Supporting Information

A Facile Solution-Phase Synthesis of Cobalt Phosphide Nanorods/ Hollow Nanoparticles

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Materials and Methods

Chemicals and Materials. Oleylamine (OAm, >70%), cobalt(II) acetylacetonate (Co(acac)₂) hydrate, trioctylphosphine (technical grade, 90%), hexane (98.5%), ethanol (100%) were all purchased from Sigma Aldrich.

Co₂P nanorods (NRs) synthesis

 $Co(acac)_2$ (0.1 g), OAm (20 mL), and TOP (1.5 mL) were mixed and magnetically stirred under a flow of nitrogen at room temperature. The solution was heated at 120 °C for 0.5 h to remove air and moisture from the reaction system. Under the protection of nitrogen, the solution was further heated to 300 °C at a heating rate of 5 °C/min and was kept at this temperature for 0.5 h. The heating source was removed, and the solution was cooled to room temperature, after which the solution was exposed to air. The black product was precipitated by adding 40 ml of ethanol, and separated by centrifugation. Finally, the product was separated and redispersed in hexane.

When 0.5 mL TOP was used in the reaction with other experimental parameters unchanged, Co_2P hollow nanoparticles (NPs) could be obtained.

Characterization. X-ray diffraction (XRD) characterization was carried out on a Bruker AXS D8-Advanced diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The

composition analyses of the samples were carried on FEI Nova Nano SEM450 with energy dispersive spectro-scopy (EDS). Samples for transmission electron microscopy (TEM) analysis were prepared by depositing a single drop of diluted clusters dispersion in hexane on amorphous carbon coated copper grids. TEM images were obtained with a Philips CM 20 operating at 200 kV. High-resolution TEM (HRTEM) and the highangle annular dark field (HAADF) images were obtained on a Fei Tecnai Osiris with an accerating votalage of 200 kV. Magnetic studies were carried out using a Quantum Design Superconducting Quantum Interface Device (SQUID) at low temperature and a Lakeshore 7404 high sensitivity vibrating sample magnetometer (VSM) with fields up to 15 kOe at room temperature.



Figures

Figure S1. XRD patterns of the as-synthesized samples with different amount of TOP: (A) 1.5 mL, (B) 0.5 mL, (C) 0.3 mL and (D) 0 mL.



Figure S2. TEM images of the as-synthesized samples with 0.3 mL mL (**A**) and 0 mL (**B**) TOP used in the reaction.



Figure S3. XRD patterns of the as-synthesized samples for different reaction time: (A) 10 min, (C) 20 min and (C) 40 min.



Figure S4. Hysteresis loops of the as-synthesized samples (A) with different amount of TOP and (B) for different reaction time.