

Supporting Information for:

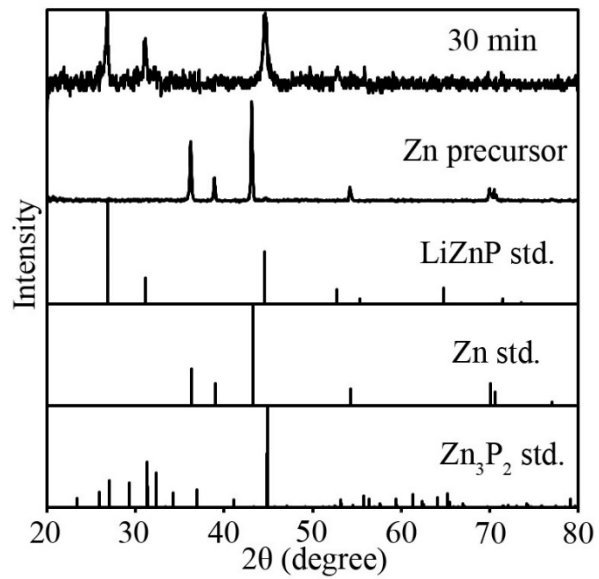
## Got LiZnP? Solution Phase Synthesis of Filled Tetrahedral Semiconductors in the Nanoregime

