Supplementary Information

Zinc Stannate Nanocubes and Nanourchins with High Photocatalytic Activity for Methyl Orange and 2,5-DCP Degradation

Zhenfei Tian, Changhao Liang,* Jun Liu, Hemin Zhang and Lide Zhang

Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics,

Hefei Institutes of Physical Science, Chinese Academy of Sciences

Hefei 230031, China

* Corresponding author. Tel.: +86 551 5591129; fax: +86 551 5591434.

E-mails: chliang@issp.ac.cn (C. H. Liang).

Preparation of $ZnSnO_3$ nanocrystalline films: The mushy mixture of $ZnSnO_3$ nanocrystals was firstly obtained by adding certain amount of ethyl alcohol, macrogol 400 (PEG-400) and Triton X-100 into the dry powder sample of urchin-like $ZnSnO_3$. Then, the prepared mixture was deposited on the conductive surface of a F-doped SnO_2 (FTO) glass substrate with certain area. After 48 hours dry at room temperature, the nanocrystals coated FTO substrate were annealed at 450°C for 120 minutes to obtain $ZnSnO_3$ films.

Figure S1 shows the characterization results of Zn and Sn based colloids by pulse laser ablation in liquids (LAL). Figure S1a and Figure S1b display the XRD patterns and TEM images of the freshly-prepared Zn colloids. The XRD analysis indicated that the mixture of ablated product consisted of ZnO, Zn and β-$Zn(OH)_2$ phases,. After ageing for several hours, the morphology and phases of product changed as showing in Figure S1c and d. The β-$Zn(OH)_2$ phase disappeared and the relative intensity of Zn phase decreased. ZnO become the main phase. The phases and morphology of Sn colloids are also shown in Figure S1e and S1f. The freshly-prepared Sn colloids consisted of amorphous SnO_2 and metal Sn phases. After longer time ageing treatment than that of Zn colloids, the amorphous SnO_2 will crystallize. Figure S1g and Figure S1h shows the phases and morphology change after ageing. The fresh colloids with high reaction activity were utilized as precursors in the following hydrothermal treatment for obtaining ternary oxides nanocrystals.

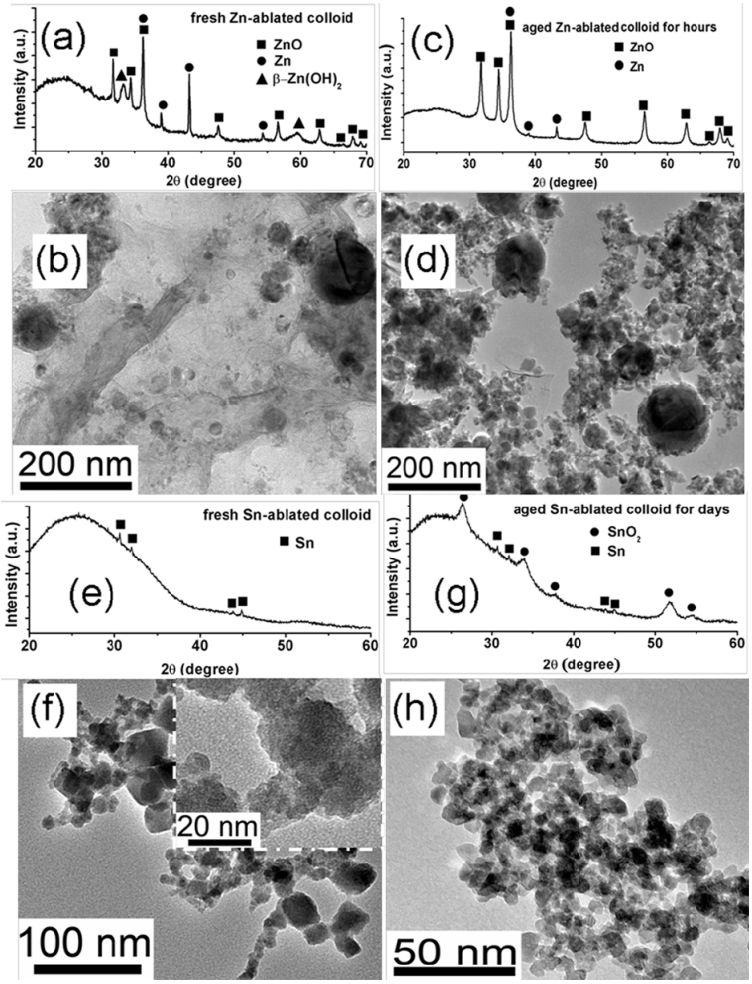

Figure S1. Morphology and phases of freshly-prepared and aged colloidal products by LAL of Zn and Sn targets. (a), (b) fresh Zn-ablated colloidal products, (c), (d) aged Zn-ablated products, (e), (f) fresh Sn-ablated colloidal products, (g), (h) aged Sn-ablated products.

Figure S2 shows the XRD patterns of products tuned by changing the concentration of ammonia. Figure S2a shows that, when 0.15 mol/L ammonia was used in reaction, the obtained product was a mixture of $ZnSnO_3$ and Zn_2SnO_4. When the amount of ammonia increased to 0.30 mol/L, only perovskite $ZnSnO_3$ phase could be found.

