Supporting Information

Synthesis of InP Branched Nanostructures by Controlling the Intermediate Nanoclusters

Yongju Kwon [a], Gyuhyun Bang [a], Jeongmin Kim [a], Anastasia Agnes [a] and Sungjee Kim*[a]

[a] Department of Chemistry, Pohang University of Science and Technology, Pohang 37673, South Korea

Experimental

Chemicals. Indium acetate ($In(Ac)_3$, 99.99%), indium chloride ($InCl_3$, 98%), myristic acid (HMy) (≥ 99%), anhydrous toluene (99.5%), 1-octadecene (ODE, 90%), acetonitrile (99.8%) were purchased from Aldrich. Tris(trimethylsilyl)phosphine ($(TMS)_3P$) (95%) was purchased from SK chemicals. All chemicals were used without further purification.

Synthetic procedures

General procedure for synthesis of 386-MSCs. 386-MSCs were synthesized using a reported method.[1] First, 0.8 mmol of $In(Ac)_3$ and 2.9 mmol of HMy in a three-necked round-bottom flask containing 20 mL ODE was degassed for 2 hours at 110 °C, then 0.4 mmol of $(TMS)_3P$ was added to the mixture and it was stirred for 2 hours under N_2 atmosphere.

Purification of 386-MSCs. As-synthesized 386-MSCs were purified with toluene as solvent and acetonitrile as anti-solvent twice by precipitation-dissolution. First, 35 mL acetonitrile was added into 0.5 mL 386-MSCs solution in conical tube and followed by centrifugation (4500 rpm, 3 minutes). After discarding transparent supernatant and drying, yellow precipitants were dissolved with 0.5 mL anhydrous toluene. 35 mL acetonitrile was added into 0.5 mL 386-MSCs solution again and followed by centrifugation (4500 rpm, 3 minutes). Final products were stored in anhydrous toluene.

General procedure for synthesis of InP NPs from molecular precursors. First, 0.4 mmol of $In(Ac)_3$ and 1.2 mmol of HMy were prepared in 12 mL ODE. The solution was degassed for 2 hours at 110 °C and cool down to room temperature, then 0.4 mmol of $(TMS)_3P$ was added to the mixture. The mixture solution was heated to 300 °C and maintained for 30 minutes under N_2 atmosphere. Heating rate is around 20 °C/min.

General procedure for synthesis of InP NPs from purified 386-MSCs. First, 12 mL ODE was degassed for 1 hour at 110 °C and cool down to room temperature. Purified 386-MSCs in toluene was added to ODE making 0.44 mM solution at room temperature and the toluene was removed under vacuum. After that, the solution was heated to 300 °C. Heating rate is around 20 °C/min. The temperature was maintained for 30 minutes and followed by cooling down.

General procedure for synthesis of InP NPs from purified 386-MSCs and $In(My)_3$. First, 0.3 mmol of $In(Ac)_3$ and 0.9 mmol of HMy were prepared in 12 mL ODE. The solution was degassed for 2 hours at 110 °C and cool down to room temperature. Purified 386-MSCs in toluene was added to $In(My)_3$ solution making 0.44 mM solution at room temperature and the toluene was removed under vacuum. After that, the solution was heated to 300 °C. Heating rate is around 20 °C/min. The temperature was maintained for 30 minutes and followed by cooling down.

General procedure for synthesis of InP NPs from as-synthesized 386-MSCs. First, 4 mL ODE was degassed for 1 hour at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into ODE at room temperature. After that, the solution containing the 386-MSCs was heated to 300 °C. Heating rate is around 20 °C/min. The temperature was maintained for 30 minutes and followed by cooling down.

General procedure for synthesis of InP NPs from as-synthesized 386-MSCs and HMy. First, 0.34 mmol of HMy were prepared in 4 mL ODE. The solution was degassed for 1 hour at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into the HMy solution at room temperature. After that, the mixture solution containing the 386-MSCs and HMy was heated to 300 °C. Heating rate is around 20 °C/min. The temperature was maintained for 30 minutes and followed by cooling down.

General procedure for synthesis of InP NPs from as-synthesized 386-MSCs and $In(My)_3$. First, 0.3 mmol of $In(Ac)_3$ and 0.9 mmol of HMy were prepared in 4 mL ODE. The solution was degassed for 2 hours at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into the $In(My)_3$ solution at room temperature. After that, the mixture solution containing the 386-MSCs and $In(My)_3$ complex was heated to 300 °C. Heating rate is around 20 °C/min. The temperature was maintained for 30 minutes and followed by cooling down.

