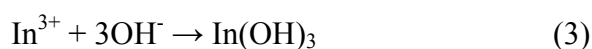*Supporting information*

Growing mechanism of In(OH)$_3$ nanostructures

The electrochemical synthesis of In(OH)$_3$ is a two step process: First, nitrate ions and H$_2$O are electrochemically reduced at the surface of the working electrode, resulting in an increase in local pH value in the vicinity of the electrode (eqs 1 and 2). Then, the increase in the local pH leads to the precipitation of indium ions as indium hydroxide (eq 3) at suitable temperatures:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

$$In^{3+} + 3OH^- \rightarrow In(OH)_3 \qquad (3)$$

For better understanding the growth mechanism of In(OH)$_3$ nanostructures, we have investigated the formation process by the aid of the controlled experiments with different deposition time. Meanwhile, we found that the morphology of In(OH)$_3$ did not change much when the electrodeposition temperature was set at 70-80 ºC. Figure 6 displays the SEM images of the samples obtained at different reaction times. As we see in Figure 6, further prolonging the electrodeposition time to 80 min，the cubic In(OH)$_3$ structure can be easily observed while nanosheet structure is slightly visible. Finally, In(OH)$_3$ nanocubes with the edge in the range of 400-600 nm were formed after electrodeposition for 120 min.
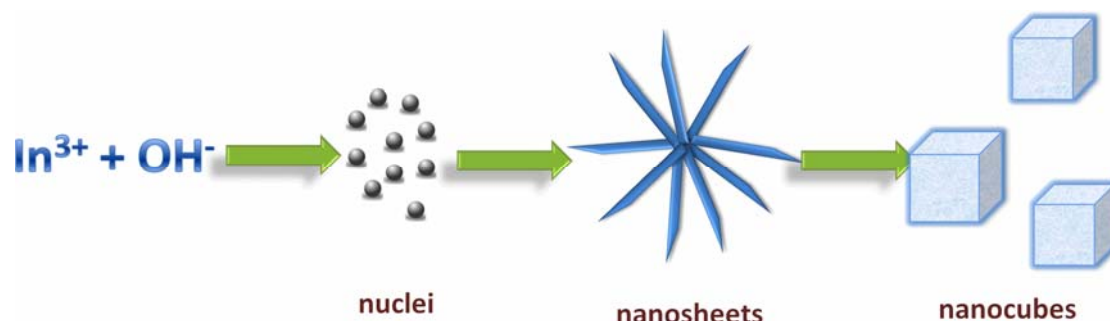
Generally, the electrodeposition process of In(OH)$_3$ can be described at the atomic level as different stages: The first involves the formation of stable nuclei, consisting of the motion of In^{3+} ions from the electrolyte to the cathode, electron transfer and the formation of adsorbed atoms, and finally the grouping of atoms to form a stable In(OH)$_3$ nucleus. The second stage consists of the isolated growth of individual In(OH)$_3$ nuclei through the incorporation of new atoms, the merging of nuclei, and the formation of continuous layers (nanosheets) over the cathode. Finally, the adjacent nanosheets are self-assembled by sharing a common crystallographic orientation. The elimination of the pairs of high energy surfaces would result in a substantial reduction in surface free energy. After the nanosheets are assembled to a stable size, they will

grow by combining with smaller unstable nuclei. In this case, the final crystal morphology is determined by the degree of supersaturation, the diffusion of the unstable nuclei to the surface of the crystals, surface, and interfacial energy, and the crystal structure. This kind of growth mode could lead to the formation of faceted particles or perfect anisotropic crystals if there is a sufficient difference in the surface energies for different crystallographic faces. In the cubic $In(OH)_3$ structure, the {001} planes contain three equivalent planes, (100), (010), and (001), which are perpendicular to three directions, [100], [010], and [001], respectively. Consequently, the cubic morphology of the sample enclosed with {001} surfaces is obtained. (See Figure 6c)

