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Ambient Pressure Syntheses of Size-Controlled Corundum-type In_2O_3 Nanocubes

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An *n*-type semiconductor, In_2O_3, existing in two phases of cubic bixbyite-type and hexagonal corundum-type, has been widely used as microelectronic device materials in solar cells, sensors, and flat-panel display.[1] While the *c*-In_2O_3 phase is easily obtained at ambient pressure, corundum-type *h*-In_2O_3 structure has been rarely prepared due to required extremely high temperatures and high pressures.[2] Because of its interesting physical properties, such as stable conductivity and structural similarity with important metal-doped oxides, such as ITO, the ambient pressure synthesis of *h*-In_2O_3 has been a long sought synthetic goal. Only recently two notable works appeared for the preparation of metastable *h*-In_2O_3 at ambient pressure, both involving the formation of hydroxyl In^{3+} intermediate species.[3,4] Gurlo et al. prepared the *h*-In_2O_3 phase from thermal decomposition of in situ generated hydroxyl-acetylacetonato In^{3+} species from the complex $In(NO)_3{\cdot}5H_2O$/methanol/acetylacetone/NH_3 mixture.[3] Yu et al. converted In(O)(OH) nanofibers to *h*-In_2O_3 by thermal dehydration and further noted that the reaction condition to the intermediate In(O)(OH) nanofiber plays an important role in deciding the final In_2O_3 phase.[4] While the above procedures were successful in providing the *h*-In_2O_3 phase at ambient pressure, the required dehydration step around 500 °C is not compatible with surfactant-assisted size controls, thus severely limiting further research opportunities due to lack of processability.

We noted that direct thermal dehydration of $In(OH)_3$ nanostructures at ambient pressure produces only *c*-In_2O_3,[5] although the intermediate $In(OH)_3$ phase formation was observed during thermolysis of hydroxyl-acetylacetonato In^{3+} species.[3] We reasoned that surfactant-coated, thus soluble in organic solvents, *h*-In_2O_3 nanoparticles might be prepared at ambient pressure if very fast dehydration of the In(O)(OH) phase can be accomplished at relatively lower temperatures. Thus we prepared small In(O)(OH) nanoparticles by surfactant-assisted solution-based methods and in situ thermally dehydrated the small In(O)(OH) nanoparticles. We could prepare, for the first time, size-controlled and soluble *h*-In_2O_3 nanocubes at ambient pressure, and herein we report the unprecedented size-selective synthesis of *h*-In_2O_3 nanocubes, the assembly of nanocubes to form an extended 2-D superstructure, as well as their optical properties.

A slurry of $In(O\text{-}^iPr)_3$ (1 mmol, Alfa, 98%), oleic acid (1 mmol, Aldrich, 90%), oleylamine (5 mmol, Aldrich, technical grade), H_2O (10 mmol), and trioctylamine (TOA, 2.5 mL, Wako, 97%) prepared in a 15 mL Pyrex pressure tube was heated at 90 °C for 24 h in an oven with a vigorous magnetic stirring. The resulting transparent solution was transferred to a 50 mL Schlenk tube, which is connected to a bubbler, and was subsequently heated in a vertical furnace at 350 °C for 4 min under a gentle N_2 flow.[6] The resulting solution was cooled to room temperature and kept at that temperature for 24 h to form white precipitates, which were subsequently washed with 10 mL of TOA to remove small In(O)(OH) or In_2O_3 nanoparticles not converted to *h*-In_2O_3 cubes, if any, and excess surfactants and, subsequently, with 10 mL of methanol to remove TOA and surfactants.[7] The resulting white powder could be redispersed in various organic solvents.

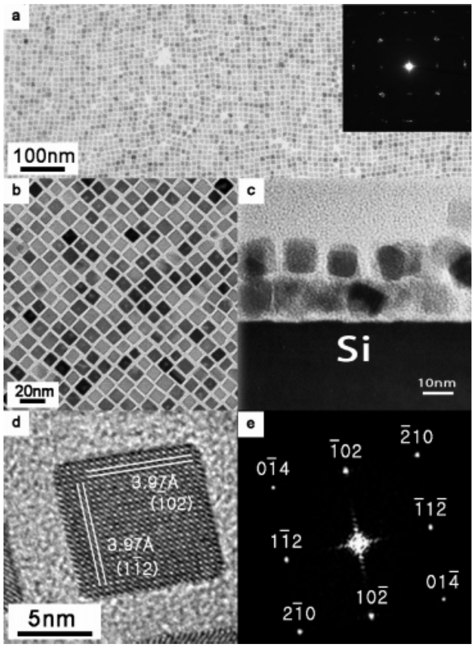

Figure 1. (a, b) TEM micrographs of 2-D arrayed 10.2 ± 1.5 nm *h*-In_2O_3 nanocubes. Inset: Selected area electron diffraction (SAED) pattern. (c) Cross-sectional view of a multilayered film of *h*-In_2O_3 nanocubes. (d) High-resolution TEM image of a single nanocube and (e) its FFT image along the ⟨241⟩ zone axis.

The XRD pattern of the white powder is in good agreement with that of the bulk *h*-In_2O_3 phase (JCPDS card No: 22-0336; see Supporting Information).[8] The morphology of the product was examined with a TEM (Transmission Electron Microscopy, LEO-912AB operated at 120 kV) study, as shown in Figure 1.

