

Large-Scale Cubic InN Nanocrystals by a Combined Solution and Vapor Phase Method under Silica Confinement

Supporting information

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Experimental section

Materials: Indium-oleate was prepared as described by Park *et al.*¹. 20 mmol indium chloride and 60 mmol of sodium oleate were dissolved in a mixture solvent composed of 40 ml ethanol, 30 ml distilled water and 70 ml hexane. The resulting solution was heated to 70 °C then kept for four hours. When the reaction was completed, the upper organic layer containing the indium-oleate complex was washed three times with 30 ml distilled water in a separate funnel. After washing, hexane was evaporated, resulting in indium-oleate complex in a waxy solid form.

In₂O₃ nanocrystals:

In₂O₃ nanocrystals were synthesized as described by Peng X. G. *et al.*². In a typical reaction indium-oleate (6 mmol), myristic acid (MA, 18 mmol), and 35 ml of 1-octadecene (ODE) were loaded in a 100 mL three-necked flask. The mixture was degassed and heated to 290 °C under a nitrogen atmosphere. When the temperature reached 290 °C, decyl alcohol (30 mmol) dissolved in 3 ml of ODE was quickly injected into the above mixture. The reaction was kept for 30 min, then stopped by removing the heater. The formed In₂O₃ nanocrystals were dispersed in hexane after wash and centrifugation.

In₂O₃@SiO₂ nanocrystals:

In₂O₃@SiO₂ nanocrystals were prepared as reported by Li Y. D. *et al.*³. The obtained In₂O₃ nanocrystals were dispersed in 450 ml hexane, and then poured into a mixture of 45 ml Triton X-100, 45 ml hexanol, 3 ml TEOS, and 13.5 ml distilled water. After that, 1.5 ml of aqueous ammonia was added to catalyze the silica-polymerization reaction. After the microemulsions were stirred at room temperature for 12 hours, the nanocrystals were isolated by adding acetone. Finally, the products were dried under 80 °C, after removing the surfactant by centrifugation and wash using ethanol.

InN@SiO₂ nanocrystals:

The obtained In₂O₃@SiO₂ nanopowders were put into a tube furnace. After being purged with NH₃ gas for 20 min, the furnace was heated to 500 °C ~ 700 °C and kept for 5 hours under NH₃ flow at 300 ml/min.

Remove silica and phase transfer:

The silica shell was removed by HF acid. The obtained InN nanocrystals were washed by distilled water three times, and then were redispersed in 50 ml distilled water. The InN nanocrystals were transferred from water to hexane according to the reference reported by Yang *et al.*⁴. The water containing InN nanocrystals was mixed with 50 ml of ethanol containing 1 ml of dodecylamine. After 3 min of stirring, 50 ml of hexane was added, and stirring was continued for 1 min. Phase transfer of InN nanocrystals from water to hexane took place quickly. Then the solution containing InN nanocrystals was heated in dodecylamine at 200 °C for 30 min. The excess dodecylamine was removed by centrifugation and wash using ethanol. Finally, the InN nanocrystals were dispersed into hexane.

Transmission Electron Microscopy (TEM):

TEM samples were prepared by immersing a 300 mesh copper grid with a ultrathin carbon film into a hexane solution containing InN nanocrystals after centrifuge at 6000 rpm for 5 min. TEM images were collected on Tecnai F20 microscopes. Size distribution of nanocrystals was determined by counting the diameter of ~200 nanocrystals measured using Adobe Photoshop.

Powder X-ray Diffraction (XRD):

The XRD measurements were performed using PANalytical X'Pert PRO MPD with a 240 mm radius goniometer using an accelerating voltage of 40 kV and a current of 40 mA. Copper K α radiation was used (1.5406 Å).

X-ray Photoelectron Spectroscopy (XPS):

The XPS measurements were carried out on PerkinElmer Physics PHI 5300.

Energy Dispersive Spectroscopy (EDS):

EDS measurements were performed using a Tecnai F20 TEM operated at 200kV. Data analysis was performed using the INCA software.

Absorption Spectroscopy:

Absorption spectra were collected on a Hitachi U4100 spectrometer at room temperature.