General procedure for synthesis of InP BNSs from 386-MSCs. First, 0.3 mmol of $In(Ac)_3$ and 0.9 mmol of HMy were prepared in 4 mL ODE. The solution was degassed for 2 hours at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into the $In(My)_3$ solution at room temperature. After that, the mixture solution containing the 386-MSCs and $In(My)_3$ complex was heated to 220 °C. Heating rate is around 20 °C/min. The temperature was maintained for 20 minutes and followed by cooling down.

General procedure for synthesis of InP HBNSs and DLNSs from 386-MSCs. First, 0.3 mmol of $In(Ac)_3$ was prepared in 4 mL ODE. The solution was degassed for 1 hour at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into the $In(Ac)_3$ solution at room temperature. After that, the mixture solution containing the 386-MSCs and $In(Ac)_3$ complex was heated to 220 °C. Heating rate is around 20 °C/min. The temperature was maintained for 20 minutes and followed by cooling down.

General procedure for synthesis of quasi-amorphous ~2 nm NPs from 386-MSCs. First, 0.3 mmol of $In(Ac)_3$ and 0.9 mmol of HMy were prepared in 4 mL ODE. The solution was degassed for 2 hours at 110 °C and cool down to room temperature. As-synthesized 386-MSCs solution with 8 mL volume was injected into the $In(My)_3$ solution at room temperature. After that, the mixture solution containing the 386-MSCs and $In(My)_3$ complex was heated to 110 °C. The temperature was maintained for 6 hours and followed by cooling down.

Size-selective purification of InP BNSs, InP HBNSs, and InP DLNSs. Size-selective purification was performed by using toluene-methanol co-solvents. First, 1 mL crude sample (InP BNSs or InP HBNSs and DLNSs) was mixed with 9 mL toluene and 4 mL methanol was added into the solution. The mixture solution was centrifuged under the condition of 3000 rpm for 3 minutes. Precipitate contains only InP BNSs or InP DLNSs without amorphous clusters.

Characterization. Absorption spectra were measured using an Agilent 8453 UV-vis spectrophotometer. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM-2100 microscope operating at 200 kV. X-ray diffraction (XRD) experiments were performed using a Dmax2500/PC (Rigaku) diffractometer with Cu Kα radiation.

