Electronic Supplementary Information

Hydrothermal Synthesis and Photoluminescent Properties of Stacked Indium Sulfide Superstructures

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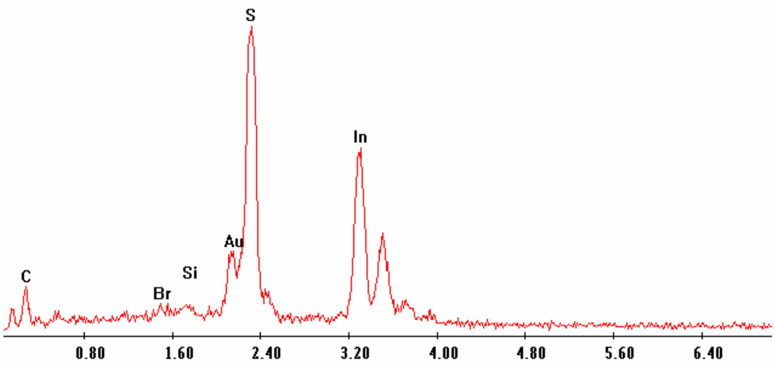

Fig. S1 EDX spectrum of In_2S_3 stacked superstructures.

FT-IR spectrum shows weak bands at 2915 and 2841cm^{-1} which are associated with asymmetric and symmetric methylene C-H stretches vibration, respectively. The band at 1463cm^{-1} arises from –CH_3 deformation and –CH_2 scissoring vibrations, while band at 723cm^{-1} is assigned to rocking vibration of methylene, suggesting that surfactant CTAB molecules remain strongly associated with the In_2S_3 crystals even after extensive washing.

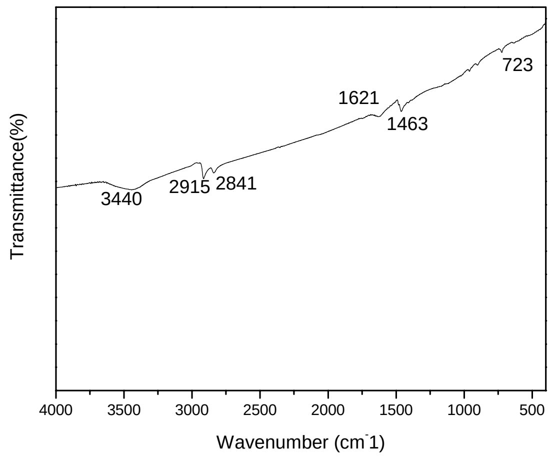

Figure S2. IR spectrum of the β-In_2S_3 nanostructures.

To depict the nature of the prepared In_2S_3 sample, thermogravimetric analysis (TGA) was carried out. TGA shows two distinct weight-loss steps in the temperature range of 20-600ºC, the first step in the region 20-450ºC corresponds to the removal of the organic surfactant of CTAB. Subsequent weight loss of 14.53% occurs between 450-600 ºC, which is approximately equal to the ideal weight loss of 14.72% when In_2S_3 is oxidized into In_2O_3 in air. The weight –loss process ceases at 550º C, and the stable residue can reasonably be ascribed to In_2O_3.

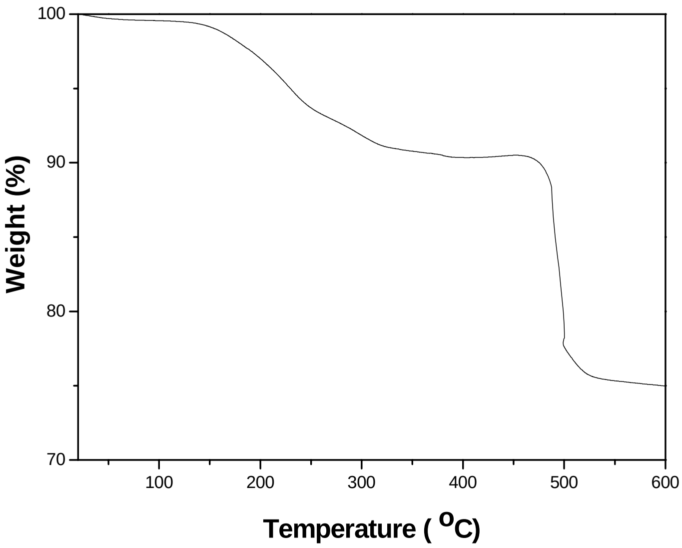

Figure S3. TGA curve of the prepared In_2S_3 sample.

