

trometer, equipped with an optical microscope ($\times 50$ objective) and liquid-nitrogen-cooled charge-coupled device (CCD) detector, using laser excitation at 514.5 nm (2.41 eV).

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Preparation and Optical Properties of Highly Crystalline, Colloidal, and Size-Controlled Indium Oxide Nanoparticles**

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Nanostructured materials display unusual chemical and physical properties that differ from those of the bulk materials and are promising for the fabrication of novel nanodevices.^[1] In particular, colloidal nanocrystals are of great interest for technological applications due to their unique size-dependent properties and excellent chemical processability.^[2] Transparent conducting oxides (TCOs) have found a variety of applications due to their best available performance in terms of

conductivity, transmissivity, excellent stability, and good surface morphology.^[3] Among them, indium oxide (In_2O_3), an n-type semiconductor with a wide bandgap of about 3.6 eV, has been widely employed as microelectronic device materials in solar cells, flat-panel displays, sensors, and architectural glasses.^[4] While previous studies mainly focused on thin films of In_2O_3 using sputtering, spray pyrolysis, and chemical vapor deposition methods,^[3,4] investigations on nanostructured In_2O_3 are quite limited. A few reports on the preparation of In_2O_3 nanoparticles^[5] and nanowires^[6] have appeared only recently in the literature. Herein we report the first preparation of colloidal, highly crystalline, and size-controlled indium oxide nanoparticles from thermal decomposition of the $\text{In}(\text{acac})_3$ precursor in the presence of a stabilizing surfactant, oleylamine, as well as their size-dependent optical properties.

The procedure for the preparation of the nanoparticles from a slurry of $\text{In}(\text{acac})_3$ in oleylamine is described in the Experimental section. A low resolution transmission electron microscopy (TEM) image of the powder obtained using a 1:12 molar ratio of $\text{In}(\text{acac})_3$ /oleylamine (sample B) is shown in Figure 1a. Nearly monodisperse spherical nanoparticles 6 nm in diameter are observed. The high-resolution TEM image in

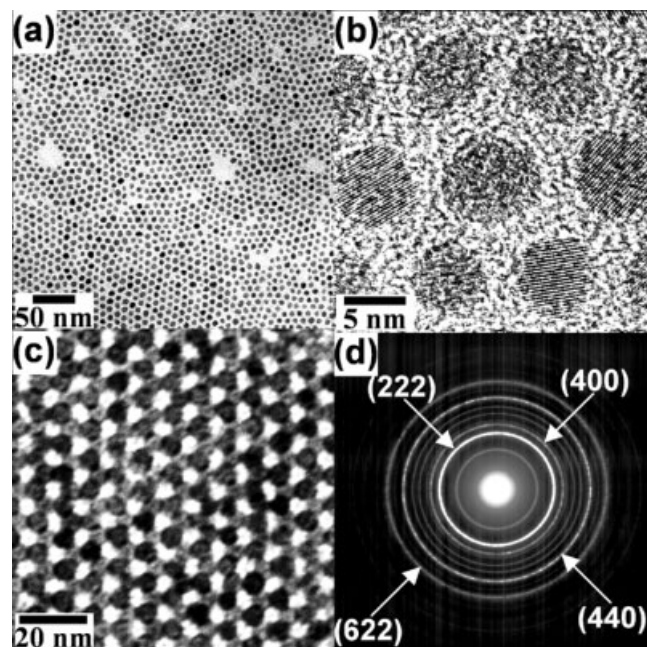


Fig. 1. TEM micrographs of 6 nm In_2O_3 nanoparticles: a) TEM image of a monolayer assembly, b) high-resolution TEM image, c) TEM image of a 3D superlattice, and d) a selected area electron diffraction pattern (SAED).

Figure 1b reveals the highly crystalline nature of these In_2O_3 nanoparticles. A 3D, close-packed In_2O_3 superlattice assembly is observed as shown in Figure 1c, when a TEM sample was prepared with a concentrated dichloromethane solution of In_2O_3 nanoparticles. The electron diffraction pattern (SAED) of the nanoparticles is consistent with cubic In_2O_3 with strong ring patterns due to (222), (400), (440), and (622) planes (Fig. 1d). Energy dispersive X-ray (EDX) analysis of the emission of the sample gives an atomic ratio of 1.47 for

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oxygen/indium, which is very close to 1.5 of the defect-free In_2O_3 phase.