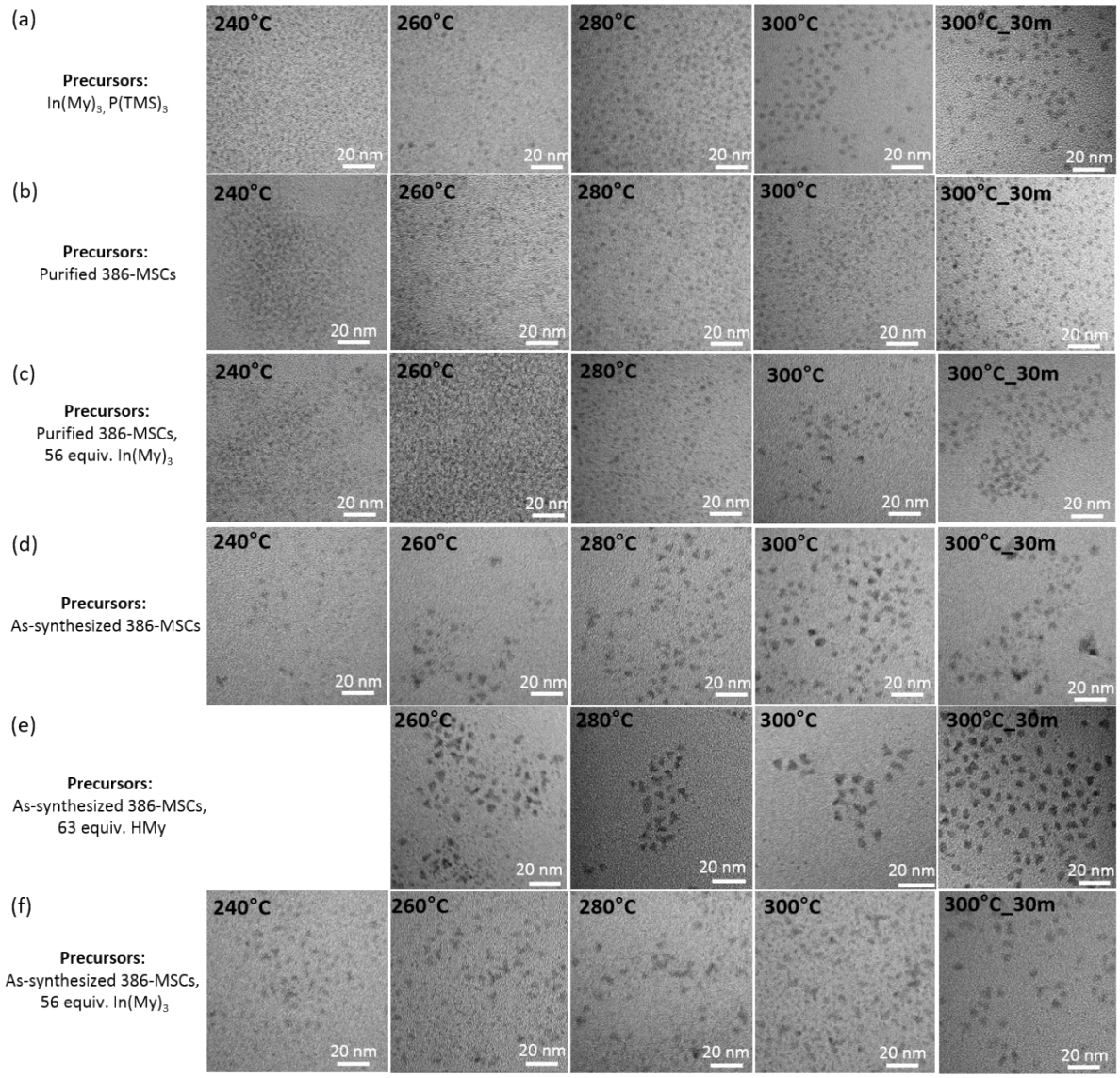

Figure S1. TEM images of aliquots taken over time during heating to 300 °C from (a) the 2:1 molar mixture of $In(My)_3$ and $(TMS)_3P$, (b) purified 0.44 mM 386-MSCs, (c) 0.44 mM 386-MSCs with additional 56 equivalents of $In(My)_3$, (d) as-synthesized 0.44 mM 386-MSCs, (e) as-synthesized 0.44 mM 386-MSCs with additional 63 equivalents of HMy, (f) as-synthesized 0.44 mM 386-MSCs with additional 56 equivalents of $In(My)_3$.