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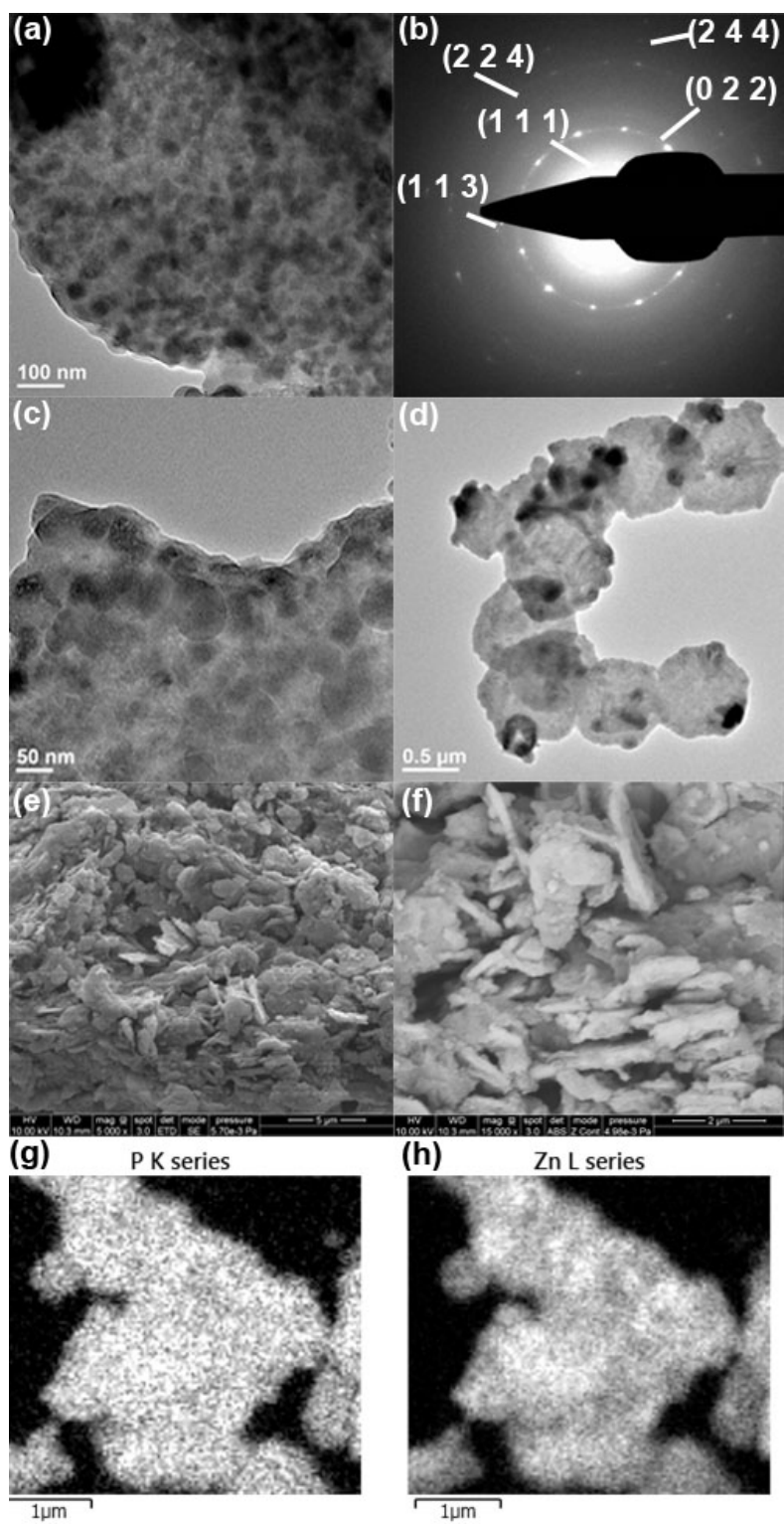
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**Synthesis:** Tri-n-octylphosphine (5 mL, TOP, 97% Strem) and lithium hydride (10-20 mg, powder 97 % Alfa-Aesar) were added to a three-neck flask in dry N<sub>2</sub> filled glove box. The flask was then degassed for 30 min followed by refilling with Ar and heating to 250 °C. Diethyl zinc (56 wt. % Zn Sigma Aldrich), in the case of LiZnP, or dimethyl cadmium (97% Strem), for the synthesis of LiCdP (1 equiv), was then immediately injected. The reaction mixture was heated to 330 °C over the course of 10 min followed by continuous stirring over the period of time indicated. The crude product was washed with toluene (10 mL) followed by centrifugation at 5000 rpm for 10 min. The washed product was washed again after adding enough toluene to re-suspend the particles (roughly 3 mL). For alternative reagents, the following were also successfully used: (Li) n-Butyllithium (2.5M in hexane Sigma Aldrich), lithiumdiisopropylamine (10 wt. % in hexane Sigma Aldrich), and phenyllithium(1.6M in diethyl ether, Sigma Aldrich); (Zn) zinc stearate (tech. grade Sigma Aldrich), and zinc chloride (97% Anhydrous, Strem); (P) triphenylphosphine (99% Acros). **Caution:** On a few instances, LiZnP prepared from n-BuLi ignited upon exposure to air. This is likely due to the presence of excess n-BuLi but needs further investigation.