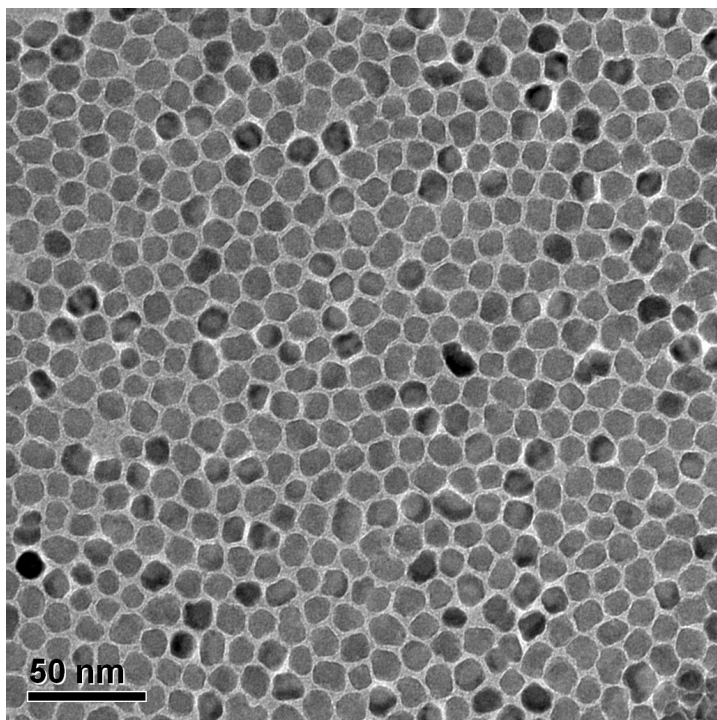


Figure S1. Nearly monodisperse In₂O₃ nanocrystals.

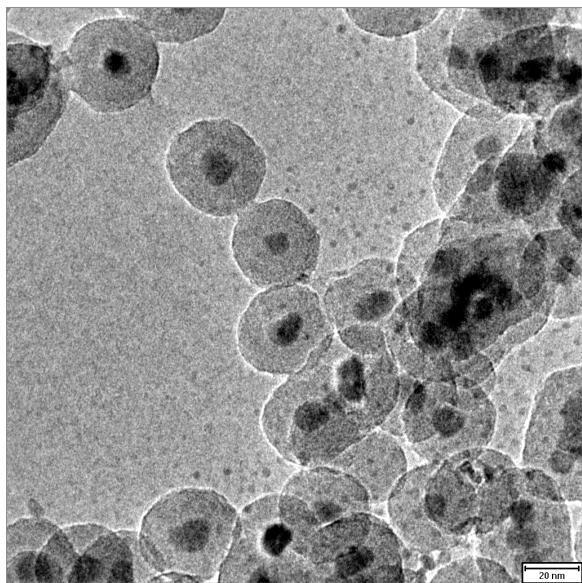


Figure S2. $\text{In}_2\text{O}_3@\text{SiO}_2$ nanocrystals by the water-in-oil microemulsion.

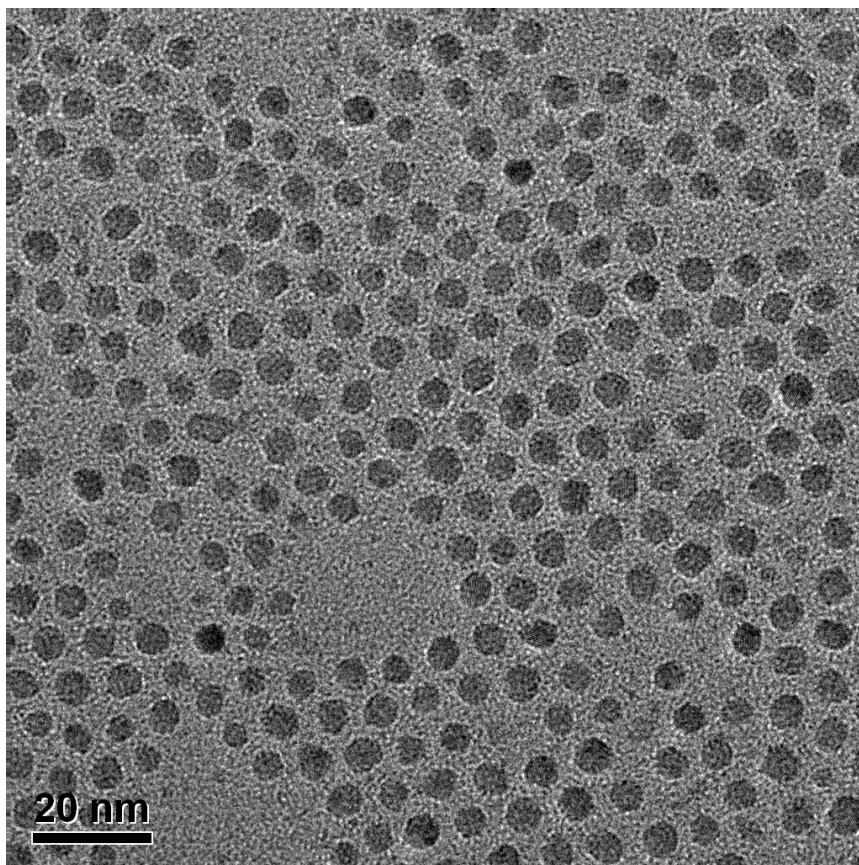


Figure S3. Nearly monodisperse InN nanocrystals after post treatments.

