Electronic Supplemental Information

Solid-State Phase Transformations in Solution: Templated Conversion of Nanoscale Nickel Phosphides

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Chemicals

All chemicals were used as received. Octyl ether was purchased from TCI America. Oleylamine (approximate C18 content 80-90%) was purchased from ACROS Organics. Tri-octylphosphine (min 97%) was ordered from STREM Chemicals. Chloroform was obtained from Fisher Chemicals and ethanol (200 proof) was purchased from Decon Labs Inc. $Ni(acac)_2$, (95%) was purchased from Alfa Aesar.

Synthesis

Hollow $Ni_{12}P_5$ nanoparticle synthesis

The synthesis procedure is adapted from our previous work on the phase control in nanoscale nickel phosphides (E. Muthuswamy, G. H. Layan Savithra, S. L. Brock, *ACS Nano*, 2011, **5**, 2402-2411)

4 mmol of $Ni(acac)_2$ is combined with octyl ether (10.0 mL), oleylamine (3 equivalents, relative to Ni) and 2 mL TOP. The P:Ni precursor ratio is 1.12. The system is degassed at 100 °C for about 15-20 minutes under partial vacuum conditions and then is raised to 230 °C under Ar. The system is maintained at 230 °C for about 60-90 minutes and then is raised to 300 °C where it is maintained for about 1 h. The final product is isolated by the addition of excess ethanol and centrifugation at RT. The isolated product is then re-dispersed in 1-2 mL of chloroform by sonication and re-precipitated by the addition of excess ethanol and centrifugation. The process is carried out twice and the product is dried under vacuum to yield the final product in a free flowing powder form.

Solid $Ni_{12}P_5$ nanoparticle synthesis

The synthesis procedure is adapted from our previous work on the phase control in nanoscale nickel phosphides. (E. Muthuswamy, G. H. Layan Savithra, S. L. Brock, *ACS Nano*, 2011, **5**, 2402-2411)

The synthesis method is the same as the hollow $Ni_{12}P_5$ nanoparticle preparation except for the change in reaction parameters. The P:Ni precursor ratio is 5.6, the oleylamine quantity is increased to 60 mmol (15 equivalents relative to Ni) and the reaction is carried out at 350 °C for about 1 h after maintaining at 230 °C for about 60-90 minutes.

Conversion of $Ni_{12}P_5$ to Ni_2P

All reactions are carried out under Ar atmosphere. Approximately 200-250 mg of hollow or solid $Ni_{12}P_5$ nanoparticles are combined with 10.0 mL octyl ether and 4.0 mL oleylamine and

degassed under partial vacuum conditions at 100 °C for about 15-20 minutes. The system is then raised to 300 °C under Ar and is maintained for about 10-15 minutes. 15 mL TOP is injected into the system and the temperature is then raised to 350-370 °C. The reaction is stopped after 3-4 h. Isolation is achieved as described for hollow $Ni_{12}P_5$ particles, above.

Characterization

Powder X-ray Diffraction (PXRD) was carried out on a Rigaku Diffractometer (RU2000) using the Kα line of a Cu rotating anode source (40 kV, 150 mA). Samples were deposited onto a zero background quartz holder with a thin layer of grease and data were acquired in the 2θ range of 20°-82° with a step size of 0.02°. PXRD patterns were processed using Jade 5.0 software and compared to Powder Diffraction Files (PDF's) from the International Center for Diffraction Data (ICDD) database.

Electron microscopy was performed using a JEOL 2010 transmission electron microscope operated at a voltage of 200 kV and a beam current of 107-108 μA with a coupled EDS detector (EDAX inc.). The images were captured using Amtv600 software provided by the Advanced Microscopy Techniques Corporation. Samples for TEM analysis were prepared by placing a drop of the sample dispersion on a carbon coated 200 mesh Cu grid. Dispersions were prepared by sonicating a small amount of the nanoparticle powder with 3-4 mL of chloroform.

Surface area and porosimetry analysis was performed by nitrogen physisorption on a Micromeritics ASAP 2010 Porosimeter at 77K after degassing at 150 ºC overnight. Surface areas were computed using the Brunauer, Emmett and Teller (BET) model, and pore characteristics were determined using the Barrett, Joyner and Halenda (BJH) model.

