1293).[17] Notably, several unknown crystalline peaks were generated when the pH approached 1. Thus, controlling the pH value within 2 and 3 during the reaction was critical to synthesize well-defined SnO$_3$O$_4$ nanostructure.

Measurements with Raman spectroscopy also confirmed the phase transformation from SnO to SnO$_3$O$_4$ at pH 5. The Raman peaks were collected with a 514 nm excitation laser. The Raman peaks of SnO at 113 and 211 cm$^{-1}$ are seen in Figure 2a. The peaks from the SnO and SnO$_3$O$_4$ structures coexisted at pH 5, as in the XRD data. As the pH decreased, the Raman peaks of SnO$_3$O$_4$ at 143 and 170 cm$^{-1}$ gradually appeared, as shown in Figure 2b. Only the Raman peaks of SnO$_3$O$_4$ existed at pH of less than 3 (Figs. 2d-e), which became more prominent with decreasing pH.[17] No other impurities were detected. The XRD and Raman spectra indicates the transition of crystal structure from tetragonal SnO to triclinic SnO$_3$O$_4$ at pH 5 and the sole existence of SnO$_3$O$_4$ when adjusting the pH between 2 and 3.

The morphology of SnO$_3$O$_4$ was observed by using scanning electron microscopy (SEM) and transmittance electron microscopy (TEM). Figure 3 shows the variation of hierarchical SnO$_3$O$_4$ morphology at different pH conditions. It was observed that the pH had a great influence on the morphology of SnO$_3$O$_4$. Indeed, if HCl was not added
into the nutrient solution, then only SnO nanoparticles aggregated together as shown in Figure 3a. At pH 5, the neighboring nanoparticles aggregated into a prickly sphere with a diameter of approximately 100 nm (Fig. 3b). As the solution became more acidic (pH = 4, Fig. 3c), the prickly surface became prominent. At pH less than 3, in which the SnO was completely transformed into the hierarchical Sn$_3$O$_4$, the prickles were dissolved and recrystallized into nanoplates as shown in Figure 3d and 3e. Figure 3f shows a magnified hierarchical Sn$_3$O$_4$ nanosphere having irregularly oriented thin nanoplates with a radius of 20 nm.

Figure 4a and 4b are TEM images that clearly show the aggregated Sn$_3$O$_4$ nanospheres covered with the protruded thin nanoplates. Figure 4c-e are the HR-TEM images of a nanoplate at different pH values. During the dissolution and recrystallization of the nanoplate, the lattice was aligned along the direction of the more thermodynamically stable plane. At pH 5, the nanoplate had conspicuous grain boundaries with an averaged grain size of 5 nm and the lattice was misaligned between the grains (Fig. 4c). At pH 2, the grain boundaries disappeared and the lattice fringes became perfectly aligned along the [111] direction with a spacing of 0.329 nm. Eventually, single crystalline triclinic phase Sn$_3$O$_4$ nanoplates were formed under strongly acidic ambient condition. However, the mechanism of the lattice alignment and the nanoplate formation have not been clearly understood.

3.2. Characterization of the hierarchical Sn$_3$O$_4$ nanostructure

The porous nature of the hierarchical Sn$_3$O$_4$ nanostructure was investigated by nitrogen (N$_2$) gas adsorption/desorption isotherms analysis via the Brunauer-Emmett-Teller (BET) method as shown in Figure 5. All the hierarchical Sn$_3$O$_4$ nanostructures followed mesoporous type (IV) isotherm with a hysteresis loop. In the case of highly mesoporous materials, a hysteresis loop is remarkable by the phenomenon of capillary condensation. The BET surface area of SnO was 8.92 m$^2$g$^{-1}$. The other hierarchical Sn$_3$O$_4$ nanostructures synthesized at different pH values had BET surface areas of 11.68, 12.26, 46.48 and 55.05 m$^2$g$^{-1}$ with decreasing pH values from 5 to 2, respectively. The amount of adsorbed nitrogen increased dramatically after complete conversion of SnO into the hierarchical
SnO$_2$. The SnO$_2$ structure synthesized at pH 2 had the highest value of BET surface area, indicating a highly porous structure caused by intensive etching in such a strongly acidic ambient condition. The inset of figure 5 demonstrates the pore size distribution of hierarchical SnO$_2$ synthesized at pH 2, revealing a maximum at 40 Å.