Smaller nanoparticles 4 nm in diameter (sample A) were obtained as shown in Figure 2a, when a 1:48 molar ratio of $\text{In}(\text{acac})_3$ and oleylamine was used for the nanoparticle preparation. In order to obtain bigger nanoparticles > 6 nm in diam-

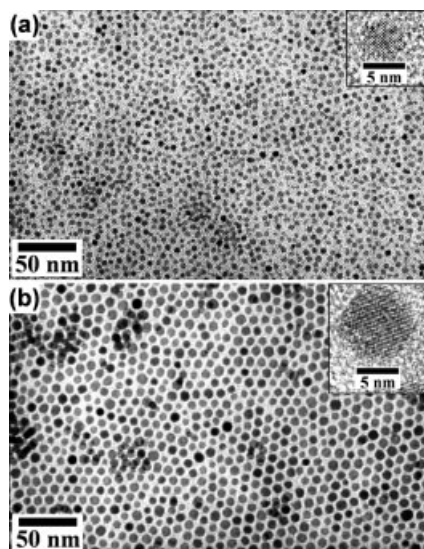


Fig. 2. TEM images of a) 4 nm and b) 8 nm In_2O_3 nanoparticles. High-resolution TEM images are inset.

eter, the reaction of $\text{In}(\text{acac})_3$ with oleylamine at a molar ratio of 1:6 was attempted. The particle size obtained, however, was still around 6 nm and was not narrowly distributed. Bigger nanoparticles with a narrow size distribution (8 nm in diameter (sample C); see Fig. 2b) were obtained by multiple additions of $\text{In}(\text{acac})_3$ (0.15 g \times 3, 1 h intervals) into a reaction mixture containing 6 nm sized In_2O_3 nanoparticles, followed by aging at 250 °C for 7 h. A similar seed-mediated growth method was successfully applied for the preparation of Fe_3O_4 nanoparticles by thermal decomposition of $\text{Fe}(\text{acac})_3$ in a mixed solvent system^[7] as well as for that of several metallic^[8] and semiconducting^[9] nanoparticles.

The X-ray powder diffraction (XRD) patterns of the three samples in Figure 3 match well with those of bulk cubic In_2O_3 reflections from (211), (222), (400), (431), (440), and (622)

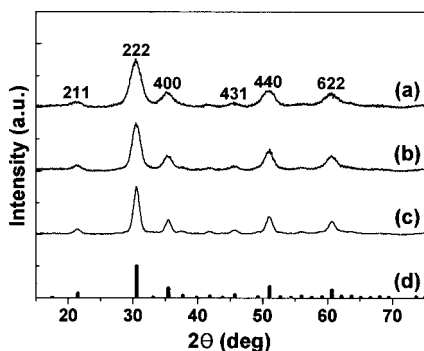


Fig. 3. X-ray diffraction patterns of a) 4 nm, b) 6 nm, and c) 8 nm In_2O_3 nanoparticles, and d) standard reflection pattern of cubic In_2O_3 (JCPDS #6-0416).

planes. These data further confirm a highly crystalline nature of In_2O_3 nanoparticles. The XRD reflection peaks become broader as the particle size decreases, which is a general size-dependent phenomenon in nanoparticles. The crystallite sizes (d_{est}) were determined for the four major reflections of the XRD data by using the Debye–Scherrer equation^[10] and are listed in Table 1. These spectroscopically estimated sizes of nanoparticles are in good agreement with mean diameters (d_{obs}) determined from the TEM images ($d_{\text{obs}}/d_{\text{est}} \approx 1$), indicating the single-crystalline and spherical nature of individual nanoparticles.

Table 1. Observed and spectroscopically estimated diameters of In_2O_3 nanoparticles.

Sample	d_{obs} [nm]	d_{est} [nm]
A	4	3.8 ± 0.2
B	6	6.0 ± 0.2
C	8	8.3 ± 0.3

Figure 4 shows the photoluminescence (PL) emission spectra (room temperature, excitation at 275 nm) of the three In_2O_3 nanoparticle samples of varying diameters. The emis-

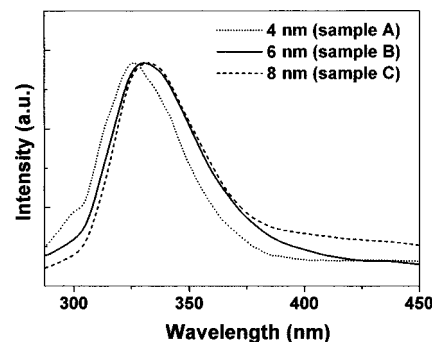


Fig. 4. Photoluminescence spectra of In_2O_3 nanoparticles.

sion maximum appear at 3.81 eV (325 nm) for 4 nm In_2O_3 , 3.76 eV (330 nm) for 6 nm In_2O_3 , and 3.73 eV (332 nm) for 8 nm In_2O_3 , and thus are blue-shifted (~60–140 meV) compared to the 3.67 eV (338 nm) of bulk In_2O_3 ,^[5b] indicating that the prepared nanoparticles are in the quantum confinement regime. The exciton Bohr diameter for indium oxide is reported to be in the range between 2.6 and 5 nm.^[4a,5a] The bandgap of the three In_2O_3 nanocrystallites, however, is little changed by variation of the particle size. A similar weak size dependence for the blue shift (110 meV) in PL has been previously reported for indium oxide nanoparticles obtained by pulsed laser ablation.^[5b] The In_2O_3 nanoparticle samples described in this paper do not show PL emission at lower energies (~400–520 nm) due to amorphous In_2O_3 or oxygen vacancies, as observed for other previously reported In_2O_3 nanoparticles^[5a] and nanowires.^[6] This observation clearly attests the formation of highly crystalline and defect-free In_2O_3 nanoparticles in the present work.