Figure 7 shows a schematic representation of the formation process of nanosheets and nanocubes, which clear deliver the detailed machanism producing these morphologies.
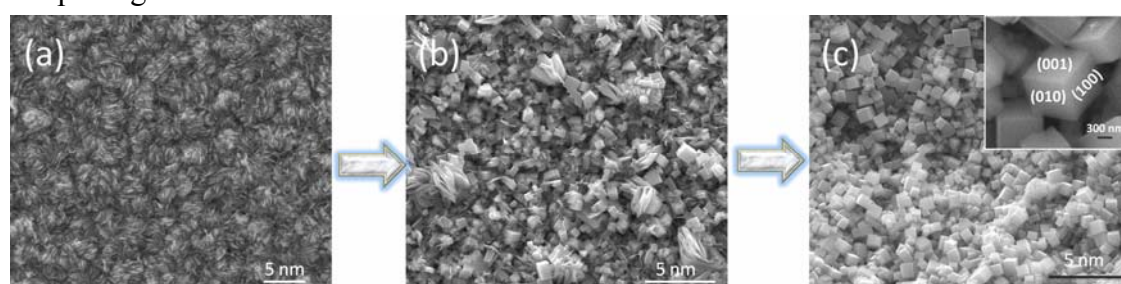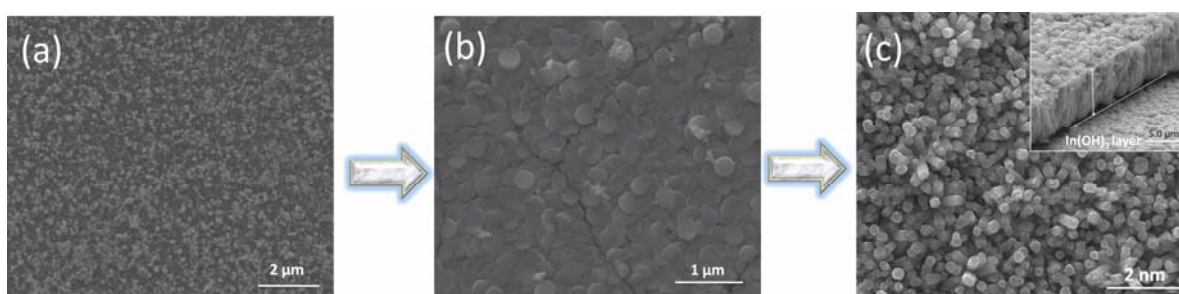

Fig. S1 SEM images of the as-synthesized samples after electrodeposition at In^{3+} concentrations of 0.008 M at 70 °C with a potential of -1.2 V (vs Ag/AgCl; current density stabilized at about 2.5 mA·cm^{-2}) for: (a) 40 min; (b) 80 min; (c) 120 min.

Fig. S2 Schematic representation of the formation process of $In(OH)_3$ nanosheets and nanocubes.

As to the synthesis of $In(OH)_3$ NRAs, the growing mechanism is slightly different.

They were prepared via cathodic electrodeposition in 0.02 M $In(NO_3)_3$ + 0.1 M NH_4Cl with a current density of 1 $mA \cdot cm^{-2}$ for 60 min at 90 °C. Figure 8 displays the SEM images of the samples obtained at different reaction times. A layer of $In(OH)_3$ nanoparticles was first occurred after 5 min electrodeposition, as shown in Figure 8a. These particles have a uniform diameter distribution about 150-200 nm. $In(OH)_3$ nanorods with a diameter about 300 nm sprouted from the layer of $In(OH)_3$ nanoparticles when the electrodeposition time prolonged to 20 min, as shown in Figure 8b. $In(OH)_3$ nanorods with diameters in the range of 300-400 nm and lengths up to 5.0 μm were formed after electrodeposition for 60 min. On the basis of the above SEM observations, the possible formation process can be defined as a seed-assisted electrochemical growth mechanism. The whole evolution process can be divided into three steps: (i) nucleation, (ii) formation of $In(OH)_3$ seed layer on the substrate, and (iii) further growth of nanorod arrays on the seed layer. $In(OH)_3$ nuclei are firstly formed via electrochemical reactions, and the process can be described as follows: OH^- ions generate by electro-reduction of NO_3^- ions on the surface of cathode. Then the OH^- ions react with In^{3+} to form $In(OH)_3$. The whole procedures are similar to eqs 1 and 3.

