

Supporting Information for:

# **Synthesis of Monodisperse Cadmium Phosphide Nanoparticles Using *Ex-situ* Produced Phosphine**

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## 1. TEM and FFT analysis of the $Cd_6P_7$ NCs

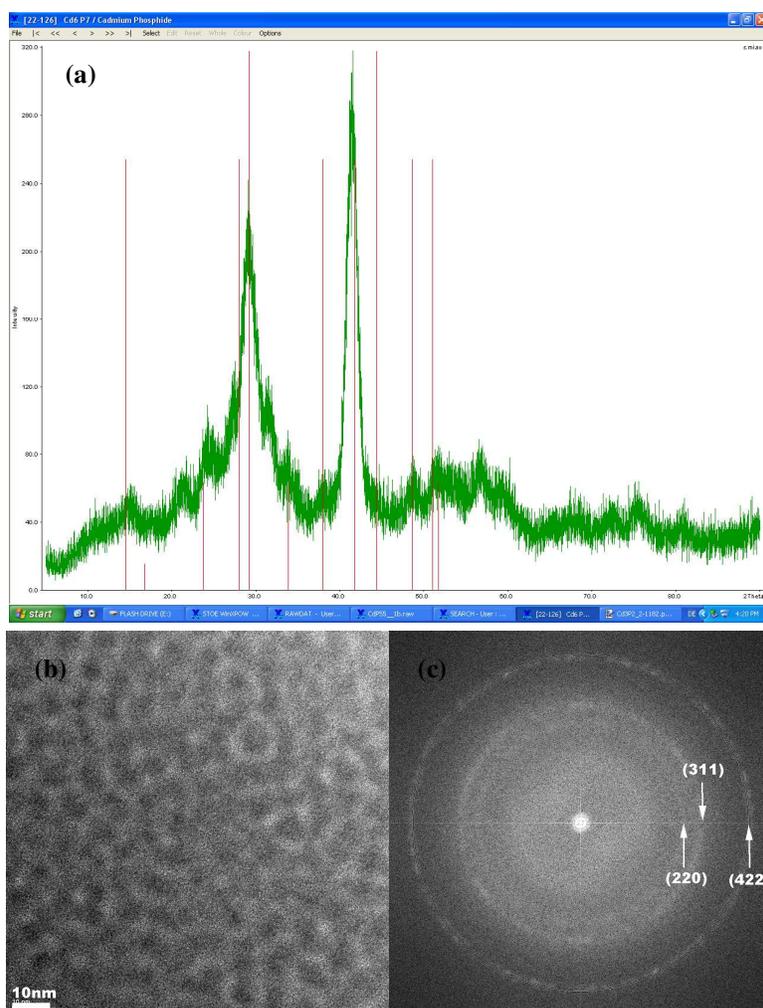


Figure S1 a) XRD pattern of cadmium phosphide QDs synthesized at 250°C with a 40 min growth-time displaying the standard XRD profile of cubic  $Cd_6P_7$  (PDF Card No. 22-0126); (b) TEM image of cadmium phosphide QDs packed multi-layer; (c) Corresponding FFT pattern, the calculated lattice parameter (d spacing) being  $0.318\pm 0.002$  nm,  $0.375\pm 0.004$  nm and  $0.220\pm 0.004$  nm, which can be indexed to the planes of (311) overlapped with (222), (220) and (422) of the cubic  $Cd_6P_7$ .

2. Synthesis of cadmium phosphide from cadmium acetylacetonate ( $\text{Cd}(\text{acac})_2$ ) and indium phosphide NCs using indium acetylacetonate ( $\text{In}(\text{acac})_3$ )

$\text{Cd}(\text{acac})_2$  or  $\text{In}(\text{acac})_3$  (2 mmol) was dissolved in 15 mL oleylamine (OLA) at  $80^\circ\text{C}$  under vacuum. After a clear solution was obtained, reaction flask was flushed with an  $\text{N}_2$  atmosphere and further heated to the desired temperature ( $120^\circ\text{C}$ ).  $\text{PH}_3$  was then bubbled into the solution using  $\text{N}_2$  as the carrier gas. The color of the reaction mixture was observed to change from straw yellow to dark red within 10 min and the reaction yields a colloidal dispersion of nanoparticles. The NCs were collected and purified with the same procedures as in  $\text{Cd}_6\text{P}_7$  synthesis from cadmium oleate.