The effect of hydrothermal temperature on the final morphology was investigated. Fig. S4 shows FE-SEM images of the samples prepared at different temperatures for 7 h. At 100ºC, the SEM image shows that the as-prepared samples are of cubic morphology of micrometer scale as shown in Fig. S4a. EDX pattern indicates that the cubic crystals are $In(OH)_3$, suggesting that thiourea did not decompose at this low temperature. Increasing the reaction temperature to 120ºC, the mixtures of cubic $In(OH)_3$ and stacked structures of In_2S_3 composed of nanoflakes were observed (Fig. S4b), indicating thiourea began to react with H_2O at this temperature to produce H_2S, and to result in the conversion of cubic $In(OH)_3$ to In_2S_3 stacks partly. And prolonging the reaction time to 24 h at this temperature, only stacked In_2S_3 composed of nanoflakes can be observed. Further increasing the reaction temperature to 180 ºC,

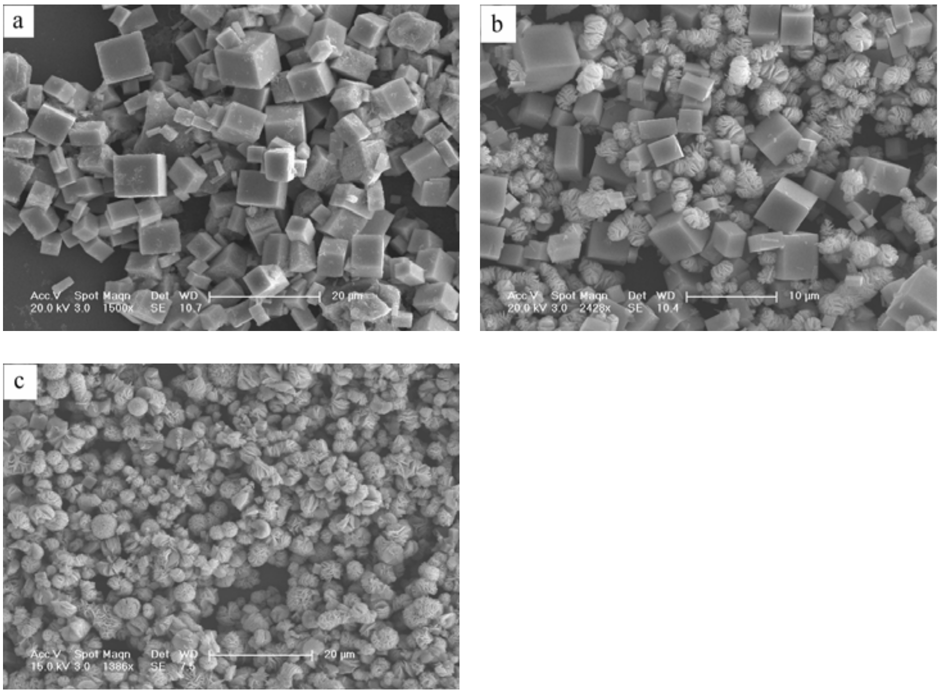

Fig. S4 FE-SEM images of the products under different hydrothermal temperatures for 7 h: (a) 100 ºC, (b) 120 ºC, (c) 180 ºC

In_2S_3 micropompons composed of nanoflakes became the main products (Fig. S4c). From the above results we can conclude that 140 ºC is the optimum temperature for the formation of stacked In_2S_3 superstructures.

In order to investigate the influence of CTAB and /or thiourea on the formation of In_2S_3 stacked structures, the following experiments were performed. The first experiment was carried out using Na_2S instead of thiourea as the sulfur source while keeping other reaction conditions the same. As a result, only nanoparticles of various shapes were obtained (Fig. S5). The main reason is likely to be that the reaction rate of $In(OH)_3$ and S^{2-} is too fast under this reaction condition. Other experiments were carried out by using an appropriate dosage of Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) or sodium dodecyl sulfate (SDS) as the template instead of CTAB, thus only microspheres (Fig. S6) or irregular polyhedra (Fig. S7) were observed by FETEM when AOT and SDS acting as "soft template", respectively. In a control experiment, without the addition of CTAB, there was no well-defined hierarchical stacks, but

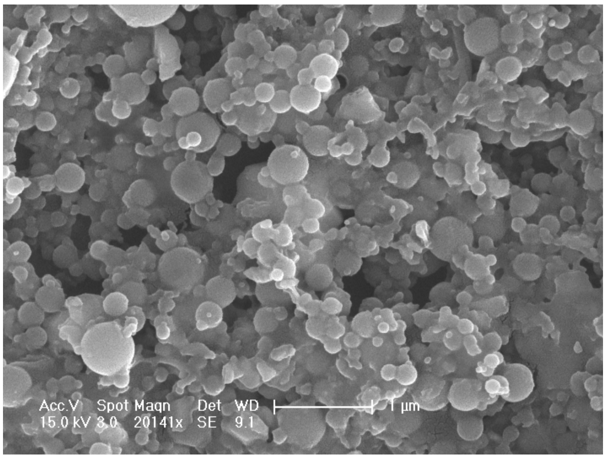

Figure S5. FE-SEM image of the as-synthesized In_2S_3 nanoparticles with Na_2S as sulfur source instead of thiourea.

rather nanoflowers composed of nanoflakes were found(Fig. S8). Based on the outcomes of above experiments, we believe that both thiourea as sulfur source and surfactant CTAB are indispensable for the formation of stacked superstructures of β-In_2S_3.