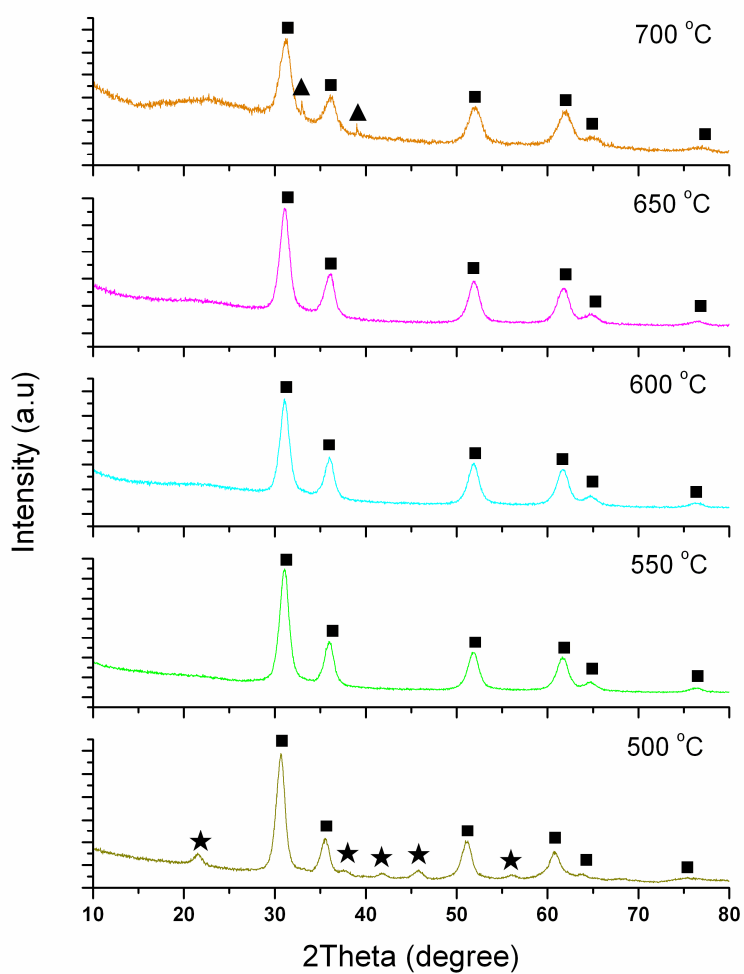


Figure S4. XRD spectra of the InN@SiO₂ obtained at different nitridation temperatures. ■-cubic phase InN(JCPDS: 88-2365); ★-cubic phase In₂O₃ (JCPDS: 89-4595); ▲- tetragonal phase In (JCPDS: 05-0642).

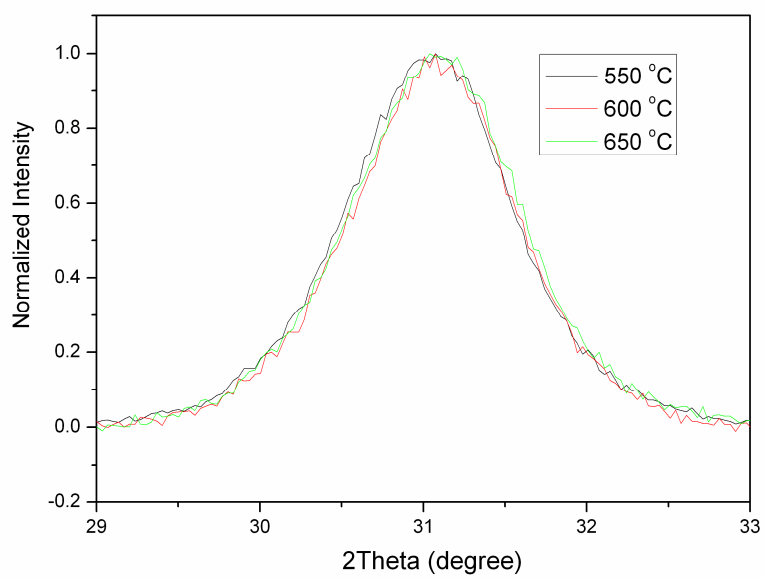


Figure S5. Local-magnification XRD spectra of the InN@SiO₂ obtained at 550 °C, 600 °C , and 650 °C.