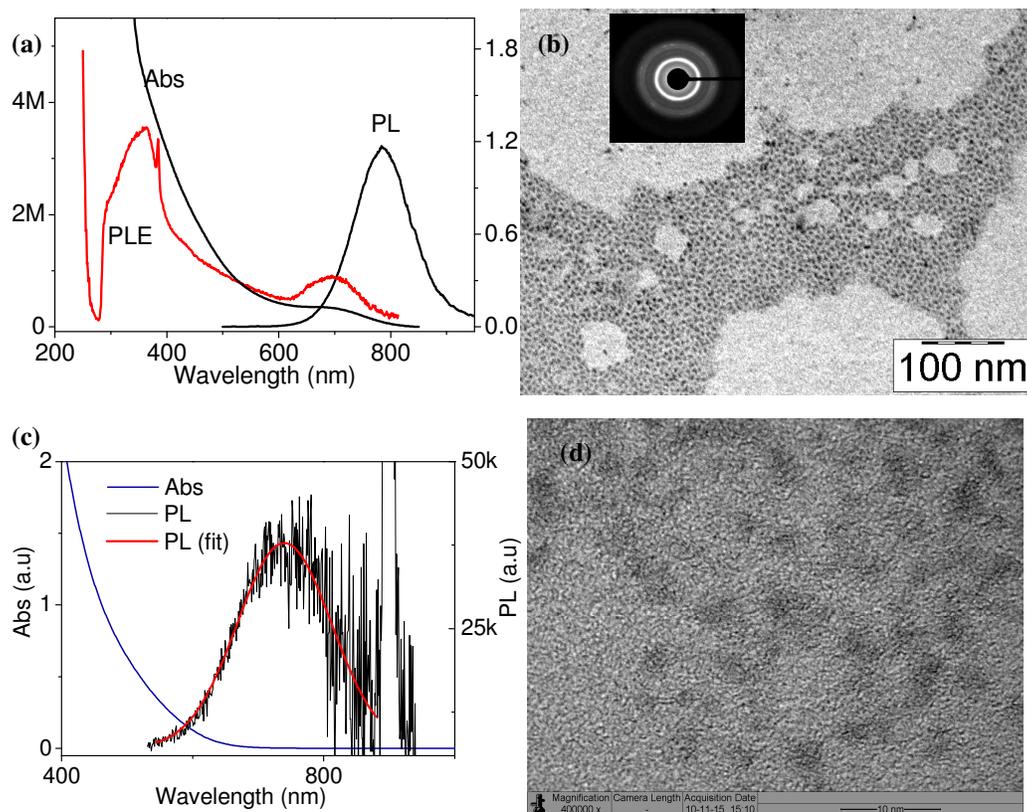


Figure S2. (a) Abs, PL, PLE spectra and (b) TEM micrograph and SAED pattern (inset) of a typical cadmium phosphide NCs synthesized at  $120^\circ\text{C}$  by bubbling a

Cd(acac)<sub>2</sub>/OLA solution with PH<sub>3</sub>; (c) Abs (blue curve), PL spectra (black) and a PL-fitted curve (red) of a typical InP QDs synthesized at 120°C by bubbling an In(acac)<sub>3</sub>/OLA solution with PH<sub>3</sub>; (d) The TEM images of the InP NCs.

### *3. Synthesis of cobalt, iron or nickel phosphide NCs*

Synthesis procedures: As the synthesis of Co<sub>2</sub>P NCs, Co(acac)<sub>2</sub> (2 mmol) was dissolved in OLA (15 mL) at 80°C under vacuum. After ~30 min, the reaction flask was flushed with an N<sub>2</sub> atmosphere and heated to 150°C. PH<sub>3</sub> was then bubbled into the solution using N<sub>2</sub> as the carrier gas after which the Co(acac)<sub>2</sub>/OLA solution becomes turbid (~20 min) as cobalt phosphide colloidal particles are produced. After cooling to room temperature, the NCs were purified by precipitation employing toluene as solvent and an isopropanol/methanol mixture as nonsolvent. The precursors for the synthesis of iron and nickel phosphide NCs are iron (III) acetylacetonate and nickel (II) acetylacetonate. The TEM images and XRD profiles of the obtained Co<sub>2</sub>P, FeP, and Ni<sub>2</sub>P and NCs are shown in the following figures.