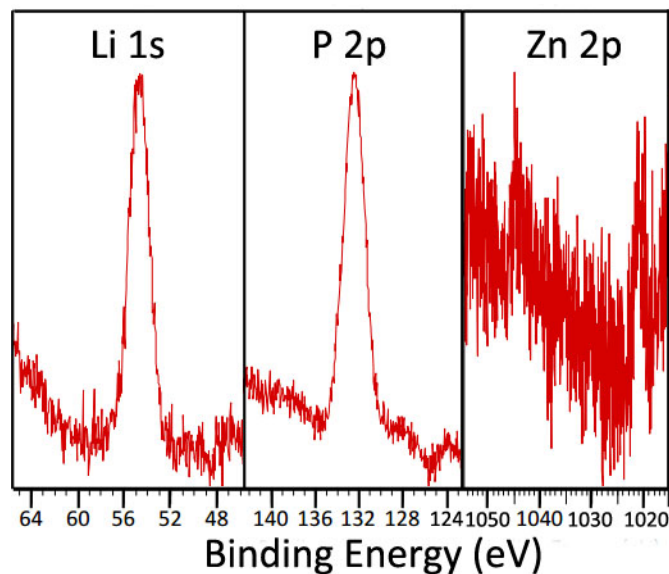
**Characterization:** Powder X-ray diffraction data were measured using Cu K $\alpha$  radiation on a Rigaku Ultima IV diffractometer. Transmission electron microscopy was conducted on carbon-coated nickel grids using a FEI Technai G2F20 field emission scanning transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolution <0.10 nm). Energy-dispersive X-ray spectroscopy was performed using area scans in STEM mode. Absorption spectra were measured with a photodiode array Agilent 8453 UV-Vis-NIR spectrophotometer. The XPS measurements were performed using a Kratos Amicus/ESCA 3400 instrument. The sample was irradiated with 240 W non-monochromated Mg K $\alpha$  x-rays, and photoelectrons emitted at 0° from the surface normal were energy analyzed using a DuPont type analyzer. The pass energy was set at 75 eV. CasaXPS was used to process raw data files. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Measurements were taken using a Netzsch STA449 F1 Jupiter® TGA/DSC instrument coupled to a Quadrupole Mass Spectrometer (QMS) and Bruker Tensor 27 FT-IR spectrometer. 10 mg sample in an alumina crucible was heated from 40 °C to 600 °C using Ar as the carrier gas and 10 °C /min for the ramp rate.



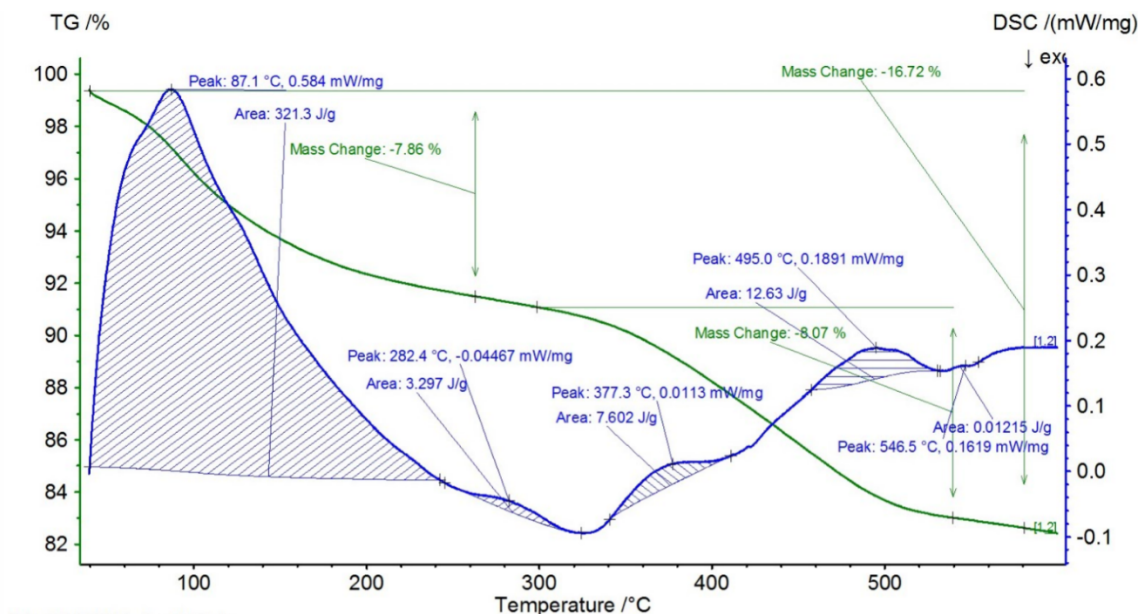
**Figure S1.** Experimental powder XRD patterns obtained for zinc metal generated *ex situ* and for nanocrystalline LiZnP using zinc metal as the Zn precursor after 30 min at 330 °C. Standard patterns of potential phases are shown for comparison.



