SUPPORTING INFORMATION

Converting Metals into Phosphides: A General Strategy for the Synthesis of Metal Phosphide Nanocrystals

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Chemicals. All metal salts were purchased from Alfa Aesar and used as received. Trioctylphosphine (90%), trioctylphosphine oxide, triphenylphosphine (99%), tetra-noctylammonium bromide (98%), sodium borohydride (98%), oleic acid, hexadecylamine (90%) and toluene were from Alfa Aesar. Octyl ether (99%), oleylamine (70%), hexanes and 1,2hexadecanediol (90%) were from Sigma Aldrich. All reactions were carried out under argon using standard air-free techniques.

Characterization. Powder x-ray diffraction was performed on a Bruker-AXS GADDS diffractometer using microdiffraction techniques. Electron microscopy and electron diffraction were performed on a JEOL 2010 transmission electron microscope.

Synthesis of metal nanoparticle precursors.

Palladium. Pd nanoparticles were synthesized using a modification of Hyeon's procedures.¹ 23.2 mg Pd(acac)₂ were heated in 2.0 mL TOP at 220 °C for 30 min, precipitated with ethanol, isolated by centrifugation, washed with ethanol, and dried under argon.

Gold. Au nanoparticles were prepared according to Grebinski's methods.² 13.1 mg $HAuCl_4 \cdot 3H_2O$ were dissolved in 0.625 mL nanopure water. Separately, 21.0 mg tetra-noctylammonium bromide was stirred in 0.825 mL toluene under argon. The aqueous Au³⁺ solution was added to the toluene solution. Then, 0.01 mL TOP dissolved in 0.200 mL toluene was added dropwise until the solution changed from clear dark red to milky white. 6.1 mg NaBH₄ in 0.500 mL nanopure water was added dropwise. The reaction was stirred 30 minutes, then the toluene layer extracted and saturated with ethanol. The particles were isolated via centrifugation, washed with ethanol, and dried under argon.

Rhodium. Rh nanoparticles were prepared by sonicating a solution of $28.4 \text{ mg RhCl}_3 \cdot \text{xH}_2\text{O}$ in 1.000 mL oleylamine and injecting the solution into 2.0 g hexadecylamine at 260 °C. The solution was then heated 1 hour at 260 °C, followed by cooling and addition of 3:1 ethanol:hexanes to precipitate particles. The particles were isolated by centrifugation, washed with 3:1 ethanol:hexanes, and dried under argon.

Platinum. Pt nanoparticles were prepared by sonicating 47.8 mg Pt(acac)₂, 42.9 mg 1,2hexadecanediol, 100 μ L oleylamine and 100 μ L oleic acid in 2.00 mL octyl ether. The solution was then heated under argon at 230 °C for 1 hour. The solution was cooled and ethanol added to precipitate particles. The particles were isolated via centrifugation, washed with ethanol and dried under argon.

Nickel. Two methods were used to prepare Ni nanoparticles of varying size and dispersity. The first method is identical to the above method for preparing Pt nanoparticles, except 85.3 mg Ni(acac)₂, 166.5 mg 1,2-hexadecanediol, 200 μ L oleylamine, 200 μ L oleic acid and 4.00 mL octyl ether were used. The second method is a modification of Hyeon's method³ in which 210.0 mg Ni(acac)₂ and 2.80 mL oleylamine were heated to 100 °C and injected into 2.5 g triphenylphosphine at 215 °C. The solution was heated at 200 °C for 30 minutes, then cooled. The particles were precipitated with ethanol, isolated via centrifugation, washed with ethanol and dried under argon.

Conversion of metal nanoparticles into metal phosphides. Conversion reactions were carried out by dispersing pre-made metal nanoparticles in TOP and injecting the solution into hot TOP, TOPO, or octyl ether as described below.

Product	Metal Nanoparticles/TOP	Solvent	Conditions
Ni ₂ P	22.2 mg Ni + 1.0 mL TOP	2.00 mL octyl ether	injected 290 °C; aged 300 °C, 2h
PdP ₂	26.1 mg Pd + 2.0 mL TOP	2.0 g TOPO	360 °C, 2h
Pd_5P_2	19.5 mg Pd(acac) ₂ *	2.0 mL TOP	300 °C, 0.5h
Au_2P_3	3.1 mg Au + 2.0 mL TOP	2.0 g TOPO	360 °C, 6h
PtP ₂	18.0 mg Pt + 1.0 mL TOP	2.0 mL TOP	370 °C, 2h
Rh ₂ P	8.7 mg Rh + 2.0 mL TOP	2.0 g TOPO	360 °C, 1h

Table 1: Synthetic variables for the conversion of metal nanoparticles into phosphides

* Pd_5P_2 particles could not be made phase-pure by injecting pre-made Pd nanoparticles dispersed in TOP into a hot solvent. Multi-phase Pd_5P_2/PdP_2 is accessible by injecting Pd particles dispersed in TOP into 330 °C TOPO. Instead, phase-pure Pd_5P_2 can be made by heating $Pd(acac)_2$ in TOP to 300 °C for 0.5 hours, during which Pd particles first form at 220 °C and are converted to Pd_5P_2 by further heating.



Figure S1. Histograms of particle size distribution for (a) Ni nanoparticles made using method 2 (from reference 3) and (b) Ni₂P formed from their reaction with TOP. The predominant particle sizes are 5 nm for Ni and 6 nm for Ni₂P.



Figure S2. (a) Powder XRD patterns for Pt, Rh and Pd nanoparticle precursors; TEM and SAED images of (b) Rh and (c) Pd nanoparticles.



Figure S3. (a) Enlarged SAED image and (b) powder XRD for PtP_2 nanocrystals, with major planes indexed.



Figure S4. TEM micrograph and EDS element mapping data for Ni_2P hollow nanospheres, showing the presence of both Ni and P in the nanostructures.



Figure S5. XRD pattern for the hollow Ni₂P nanospheres shown in Figures 3 and S4.



Figure S6. TEM micrographs showing metal nanoparticle precursors (Pt, Rh, Pd) and the metal phosphide products (PtP₂, Rh₂P, PdP₂) that are derived from them via reaction with TOP. For PdP₂, the Pd nanoparticle precursors are much smaller than the PdP₂ products, implying that more than one Pd nanoparticle serves as a precursor for the formation of a single PdP₂ particle. This, in turn, implies a slightly different reaction pathway for the formation of PdP₂ compared to the other metal phosphides, which more closely match the shape and size dispersity of the metal nanoparticle precursors.

¹ (a) Son, S. U.; Jang, Y.; Yoon, K. Y.; Kang, E.; Hyeon, T. *Nano Lett.* **2004**, *4*, 1147-1151. (b) Kim, S.-W.; Park, J.; Jank, Y.; Chung, Y.; Hwang, S.; Hyeon, T.; Kim, Y. W. *Nano. Lett.* **2003**, *3*, 1289-1291.

² Grebinski, J. W.; Richter, K. L.; Zhang, J.; Kosel, T. H.; Kuno, M. J. Phys. Chem. B 2004, 108, 9745-9751.

³ Park, J.; Kang, E.; Son, S. U.; Park, H. M.; Lee, M. K.; Kim, J.; Kim, K. W.; Noh, H.-J.; Park, J.-H.; Bae, C. J.; Park, J.-G.; Hyeon, T. *Adv. Mater.* **2005**, *17*, 429-434.