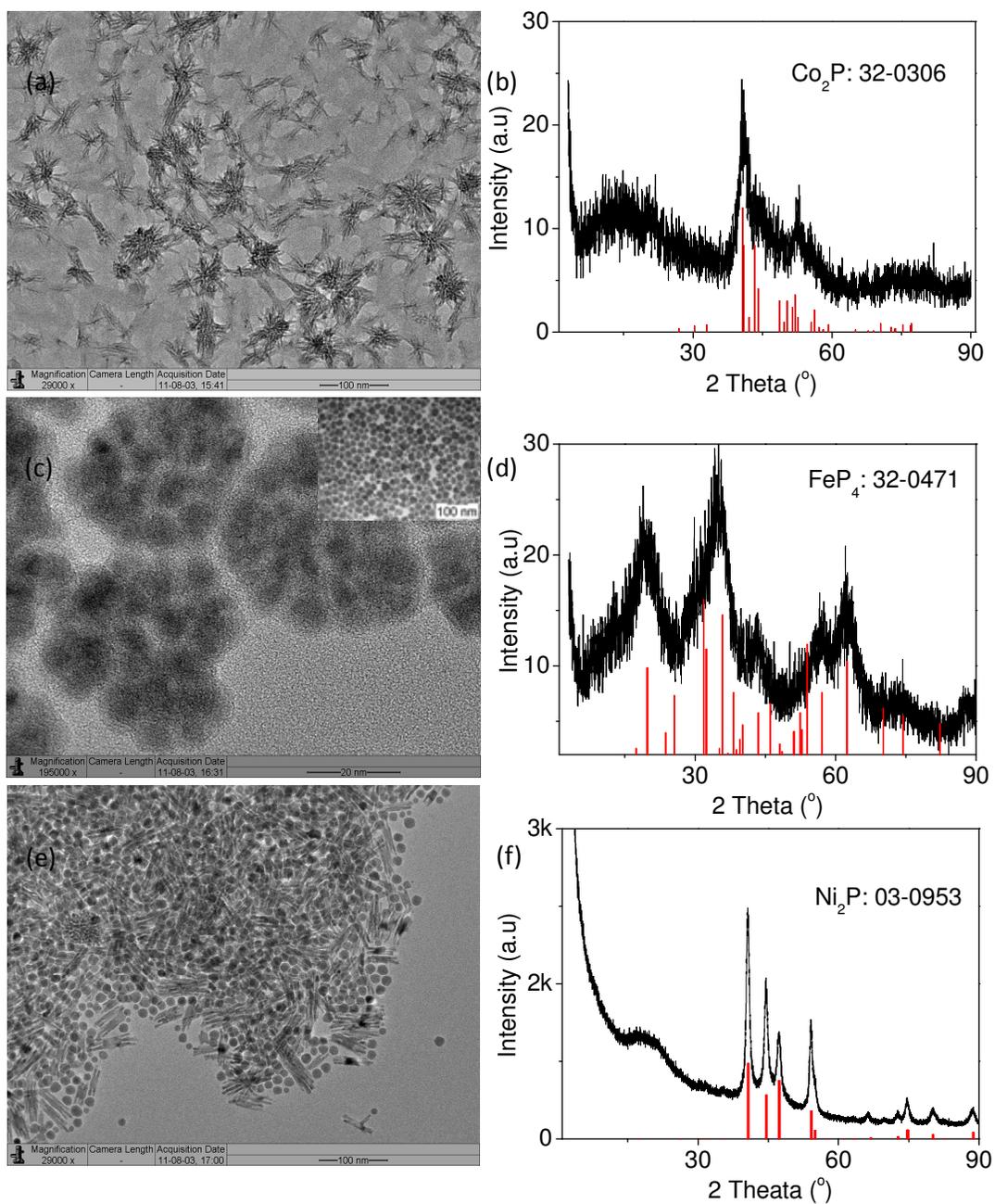


Figure S3 TEM images and XRD profiles of  $\text{Co}_2\text{P}$  (a. b),  $\text{FeP}_4$  (c, d) and  $\text{Ni}_2\text{P}$  (e, f) NCs synthesized by bubbling  $\text{PH}_3$  into  $\text{Co}(\text{acac})_2$ ,  $\text{Fe}(\text{acac})_3$  and  $\text{Ni}(\text{acac})_2$  in OLA, respectively.

#### 4. ESR measurement

Experiment: A JEOL JES-FA200 Electron Spin Resonance Spectrometer was used to obtain ESR spectra. Spectra were recorded at room temperature in the 0~50 mT range. The diphenylpicrylhydrazyl (dpph) radical ( $g = 2.0036$ ) was used to standardize the klystron frequency. The ESR spectrum was obtained with the purified Cd<sub>6</sub>P<sub>7</sub> QDs and MSCs dissolved in absolute toluene which was kept in a 4 mm diameter quartz tube. Spectra were recorded as a first derivative with modulation frequency 100 kHz. The settings used in recording the ESR spectra were as follows: modulation amplitude is 10 G, frequency is 9.15138 GHz, and power is 0.9980 mW.