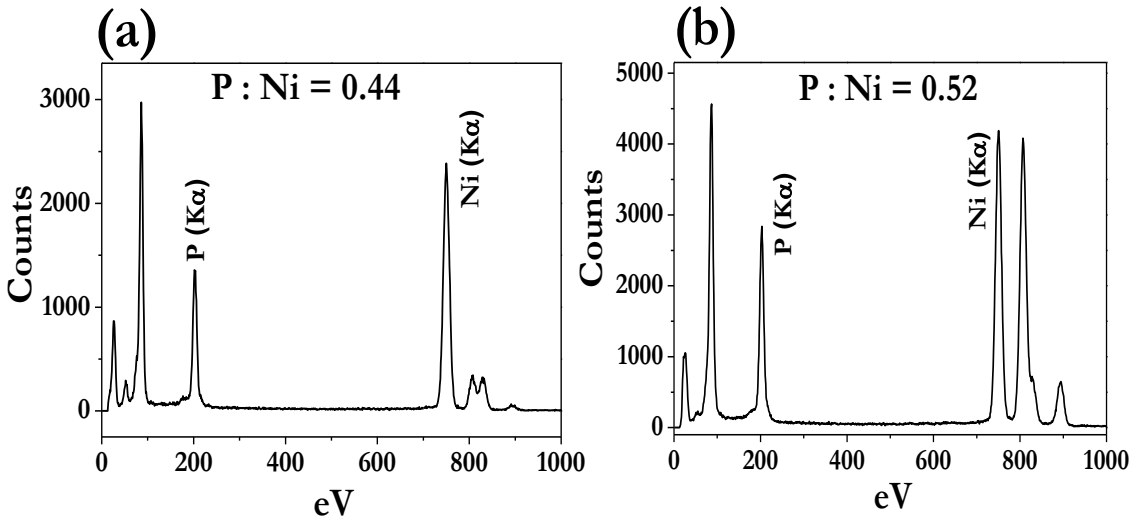

Figure S1. EDS patterns of (a) hollow $Ni_{12}P_5$ nanoparticles and (b) hollow Ni_2P nanoparticles. The expected values for $Ni_{12}P_5$ and Ni_2P are 0.42 and 0.5, respectively.

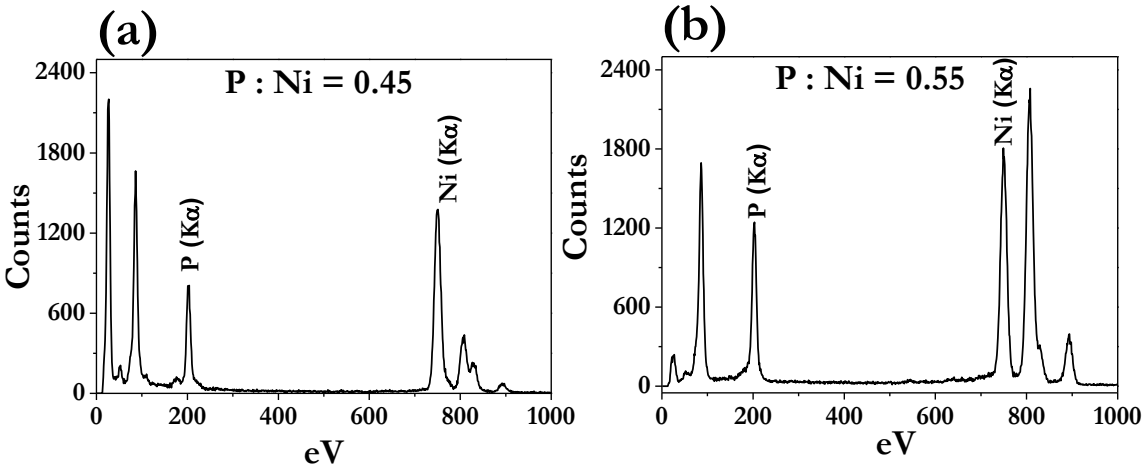

Figure S2. EDS patterns of (a) solid $Ni_{12}P_5$ nanoparticles and (b) solid Ni_2P nanoparticles. The expected values for $Ni_{12}P_5$ and Ni_2P are 0.42 and 0.5, respectively.

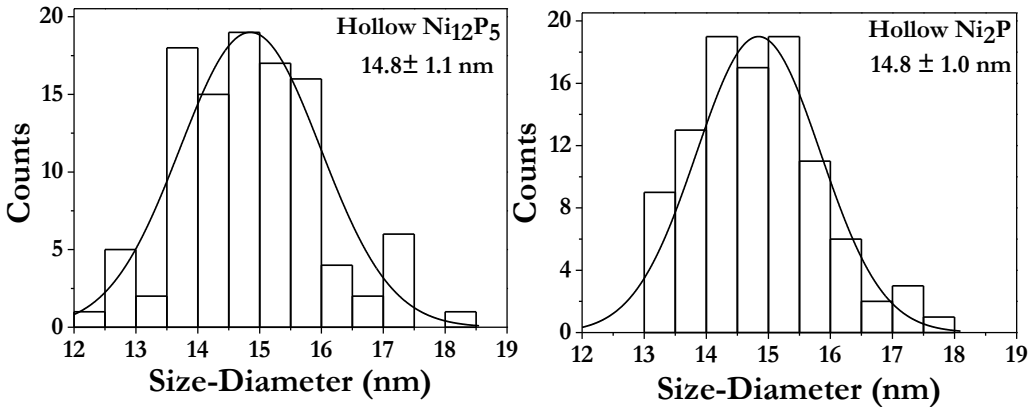

Figure S3. Size distribution histograms indicating almost negligible change between the size of the precursor (hollow $Ni_{12}P_5$) and product (hollow Ni_2P).