Fig. S3 SEM images of the as-synthesized samples after electrodeposition at 0.02 M $In(NO_3)_3$ + 0.1 M NH_4Cl at 90 °C with a current density of 1 $mA \cdot cm^{-2}$ for: (a) 5 min; (b) 20 min; (c) 60 min.

As the concentration of $In(OH)_3$ has reached supersaturation, $In(OH)_3$ nuclei form. Then the nuclei grow into a layer of $In(OH)_3$ particles as a seed layer for further growth of nanorod arrays. With deposition time increasing, the nanorods gradually occur on the surface of the $In(OH)_3$ seed layer and finally form nanorod arrays. The

formation of rod structure can be attributed to preferential one dimensional orientation of the seed layer along the [100] growth direction at an early stage. In this case, it is suggested that the relatively low current density (1 mA·cm^{-2}) might play an important role in deciding the final morphology. During electrodeposition, the working electrode is parallel to the counter electrode, and thus, the electric field can be regarded as perpendicular to the substrate. At a relatively low deposition rate (1 mA·cm^{-2}), the atomic arrangement rate along the electric field direction would be increased, resulting in preferential growth perpendicular to the substrate and formation of a rod structure. Therefore, the growth rate of [100] is faster than that of [010] and [001]. However, a relatively high deposition rate (corresponding to 2.5 mA·cm^{-2}) would not give the atoms time to arrange their sites. Because the surface of the substrate was not smooth, the electric field would have random orientations .As a result, the growth rate of [100], [010], and [001] would be almost the same.

It is noted that the concentration of indium nitrate (0.02 M) is higher than that of cubes and sheets (0.008 M), which means a lower pH value in the reaction solution. Thus, the concentration of OH$^-$ also would be lower, resulting in a lower nucleation rate of $In(OH)_3$. The nucleation and growth are the key factors in the formation of nanostructures. Various nanostructures could be obtained by adjusting the rate of nucleation and growth. In our case, the NH_4Cl not only plays a role as supporting electrolyte but also as reactant. During the electrodeposition, NH_4^+ ions in deposition solution will move to the cathode and obtain electrons to form NH_3. The produced NH_3 can integrate In^{3+} ions to form the complexes $[In(NH_3)_6]^{3+}$, resulting in the decrease of the concentration of In^{3+} ions, and hence lower the deposition rate of $In(OH)_3$. On the other hand, NH_4^+ ions can also react with the OH$^-$ produced from eqs 1 to form NH_3 and decrease the concentration of OH$^-$ ions, which further lower the deposition rate of $In(OH)_3$. It is difficult for the $In(OH)_3$ nanostructures to agglomerate when the formation rate $In(OH)_3$ is slow enough.[1] In addition, the NH_4^+ can be adsorbed on the special crystal faces of nanomaterials.[2] Herein, NH_4^+ ions may also be adsorbed on the surface of $In(OH)_3$ nuclei and promote the anisotropic growth of crystals. Based on the results and discussion, the morphology of $In(OH)_3$

nanorods can be readily tuned by adjusting the concentration of $In(NO_3)_3$, NH_4Cl and applied potential.

[1]C. Hu, H. Liu, W. Dong, Y. Zhang, G. Bao, C. Lao and Z. L. Wang, *Adv. Mater.*, 2007, **19**, 470.

[2]L. N. Wang and M. Muhammed, *J. Mater. Chem.*, 1999, **9**, 2871.