The effective g-factor is determined according to the equation:  $g = \frac{h\gamma}{H\mu_B}$ , where  $h$  is Planck's constant,  $\gamma$  is the microwave frequency and  $\mu_B$  is the Bohr magneton. It is indicated that g-factor of 4.97 is due to transition metal that has unpaired electron, herein only cadmium ions are present in this system. We assigned this ESR signal comes from partially reductive Cd<sup>δ+</sup> ions arising from polaronic self-trapping of electrons introduced by oxygen deficiency at Cd<sup>2+</sup> sites to generate localised 5s1 states. Perfect Cd<sup>2+</sup> crystals (CdS or CdO) do not exhibit ESR signals. Therefore, there have to be Cd<sup>δ+</sup> ions or some immediate chemical valence between Cd<sup>+</sup> and Cd<sup>2+</sup> in our system. This result further supports the cubic structure of cadmium phosphide which has a formula of Cd<sub>6</sub>P<sub>7</sub>.

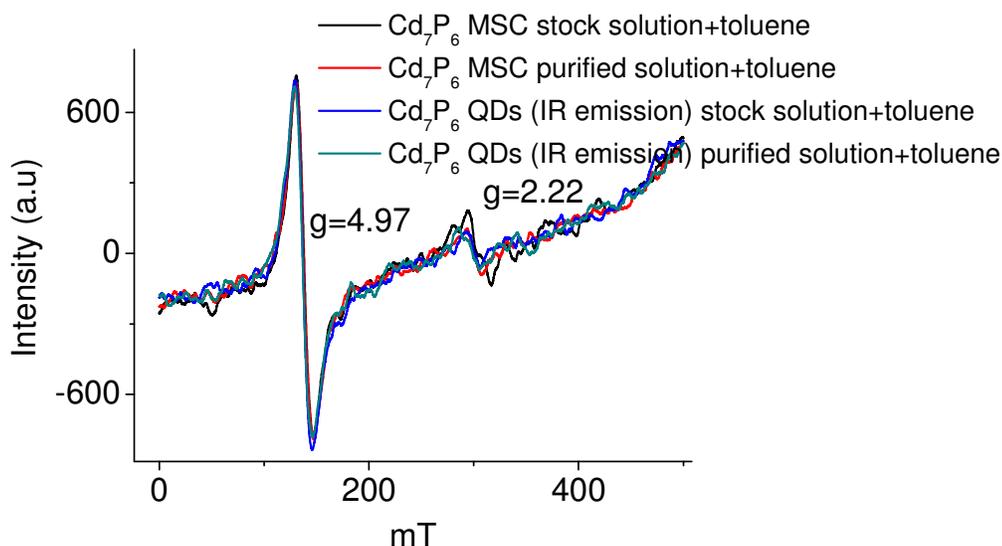


Figure S4 ESR spectra of cadmium phosphide QDs and MSCs dissolved in absolute toluene. The sample of cadmium phosphide NCs was synthesized by bubbling  $\text{PH}_3$  in cadmium oleate/ODE system without adding TOPO. The sample was purified by the standard precipitation-dissolution procedure employing toluene as solvent, and an isopropanol/methanol mixture (isopropanol/methanol=2:1, v/v) as a non-solvent. (unpurified solution contains ODE,). Unpurified solution or the stock solution contains ODE,  $\text{Cd}_6\text{P}_7$  NCs and some unreacted cadmium oleate.

5. *Formation of cadmium metal nanoparticles during the heating process of CdO/OA/ODE system*

To confirm the ease of reduction of cadmium oleate in ODE at a high temperature, a mixture of 2 mmol of CdO and 4mmol of oleic acid was mixed in 15mL ODE, and heated to 270°C for 20min under Ar flow. It was observed that initially the solution becomes colorless due to the formation of cadmium oleate (Figure S4a) but within

about 40min upon further heating (Figure S4b), the solution grows turbid and a cadmium metal mirror forms on the wall of the flask after approx. 60 min (Figure S4c). Metallic nanoparticles were retrieved from the reaction flask, rinsed with acetone and identified by X-ray diffraction (XRD) analysis (Figure S4d).