UV-Vis. absorption spectra of the SnO$_2$ structures are shown in Figure 6. In the case of SnO, there was no absorption in the UV wavelengths and comparatively negligible absorption in the visible wavelengths. The respective absorption edges of the SnO$_2$ structures are 397, 445, 480 and 550 nm with decreasing pH values from 5 to 2, respectively. By using the equation of $E_g = 1240/\lambda$ (λ = the wavelength of absorption edge), the corresponding band gap of the SnO$_2$ structures are calculated to be 3.12, 2.78, 2.58 and 2.25 eV, respectively. These results indicate that the band gap of hierarchical SnO$_2$ nanostructure becomes lower with decreasing pH. In comparison, the commercially available P25 (TiO$_2$, Degusa) photocatalyst had an absorption edge of 350 nm, corresponding to a band gap of 3.54 eV, and a negligible absorbance at visible wavelengths.

3.3. Photocatalytic activity of the hierarchical SnO$_2$ nanostructure

The photocatalytic activity of the mesoporous hierarchical SnO$_2$ nanostructure synthesized at pH 2 was tested by measuring the photo-decomposition of MO under one-Sun condition (air mass 1.5). The P25 photocatalyst was also tested to compare its performance with the synthesized SnO and SnO$_2$ structures. Because the P25 (TiO$_2$) has the merits of inexhaustible abundance with no photo-corrosion and non-toxicity,[34-36] many research groups have studied the photocatalytic phenomena of TiO$_2$ under irradiation with UV light.[37-40] However, because of its wide band gap, the TiO$_2$ cannot excite electrons at the valence band under irradiation with visible light as shown in Figure 6. For direct comparison, the same amount of each photocatalyst (0.05 g) was added into an excessively concentrated (30 vol. %) MO solution in 100 ml deionized water to measure the photocatalytic ability in such an extreme condition.

Usually, the MO has been used as a pH indicator and utilized in various industrial fields such as textile, printing, paper, food and so on. However, it has mutagenic side-effects and often pollutes the environment. Thus, the elimination of MO in solution is necessary for the environment and healthy life. When the photocatalyst absorbs light from the Sun or an artificial light source, it produces
pairs of electron and hole. The generated holes attack the surrounding water molecules to generate hydroxyl radicals (·OH) at the surface of photocatalysts as depicted in the following photo-oxidation mechanism:

\[
\text{Metal oxide} + \text{hv} \rightarrow e^-_{\text{CB}} + h^+_{\text{VB}} \quad (1)
\]

\[
h^+_{\text{VB}} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \quad (2)
\]

It is known that the hydroxyl radical has the second largest oxidation potential of 2.8 V among several common oxidants including fluorine (3.03 V), ozone (2.07 V), hydrogen peroxide (1.77 V) and chloride (1.36 V). Therefore, the ·OH can rapidly attack and cleave the aromatic rings of organic pollutants.[41]

Figure 7a represents the variation of MO concentration (C/C₀) as a function of exposure time under one-Sun condition. The decomposition efficiency of the photocatalyst is defined as follows:

\[
\text{Photo-decomposition} \% = (1 - \frac{C}{C_0}) \times 100 \% \quad (3)
\]

where, C₀ is the initial concentration of MO solution before irradiation and C is its concentration after irradiation. After 1 hour exposure under one-Sun condition, no decomposition of MO was observed in the case of SnO because it had a small BET surface area and a negligible light absorbance over entire wavelengths. In the case of P25, the photo-decomposition proceeded slowly; 80 % of the MO remained after 15 min exposure and it took 1 hour to decompose all the MO contents because this photocatalyst was active only at UV wavelengths. Unlike the P25, the mesoporous hierarchical SnO₃ nanostructure synthesized at pH 2 demonstrated a rapid photo-decomposition owing to its narrow band gap, enabling to absorb the intense visible and UV light concurrently. The MO was completely decomposed within 15 min with only 0.05 g of SnO₃ photocatalyst. Comparison of photocatalytic activity of P25 vs. SnO₃ under UV light or visible light illumination was illustrated in Fig. S1 of the Electronic Supplementary Material (ESM). The SnO₃ had a much higher photocatalytic activity in both cases.