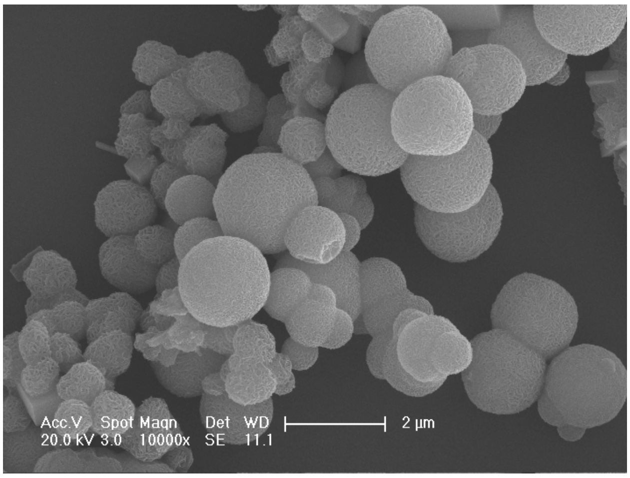

Figure S6. FE-SEM image of the as-synthesized In_2S_3 microspheres in the presence of AOT as template.

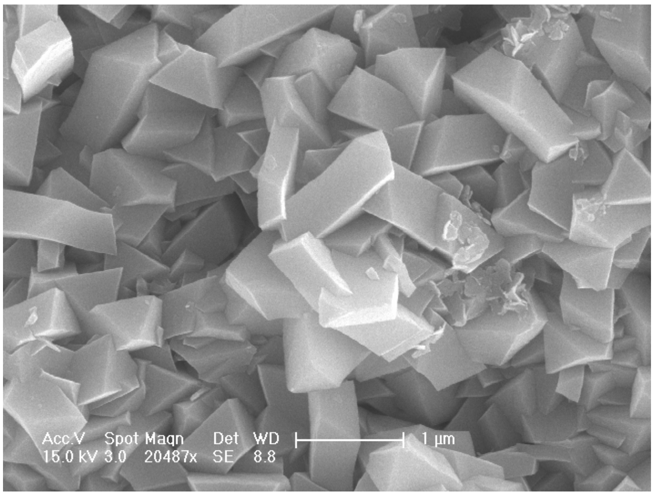

Figure S7. FE-SEM image of the as-synthesized In_2S_3 irregular polyhedra in the presence of SDS as template.

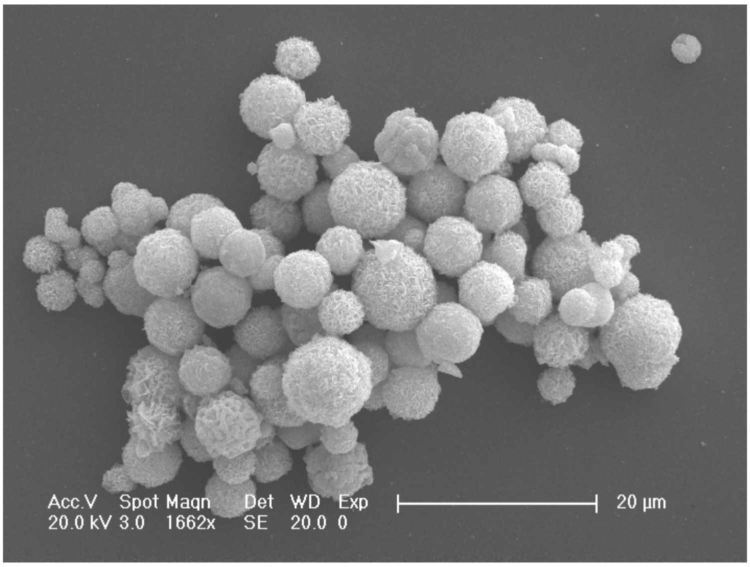

Figure S8. FE-SEM image of the as-synthesized In_2S_3 nanoflowers without any surfactants.

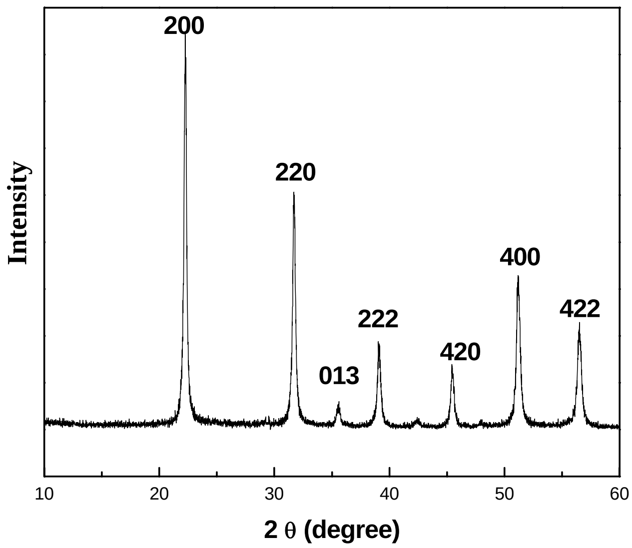

Figure S9. XRD pattern of $In(OH)_3$ nanorod bundles.