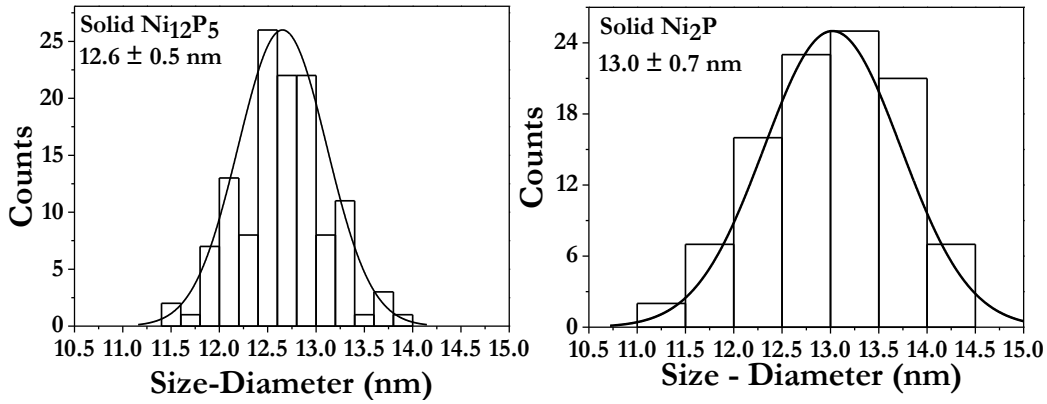

Figure S4. Size distribution histograms indicating almost negligible change between the size of the precursor (solid $Ni_{12}P_5$) and product (solid Ni_2P).

Table S1. Table indicating particle and void size, pore volume, average pore size and theoretical and BET surface area of the hollow nickel phosphide nanoparticles.

Hollow sample	TEM particle size (nm)	TEM void size (nm)	BJH pore volume (cm^3/g)	BJH avg. pore size (nm)	Theoretical surface area (m^2/g)	BET surface area (m^2/g)
$Ni_{12}P_5$	14.8	4.2	0.09	6.6	58.7	67.3
Ni_2P	14.8	4.2	0.063	6.9	60.1	17.3

Table S2. Table indicating particle size, pore volume, average pore size and theoretical and BET surface area of the solid nickel phosphide nanoparticles.

Solid Sample	TEM Particle Size (nm)	BJH Pore Volume (cm^3/g)	BJH Avg. Pore Size (nm)	Theoretical Surface Area (m^2/g)	BET Surface Area (m^2/g)
$Ni_{12}P_5$	12.6	0.031	5.4	63.2	43.6
Ni_2P	13.0	0.039	7.9	62.7	16.7

Templated reactions with iron phosphides

Fe_2P Nanorod Synthesis

The synthesis procedure is adapted from our previous work (E. Muthuswamy, P. R. Kharel, G. Lawes, S. L. Brock, *ACS Nano*, 2009, **3**, 2383-2393)

0.7 mL of $Fe(CO)_5$ (99.999% metal basis purity, Sigma Aldrich) was injected into a degassed system of octadecene (20.0 mL, 90% tech., Sigma Aldrich) and oleylamine (0.3 mL, C18 content 80-90%) maintained at 200 °C under Ar. The system is aged for about 20 minutes at 200 °C allowing the formation of monodisperse Fe nanoparticles. The transformation to phase-pure Fe_2P is effected by injecting 5.0 mL TOP into the hot Fe nanoparticles and subsequently raising the system to 350 °C. The reaction is brought down to RT after 24 h at 350 °C. The final product is isolated by centrifugation with excess ethanol. The product is then re-dispersed in a small quantity of pyridine by sonication and re-precipitated again by centrifugation with excess ethanol. The process is repeated one more time and the black product is dried under vacuum to yield a free flowing powder.