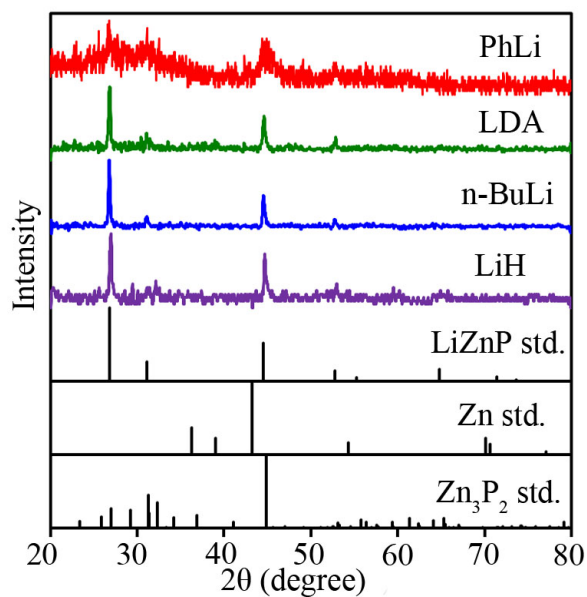
**Figure S2.** TEM image of nanocrystalline LiZnP particles (a, c, d). SAED of LiZnP from (a) with the visible reflections labelled with their corresponding lattice planes (b). SEM images of nanocrystalline LiZnP (e, f). Elemental mapping of phosphorus and zinc given in (g) and (h), respectively.



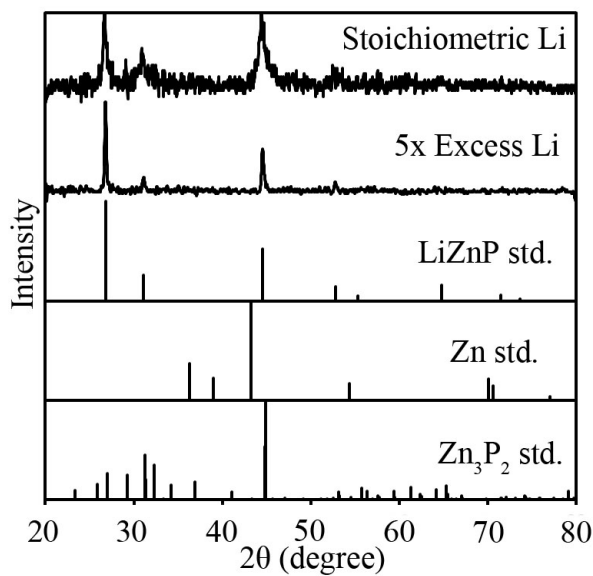
**Figure S3.** XPS of LiZnP nanocrystals prepared using TOP, LiH, and Et<sub>2</sub>Zn at 330 °C for 30 min. Spectra contained two major peaks corresponding to Li<sup>+</sup> bound to oxygen (with a binding energy of 55 eV)<sup>1</sup> and P<sup>5+</sup> bound to oxygen (with a binding energy of 133 eV).<sup>2</sup> XPS is a surface technique that only probes the first 5 nm with the majority of signal coming from the first 1-2 nm. For this reason, a large quantity of excess ligands bound to the particle surface could explain the lack of a Zn signal (see also TEM and thermal analysis). With knowledge that the nanocrystals were most likely not measured, it is feasible to assign the peaks corresponding to Li and P to excess LiOH and TOPO, respectively. This large excess of surface ligands accounts for the aggregation and difficulty in discerning discrete particles by TEM imaging.