Figure 7b and 7c present the variation of the absorption spectra of MO solution with different exposure times when using the SnO₃ and P25, respectively. In the case of SnO₃ photocatalyst, the intensity of the MO absorption peak (λ = 485 nm) was dramatically attenuated (Figure 7a). After 15 min exposure, the color of the MO solution became bleached as shown in the inset of Figure 7b, suggesting that the entire MO was completely decomposed within 15 min. In contrast, the MO absorption peak gradually decreased with exposure time when using the P25. The inset of Figure 7c confirms the gradual color change of the solution with exposure time.

The photo-decomposition rate of MO can be calculated by the following equation:[14]

\[
-\ln\left(\frac{C}{C_0}\right) = \kappa t \quad (4)
\]
where $\kappa$ (min$^{-1}$) is the photo-decomposition rate constant. The $\kappa$ value of each photocatalyst after 15 min irradiation is summarized in Table 1. The Sn$_3$O$_4$ exhibited much faster photo-decomposition activity compared with the other two photocatalysts. The $\kappa$ value of Sn$_3$O$_4$ is $1.73 \times 10^{-1}$ min$^{-1}$ under one-Sun condition, which is a 90.86 % enhancement compared to that of P25 ($1.58 \times 10^{-2}$ min$^{-1}$). Considering the complete removal of the extremely concentrated MO solution (30 vol. %), the photocatalytic ability of the hierarchical Sn$_3$O$_4$ nanostructure is superb. The excellent performance can be ascribed to its large surface area, permitting widespread contact to the MO solution, and its narrow band gap, which effectively utilizes the visible light of the Sun.

The used Sn$_3$O$_4$ photocatalysts were collected by centrifugation and recycled in the subsequent photocatalytic activity test to check the durability for repeatable use. No significant change in photocatalytic activity was observable in 5 successive tests (S2 in the ESM).

4. Conclusion
Hierarchical Sn$_3$O$_4$ nanospheres covered with nanoplates were synthesized via a simple hydrothermal method in strongly acidic ambient condition. X-ray diffraction and Ra-man spectroscopy evidenced that only triclinic Sn$_3$O$_4$ was produced from SnO at pH 3 by dissolution and recrystallization. During recrystallization, the lattice of the nanoplate was aligned along the thermodynamically stable [111] plane. The hierarchical Sn$_3$O$_4$ nanostructure (0.05 g) possessed an ability to fully decompose 30 vol. % MO in 100 ml deionized solution in 15 min under one-Sun condition with a decomposition rate of $1.73 \times 10^{-1}$ min$^{-1}$, which is a 90.86 % enhancement compared with that of the commercially available P25. The high photo-decomposition activity of the hierarchical Sn$_3$O$_4$ nanostructure was resulting from a BET surface area of 55.05 m$^2$g$^{-1}$ and its narrow band gap of 2.25 eV, which is capable of absorbing the visible light.

### Acknowledgements
This work was supported by the Basic Science Research program through the National Research Foundation of Korea funded by the Pioneer Research Center Program (NRF, No. 2014M3C1A3016468) and the GIST Specialized Research Project provided by GIST.

### Electronic Supplementary Material: Experimental details and additional data. This material is available free of charge via the Internet at http://dx.doi.org/10.1007/sxxxxx-xxxx-xxxx-x.

### References

8. Wang, H. J.; Sun, F. Q.; Zhang, Y.; Li, L.; Chen, H.; Wu, Q.; Yu. J. C. Photochemical growth of nanoporous SnO at