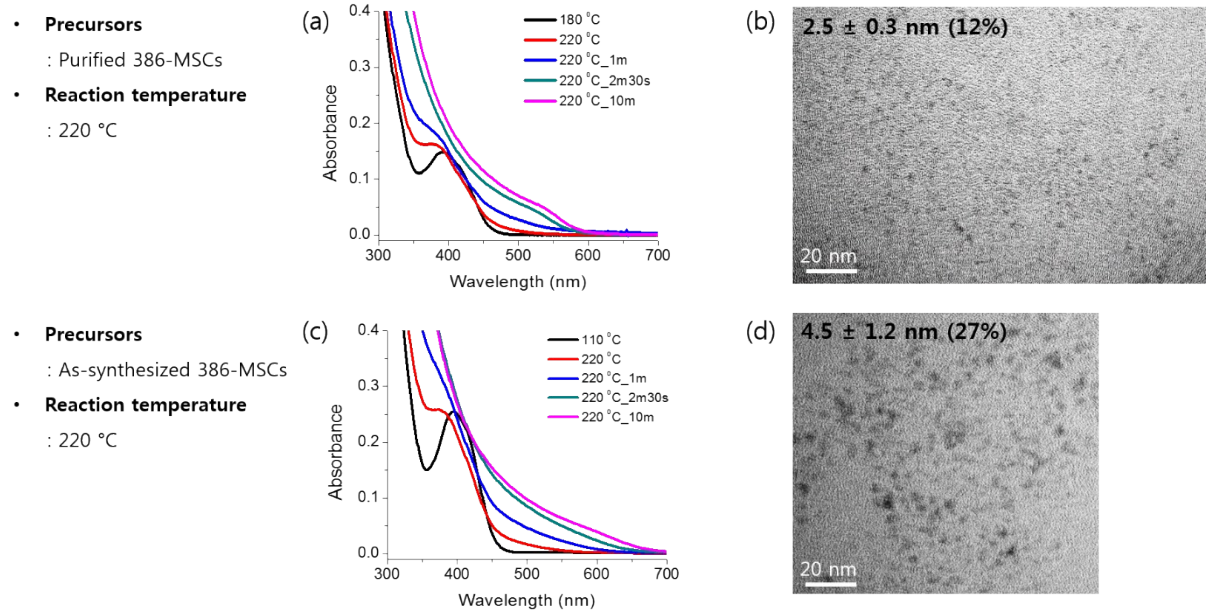

Figure S2. UV–vis absorption spectra of aliquots taken over time upon heating to 220 °C and TEM images of the final samples for the heat-up reactions of: (a, b) purified 0.44 mM 386-MSCs, (c, d) as-synthesized 0.44 mM 386-MSCs.