For the TEM analysis, a TEM grid was immersed in a dilute toluene solution containing the sample, and the solution was allowed to evaporate slowly at room temperature. The TEM image reveals a well-ordered extended 2-D superstructure of 10.2 ± 1.5 nm *h*-In_2O_3 nanocubes (Figure 1a,b). Cross-sectional view of the multilayered film of *h*-In_2O_3 nanocubes clearly shows the cube-

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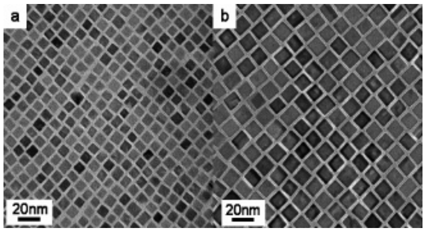

Figure 2. TEM micrograph of (a) 8.0 ± 0.8 nm and (b) 12.3 ± 1.1 nm h-In_2O_3 nanocubes.

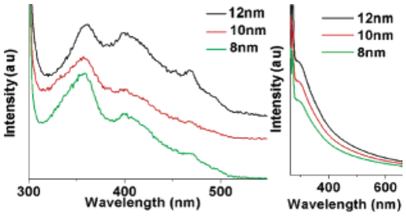

Figure 3. PL spectra and UV absorption of h-In_2O_3 nanocubes.

like morphology for the h-In_2O_3 nanostructures (Figure 1c). The 2-D superstructure of h-In_2O_3 nanocubes could grow as large as 1 μm × 1 μm, and we believe this is possible by the strong lateral interaction between surfactant-modified nanocubes and excellent size homogeneity of the cubes; the maximum standard deviation allowed for 2-D superlattice formation seems to be around 16% (see Supporting Information Figure S11). Recently, a similar technique was employed to fabricate an extended 2-D array of gold nanoparticles.[9] A high-resolution TEM (Tecnai F20 operated at 200 kV) image of a single nanocube and its corresponding FFT image are also consistent with the phase assignment by XRD (Figure 1d,e).

The XRD pattern for the white powder obtained by initial low-temperature hydrolysis of In(O-^{i}Pr)$_3$ at 90 °C for 24 h and precipitation by added methanol corresponds to the In(O)(OH) phase (JCPDS card No: 17-0549), and the white powder is composed of very small nanoparticles (<5 nm in diameter) as demonstrated by TEM analysis (see Supporting Information). Due to the small size of In(O)(OH) nanoparticles, the dehydration step would not necessitate very high temperatures, thus compatible with organic solvents and surfactants used for nanoparticle synthesis. In fact, TGA study of the In(O)(OH) nanoparticles shows that the weight loss of the hydrolyzed sample starts around 250 °C, indicating the onset of a dehydration step at that temperature (see Supporting Information). Facile dehydration of small In(O)(OH) nanoparticles would conveniently result in the h-In_2O_3 nanoparticles, whose growth behavior would be limited and controlled by the nature of solvent and surfactants present in the reaction mixture. When a direct thermal decomposition of In(O-^{i}Pr)$_3$ in the absence of water at 350 °C was performed, only c-In_2O_3 nanoparticles with a broad size distribution were obtained (see Supporting Information). This further indicates that the formation of small In(O)(OH) nanoparticles is an indispensable step toward the formation of h-In_2O_3 nanocubes.

The size of the nanocubes could be further modified by simply changing the amounts of surfactants; 8.0 ± 0.8 and 12.3 ± 1.1 nm h-In_2O_3 nanocubes of excellent size homogeneity are obtained with surfactant ratios of 1/7 and 1/3 (oleic acid/oleylamine), respectively, under otherwise the same conditions (Figure 2).

The photoluminescence (PL, room temperature, excitation at 290 nm) emission and UV absorption behaviors of the three samples in chloroform are shown in Figure 3. The PL behaviors of all three samples are nearly identical; three emission signals appear at 360, 400, and 470 nm, indicating very similar electronic structures for the three samples. Similar blue PL emissions stemming from, presumably, the systematic oxygen vacancy have been recently documented for c-In_2O_3 nanoparticles.[10] While PL emission of In_2O_3 in the UV range at room temperature is rare, small In_2O_3 nanoparticles, although documented only for the c-In_2O_3 phase, with a high crystallinity seem to be capable of emitting a PL signal in the UV range.[10−12] All three samples show UV absorption maxima around 300−310 nm, which is blue-shifted from the band gap at 330 nm (3.75 eV) of the bulk h-In_2O_3,[13] from the existence of a weak quantum confinement effect.[9]

In summary, we have reported the first preparation of size-controlled h-In_2O_3 nanocubes at ambient pressure as well as their optical properties. The prepared h-In_2O_3 nanocubes exhibit good solubilities in organic solvents and form extended 2-D arrays due to the excellent size homogeneity and strong lateral face-to-face interactions. The fabrication of thickness-controlled h-In_2O_3-based thin films and their electrochemical and optoelectronic property measurements are currently underway.

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Supporting Information Available: XRD and additional TEM data of h-In_2O_3 nanocubes, In(O)(OH) nanoparticles from hydrolysis of In(O-^{i}Pr)$_3$, and c-In_2O_3 nanoparticles from thermal decomposition of In(O-^{i}Pr)$_3$. TGA study of In(O)(OH) nanoparticles. Additional spectral data for the h-In_2O_3 nanocubes and surfactants. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) *CAUTION!* The abrupt pressure buildup by the water vapor at high temperatures can be dangerous. Therefore, the experiment should be carried out under an efficient fume hood with a proper shielding. The N_2 flow is intended to remove the formed water vapor from the reaction system.

(7) TOA cannot act as an effective surfactant for h-In_2O_3. For the solubility of h-In_2O_3 nanoparticles, the nanoparticle surface modification by oleylamine or oleic acid is absolutely necessary.

(8) Rigaku D/MAX-RC (12 kW) diffractometer using graphite-monochromatized Cu Kα radiation at 40 kV and 45 mA.

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