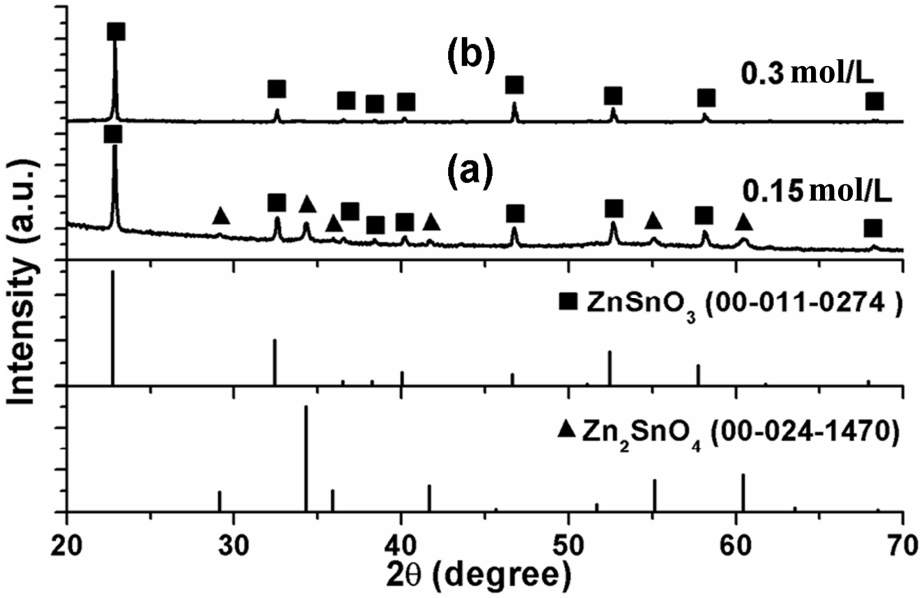

Figure S2. XRD patterns of the tunable zinc stannate phases by changing the concentration of ammonia, (a) 0.15 mol/L, (b) 0.30 mol/L.

Figure S3 gives the evolved morphologies of the final products with different amount of ammonia added. When ammonia in concentration of 0.15 mol/L was added, the amount of cube-like structure decrease as showing in Figure S3a in compared with morphology of product without ammonia added (Figure 2a). Meanwhile, a lot of nanocrystals with smaller size formed. When the concentration of ammonia increased to 0.30 mol/L (Figure S3b), the cube-like Zn_2SnO_4 structure completely disappeared. As the concentration of ammonia is 0.6 mol/L (Figure S3c), the product consisted of nanoplates (SEM image indicated) with fine rods at the edge. As the added concentration further increased to 1.5 mol/L, as Figure S3d shown, the nanoplates begin to evolve into urchin-like structure.

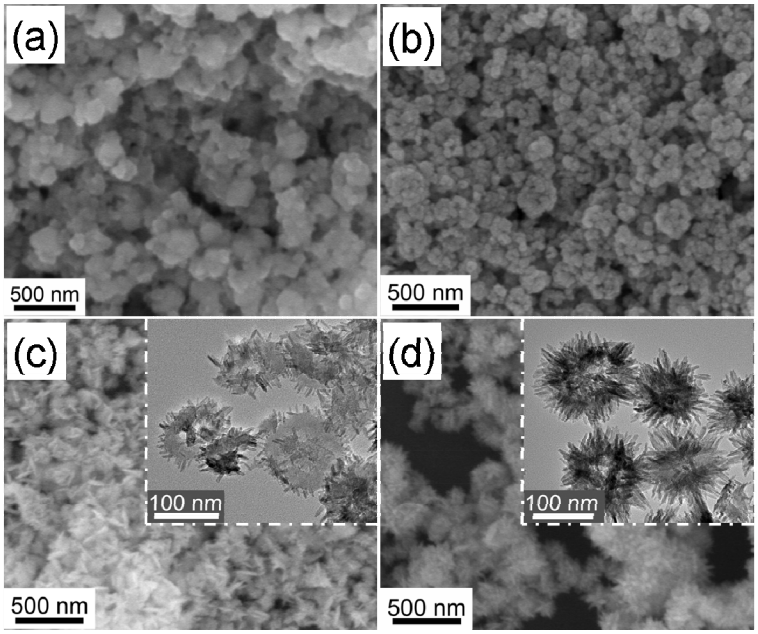

Figure S3. SEM and TEM images of as-synthesized zinc stannate nanostructures with different amount of ammonia added. (a) 0.15 mol/L, (b) 0.30 mol/L, (c) 0.60 mol/L, (d) 1.5 mol/L.

Figure S4 displays the local enlarged UV spectra of Figure 8c, indicating the degradation of 2,5 dichlorophenol (2,5-DCP) under ultraviolet-light irradiation. With $ZnSnO_3$ catalyst used (Figure S4a), spectrum with peak located around 280 nm of B-band of benzene ring disappeared. However, for the blank comparison, the intensity of B-band did not show decrease except for their peaks profile changed slightly as time going.

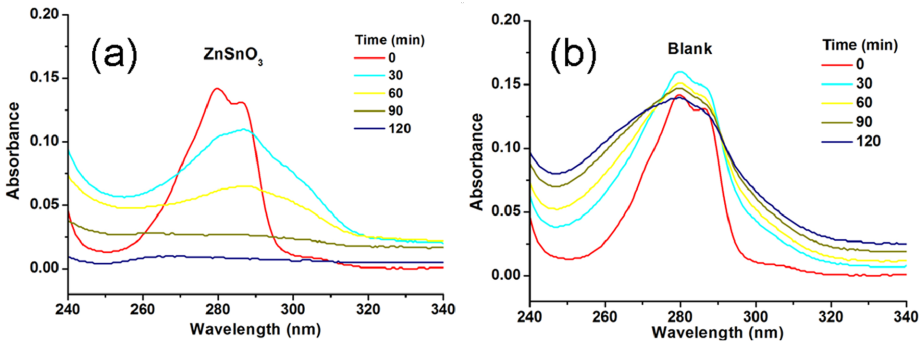

Figure S4. Local enlarged UV spectra of 2,5-DCP degradation under UV-light irradiation, (a) urchin-like $ZnSnO_3$ added, (b) blank for comparison.