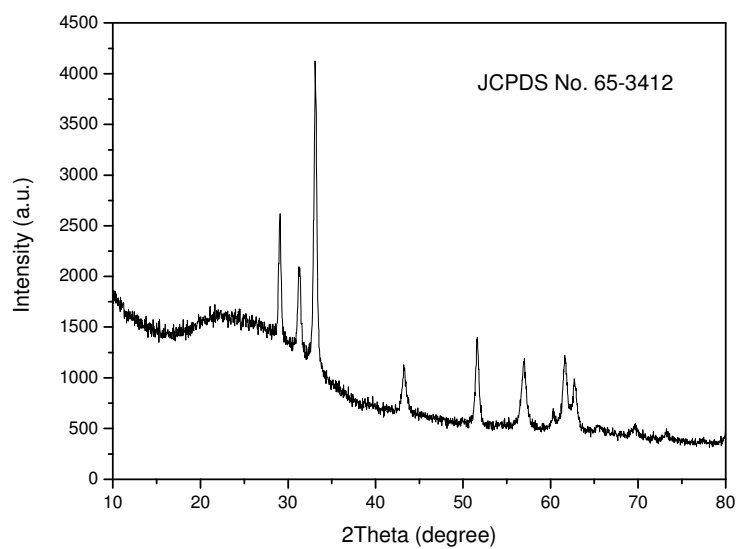


Figure S6. The InN nanocrystals obtained by the In_2O_3 nanocrystals without silica shell exhibit hexagonal phase. (JCPDS No. 65-3412)

To further confirm the formation of InN and acquire the chemical states of InN nanocrystals, the X-ray photoelectron spectra (XPS) of InN nanocrystals were investigated, after removing the silica shell. Figure S6 shows that the In core spin-orbit splits into the 3d_{5/2} peak at 444.8 eV and 3d_{3/2} peak at 452.3 eV (Figure 3a), and the peak at 397.3 eV corresponds to the N1s (Figure 3b); these values are in agreement with the reported values.⁵⁻⁷ Through calculating the integral of the peak, the atomic ratio of In : N can be obtained as 1.02 : 1. This result is consistent with that from Energy Dispersive Spectroscopy (EDS). No obvious peaks of silicon and oxygen were observed in the XPS and EDS spectra, which indicate that the silica shells were completely removed.

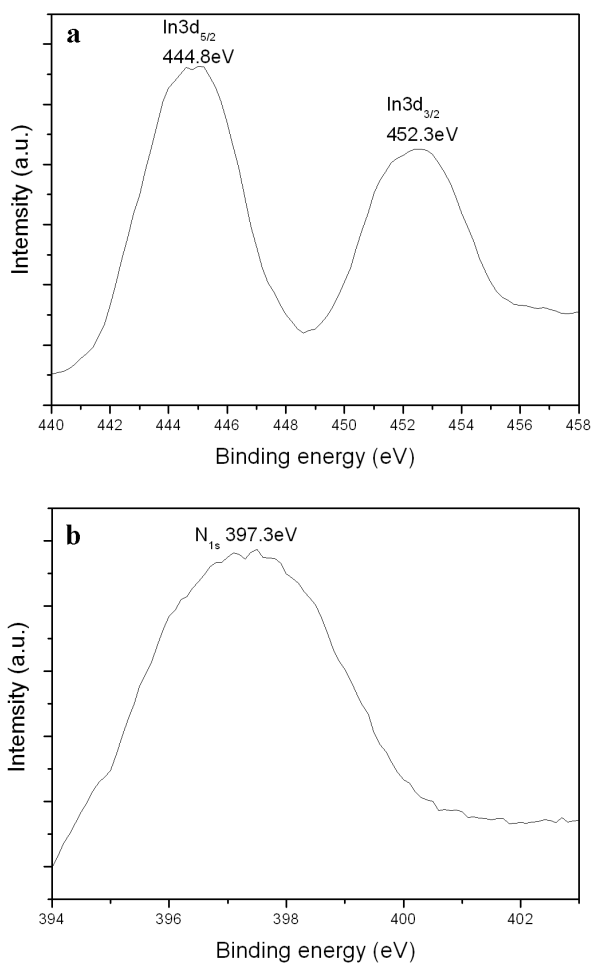


Figure S7. XPS spectra of (a) the In 3d_{5/2} and In 3d_{3/2}, and (b) the N_{1s} for InN nanocrystals after removing the silica shell by HF acid.