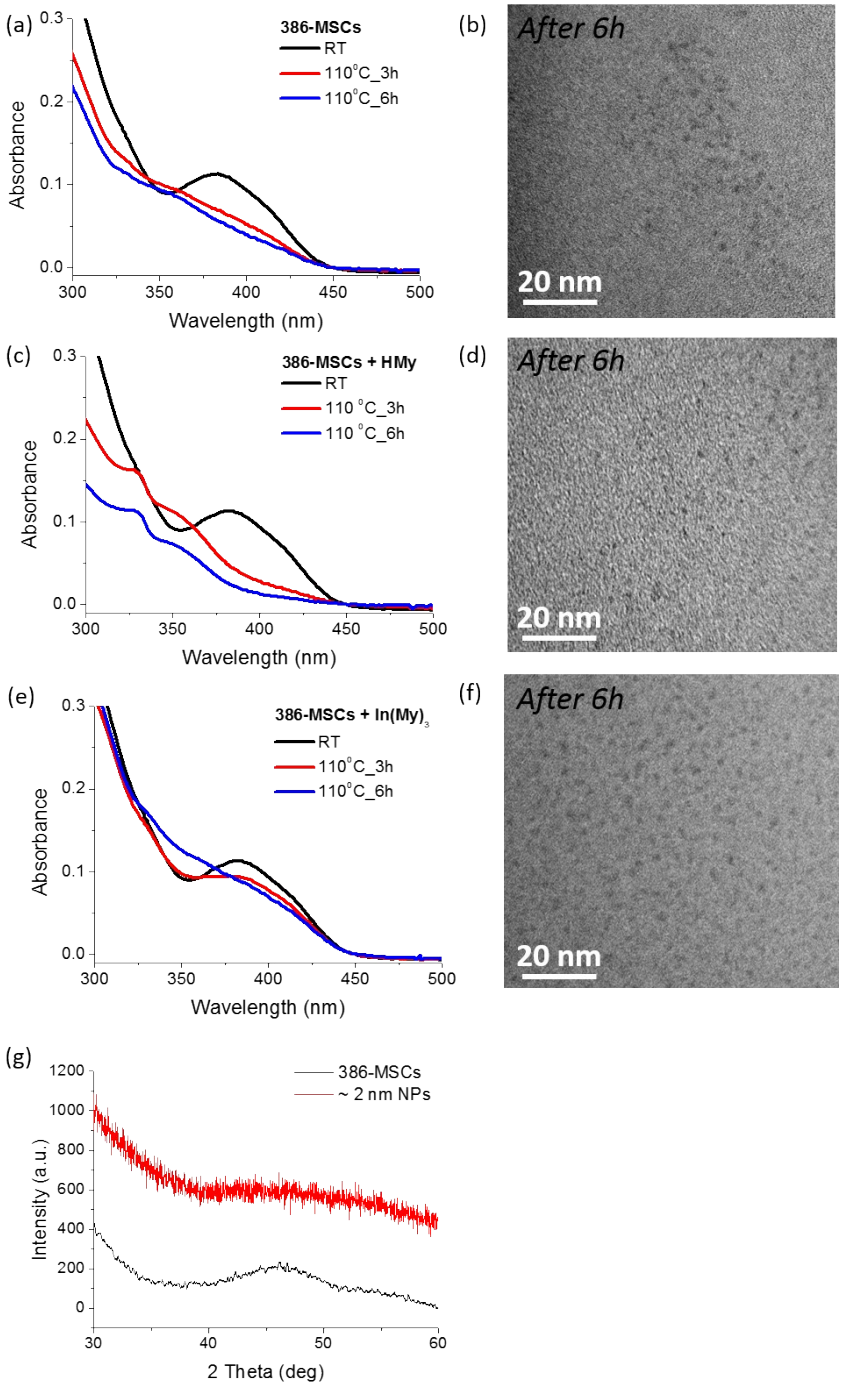

Figure S3. UV−vis absorption spectra of aliquots taken over time upon heating at 110 °C and TEM images of the final samples for the reaction of: (a,b) as-synthesized 386-MSCs, (c,d) as-synthesized 386-MSCs with additional 56 equivalents of HMy, (d,e) as-synthesized 386-MSCs with additional 56 equivalents of $In(My)_3$. (g) XRD patterns of 386-MSCs and 2 nm InP NPs which were synthesized by reacting 386-MSCs and 56 equivalents of $In(My)_3$ at 110 °C for 6 hours.

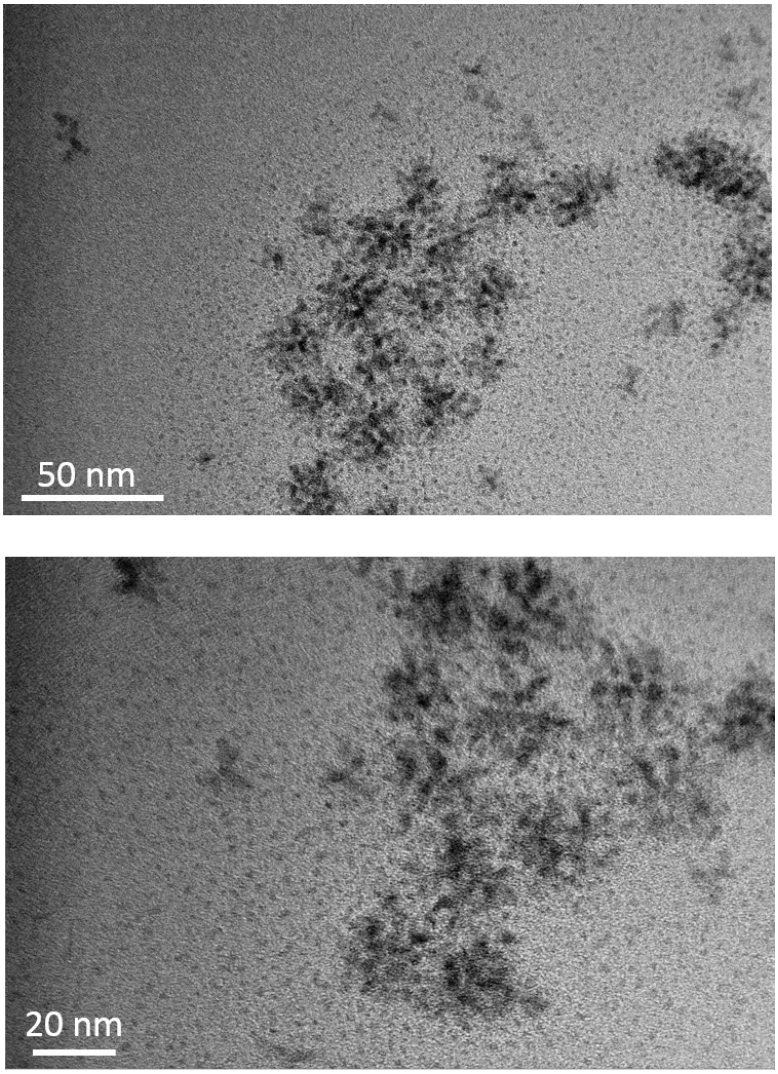

Figure S4. TEM images of InP HPNSs and DLNSs formed by the reaction of 386-MSCs and 56 equivalents of $In(Ac)_3$.

Table S1. The In/P atomic ratios of 386-MSCs, 2 nm amorphous NPs, and BNSs.

	In	P
386-MSCs	1	0.54
2 nm Amorphous NPs	1	0.33
BNSs	1	0.71

Reference

1. Gary, D. C.; Terban, M. W.; Billinge, S. J. L.; Cossairt, B. M., Two-Step Nucleation and Growth of InP Quantum Dots via Magic-Sized Cluster Intermediates. *Chemistry of Materials* **2015,** *27* (4), 1432-1441.