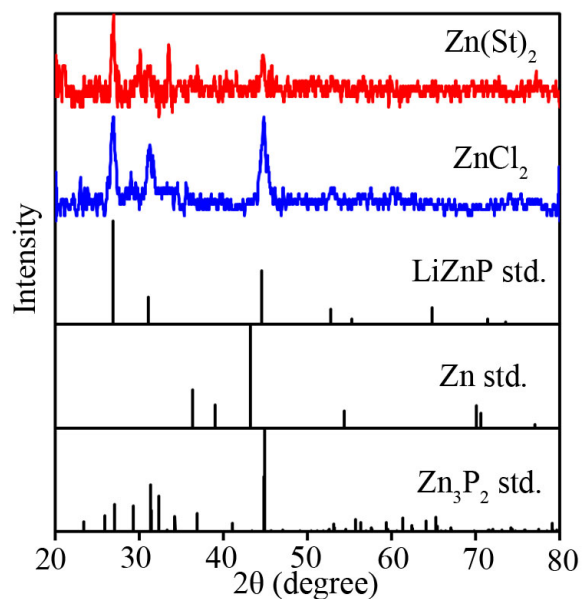
**Figure S4.** TGA/DSC data for LiZnP nanocrystals prepared using TOP, LiH, and Et<sub>2</sub>Zn at 330 °C for 30 min. Broad mass loss from 250-500 °C is consistent with decomposition of TOPO ligands on the surface of the nanocrystals.



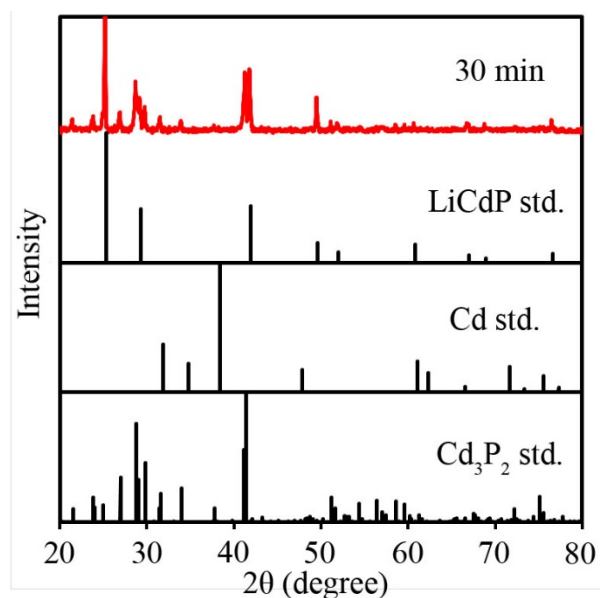
**Figure S5.** Experimental powder XRD patterns obtained for nanocrystalline LiZnP using LiH, n-BuLi, LDA and PhLi as the lithium source for 30 min at 330 °C. Standard patterns of potential phases are shown for comparison.



**Figure S6.** Experimental powder XRD patterns obtained using varying stoichiometry of n-BuLi relative to  $\text{Et}_2\text{Zn}$  for 30 min at 330 °C. Standard patterns of potential phases are shown for comparison. Particle size is found to be 25 nm in the case of excess n-BuLi and 10 nm for stoichiometric n-BuLi.



**Figure S7.** Experimental powder XRD patterns obtained using n-BuLi with  $\text{ZnCl}_2$  (bottom exp. pattern) and LiH with  $\text{Zn}(\text{St})_2$  (top exp. pattern) for 30 min at 330 °C. Standard patterns of potential phases are shown for comparison.



**Figure S8.** Experimental powder XRD pattern obtained for nanocrystalline LiCdP after 30 min at 330 °C. Standard patterns of potential phases are shown for comparison. The ratio of LiCdP to  $\text{Cd}_3\text{P}_2$  was simulated to be 2:1.

## References.

- <sup>1</sup>Suo, L.; Hu, Y.-S.; Li, H.; Armand, M.; Chen, L. *Nat. Commun.* **2013**, *4*, 1481.
- <sup>2</sup>Luber, E. J.; Mobarok, M. H.; Buriak, J. M. *ACS Nano* **2013**, *7*, 8136–8146.