Fe_2P to FeP Conversion

The conversion of Fe_2P to FeP (impure) involved two reactions. In the first reaction, approximately 300 mg of the as-synthesized Fe_2P sample was taken along with 20.0 mL

octadecene and was heated to 200 °C under Ar. In another flask, 15 mL TOP was heated to 350 °C. The hot Fe_2P dispersion in octadecene was cannulated into the pre-heated TOP at 350 °C and the system was raised to 370 °C. The reaction was carried out for 8 h at 370 °C. Isolation of the final product was carried out similar to the process described for the Fe_2P nanorods above. PXRD revealed the product to be a mixture of Fe_2P and FeP. The isolated product was again subjected to a similar treatment with TOP (15 mL) for a longer reaction time, 27 h at 370 °C. The PXRD pattern indicated that the major product this time was FeP (Figure S5).

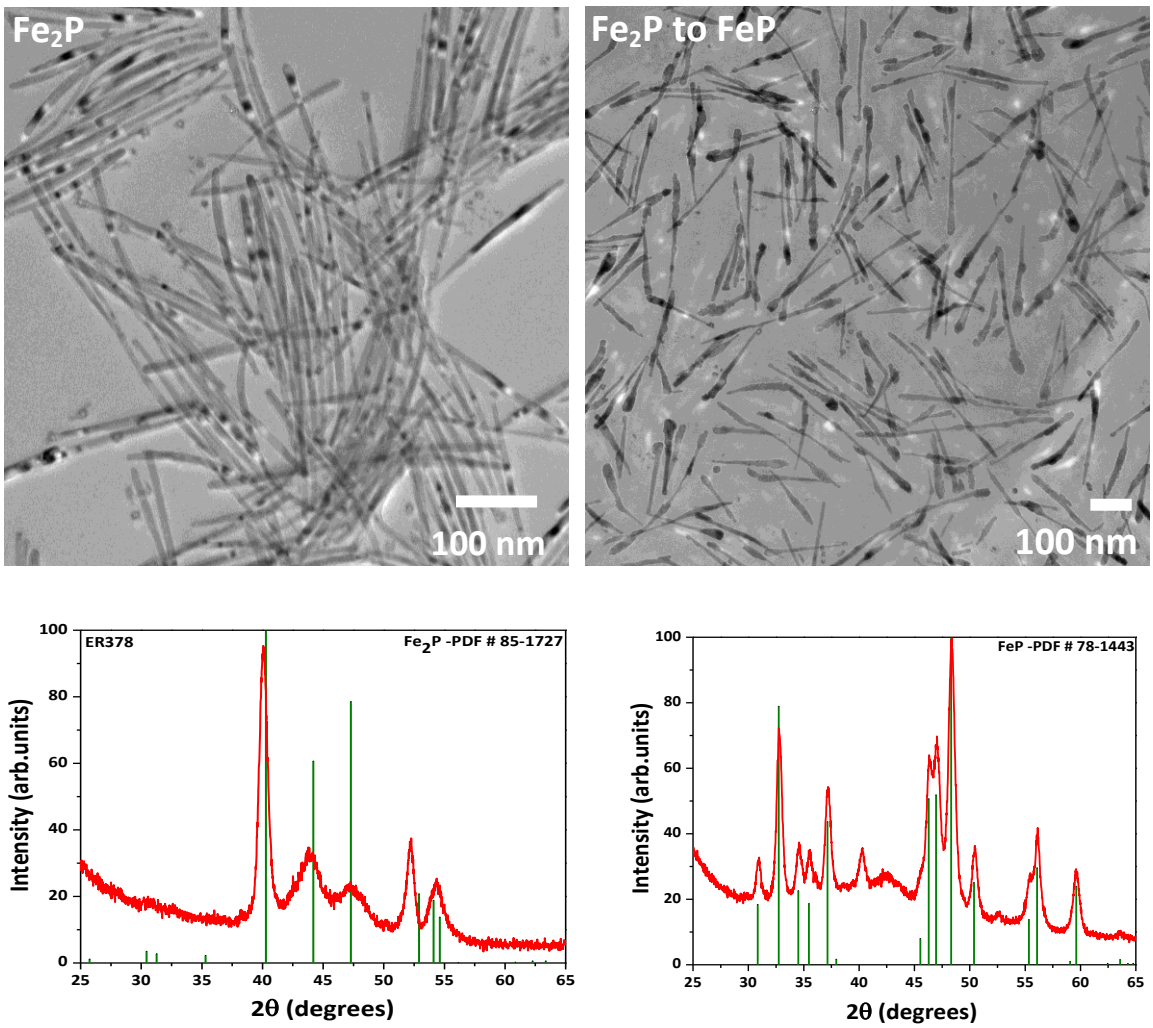

Figure S5. TEM (top) and PXRD (bottom) data for Fe_2P nanorods (left) and the majority-phase FeP nanorods that result from reaction of Fe_2P nanorods with additional phosphorus source (trioctylphosphine). Residual Fe_2P is evident in the PXRD pattern of FeP from the peak at 40° 2θ.