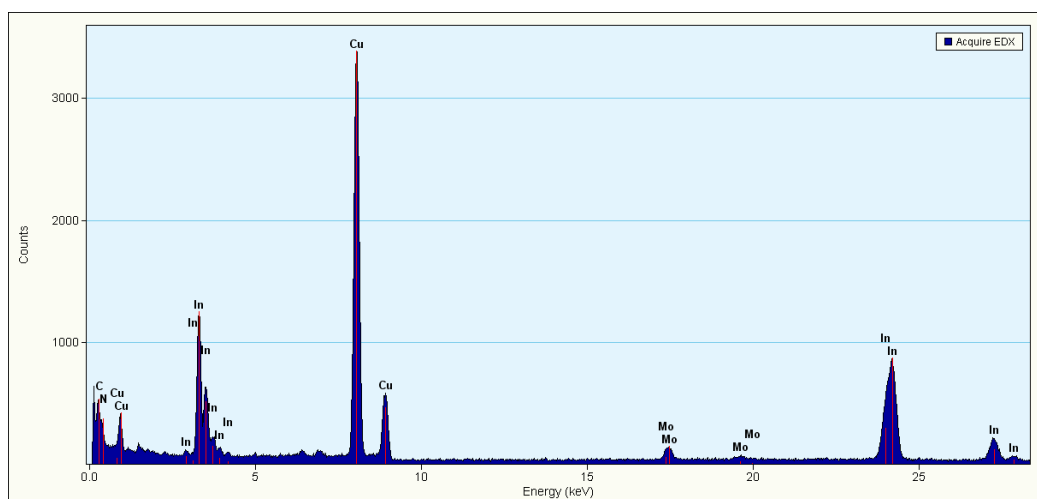


Figure S8. EDS spectrum of InN nanocrystals.

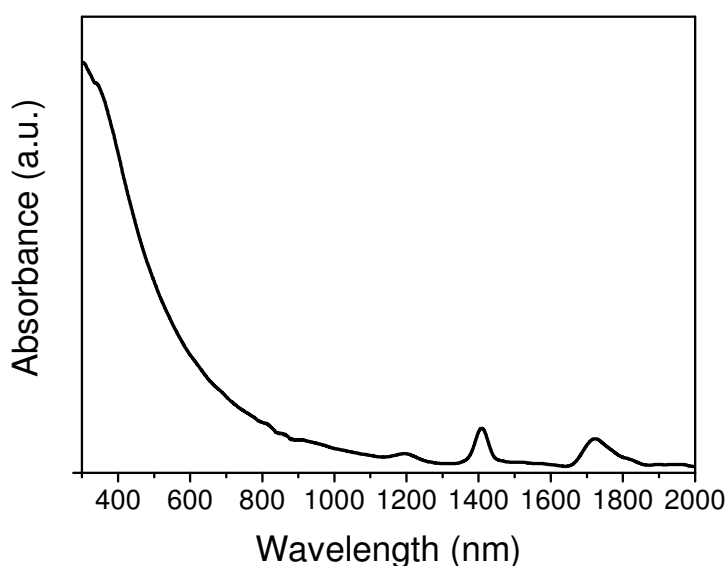


Figure S7. Absorption spectrum of InN nanocrystals.

The InN nanocrystals with organic capping ligands (*without silica shells*) dispersed in tetrachloroethylene were used for absorption measurements. The absorption spectrum of InN nanocrystal colloidal solution exhibits two absorption peak around 1722 nm and 1408 nm, and a slightly absorption peak around 1196 nm. Given the complications of surfaces, doping levels and free electron concentrations of InN nanocrystals, we could not conclusively extract the band structure information from the absorption spectra.

References:

- (1) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, 3, 891.
- (2) Arun Narayanaswamy, Huifang Xu, Narayan Pradhan, Myeongseob Kim, and Xiaogang Peng, *J. Am. Chem. Soc.* 2008, 130(29), 9240–9241.
- (3) Jian-Ping Ge, Sheng Xu, Jing Zhuang, Xun Wang, Qing Peng, and Ya-Dong Li, *Inorg. Chem.* 2006, 45(13), 4922-4927.
- (4) Jun Yang, Edward H. Sargent, Shana O. Kelley and Jackie Y. Ying *Nat. Mater.* 2009, 8, 683-689.
- (5) Xiong, Y.; Xie, Y.; Li, Z.; Li, X.; Zhang, R. *New J. Chem.* 2004, 28, 214 – 217.
- (6) Hsieh, J. C.; Yun, D.S.; Hu, E.; Belcher, A.M. *J. Mater. Chem.* 2010, 20, 1435-1437.
- (7) Wanger, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. in *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Eden Prairie, 1978.