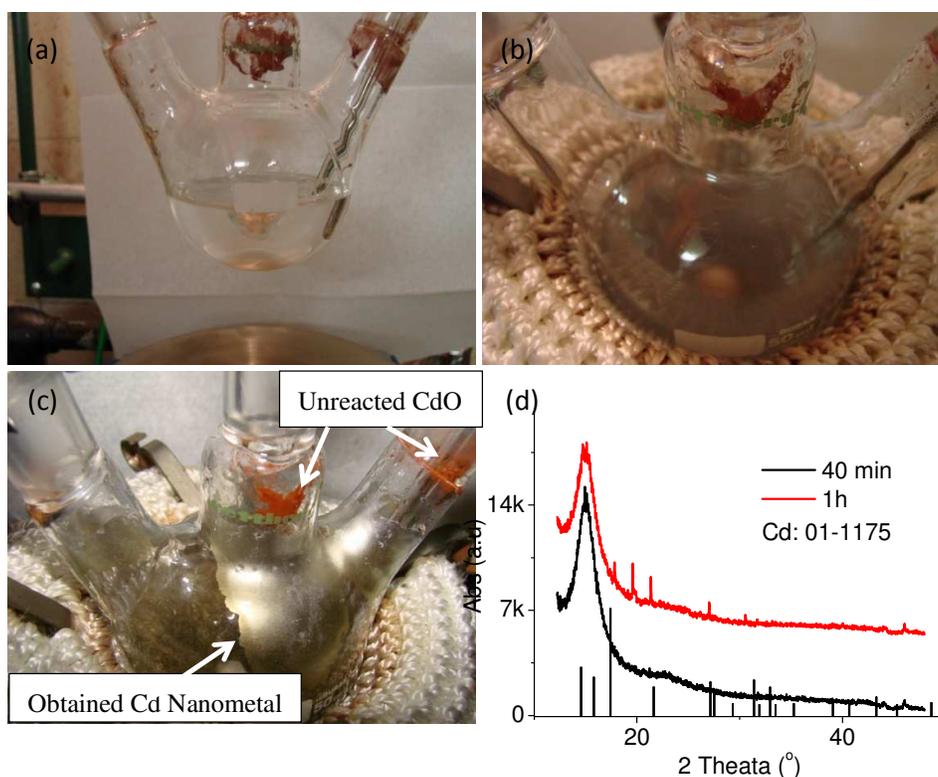


Figure S5 Photographs recorded during the heating process ((a): 20min; (b) 40min; (c): 1h) of cadmium oleate/ODE solution, which displayed the transformation from colorless cadmium oleate to cadmium metal. The red material present in the neck of the flask is unreacted CdO that is attached on the inside of the glass. The mirror-like substance on the flask wall is cadmium metal; (d) XRD profiles of the sample obtained by heating cadmium oleate/ODE with different time (black: 40min; red: 1h) under  $N_2$  atmosphere.

6. Characterizations of Pb metal nanoparticles

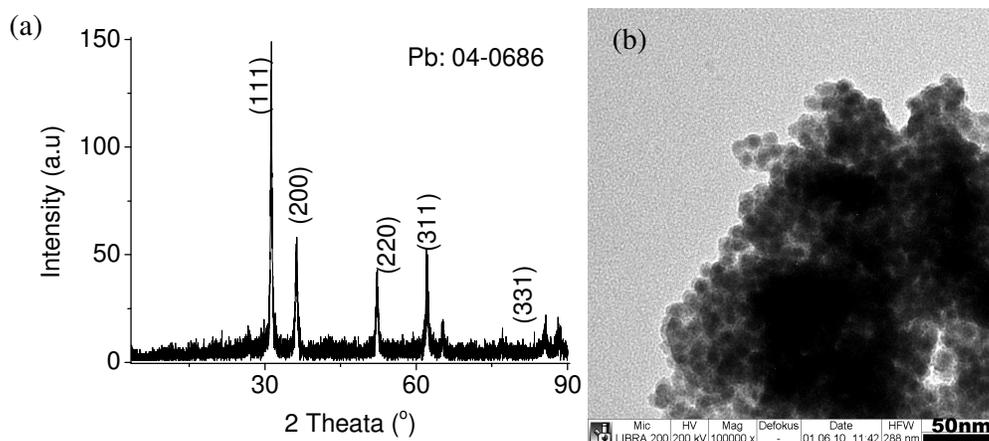


Figure S6 XRD profile (a) and TEM image (b) of Pb metal nanoparticles prepared by bubbling  $\text{PH}_3$  into lead oleate/ODE at  $150^\circ\text{C}$ .