In summary, we have prepared soluble, highly crystalline, monodisperse, and size-controlled In_2O_3 nanoparticles by thermal decomposition of $\text{In}(\text{acac})_3$ in oleylamine under inert atmosphere. The oxygen in the nanoparticles apparently originates from the acetylacetonate ligand in the $\text{In}(\text{acac})_3$ precursor. The particle size of In_2O_3 can be easily manipulated by changing the experimental conditions, and a weak size dependence of photoluminescence is demonstrated. The high solubility of the prepared oleylamine-capped In_2O_3 nanoparticles in various organic solvents and the ready formation of a superlattice on a flat surface promise potential utilization of their size-dependent properties and the facile fabrication of nanodevices.

Experimental

Preparation of 6 nm In_2O_3 Nanoparticles (Sample B): A slurry of 0.3 g $\text{In}(\text{acac})_3$ in 2.34 g oleylamine (1:12 molar ratio) was heated at 250 °C for 7 h under an atmosphere of argon, and the resulting reaction mixture was cooled to room temperature to form a brown, viscous oil. Dichloromethane (10 mL) was added to enhance the fluidity of the reaction mixture, and insoluble precipitates were removed by centrifugation. To the resulting brown solution was added excess ethanol (40 mL) to form a pale yellow precipitate. Centrifugation and repeated washing with ethanol gave a pale yellow powder, which can be easily re-dispersed in various organic solvents such as hexane, toluene, and dichloromethane.

Preparation of 4 nm In_2O_3 Nanoparticles (Sample A): A slurry of $\text{In}(\text{acac})_3$ (0.075 g, 0.18 mmol) and oleylamine (2.34 g, 8.73 mmol, 48 equiv.) was used.

Preparation of 8 nm In_2O_3 Nanoparticles (Sample C): A slurry of $\text{In}(\text{acac})_3$ (0.30 g, 0.73 mmol) and oleylamine (2.34 g, 8.73 mmol, 12 equiv.) in a 100 mL Schlenk flask connected to a bubbler was purged with argon for 20 min and then heated at 250 °C for 7 h under an argon atmosphere. Solid $\text{In}(\text{acac})_3$ (0.15 g, 0.36 mmol) was added to the reaction mixture against an argon stream and the resulting solution was heated at 250 °C for 1 h; this step was repeated once more. Additional $\text{In}(\text{acac})_3$ (0.15 g, 0.36 mmol) was added, and the reaction mixture was aged at 250 °C for 7 h under an argon atmosphere.

Characterization of In_2O_3 Nanoparticles: The prepared nanoparticles were characterized by XRD (Rigaku D/MAX-RC (12 kW) diffractometer using graphite-monochromatized $\text{Cu K}\alpha$ radiation at 40 kV and 45 mA), TEM (low resolution: Omega EM912 operated at 120 kV; high resolution: Philips F20Tecnai operated at 200 kV), selected area electron diffraction (SAED) patterns attached to EM912, and energy dispersive X-ray analysis (EDX) attached to EM912. UV-vis absorption spectra were recorded on a Jasco V530 spectrophotometer. Photoluminescence measurements (Spex Fluorolog-3) were performed using an excitation wavelength of 275 nm with a 450 W Xe arc lamp at room temperature. Samples for TEM investigations were prepared by putting an aliquot of dichloromethane solution of In_2O_3 nanoparticles onto an amorphous carbon substrate supported on a copper grid. The excess liquid was then wicked away with tissue, and the grid was allowed to dry at room temperature.

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Low Molecular Weight Gelators with Hexagonal Order in Their Liquid-Crystal Phases and Gel States: 5-Cyano-2-(3,4,5-trialkoxybenzoylamino)tropones**

By Masashi Hashimoto, Seiji Ujiie, and Akira Mori*

Self-assembled systems such as gelling agents and liquid crystals receive much attention from both theoretical and practical viewpoints. In order for these self-assemblies to form, however, it is important to control the intermolecular interactions in such a way that they enable the directed organization of the molecules, but avoid transformation to a crystalline state. For example, in the case of liquid crystals,^[1] soft side chains are introduced to a hard core to prevent crystallization, whereas a chiral center introduced into a molecule for the preparation of gelling agents prevents tight packing.^[2] We have recently prepared troponoid liquid crystals and observed that they have higher thermal mesophase stability compared to the corresponding benzenoids.^[3] For example, compounds **1** and **2** (5-cyanotropones with a 4-alkoxybenzoyloxy and a 4-alkoxybenzoylamino group at C(2), see Scheme 1) formed a more tightly interdigitated head-to-tail bilayer smectic A phase than benzenoids **3** and **4**. This was facilitated through the dipole-dipole interaction between antiparallel troponone rings as well as the interaction between a cyano and a benzoyl group.^[4]

In this paper, we report the synthesis and self-organizing properties of 5-cyanotroponoids **5** and **6** with a 3,4,5-trialkoxybenzoyloxy and a 3,4,5-trialkoxybenzoylamino group at C(2).

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