

Magic-Sized Cd₃P₂ II-V Nanoparticles Exhibiting Bandgap Photoemission

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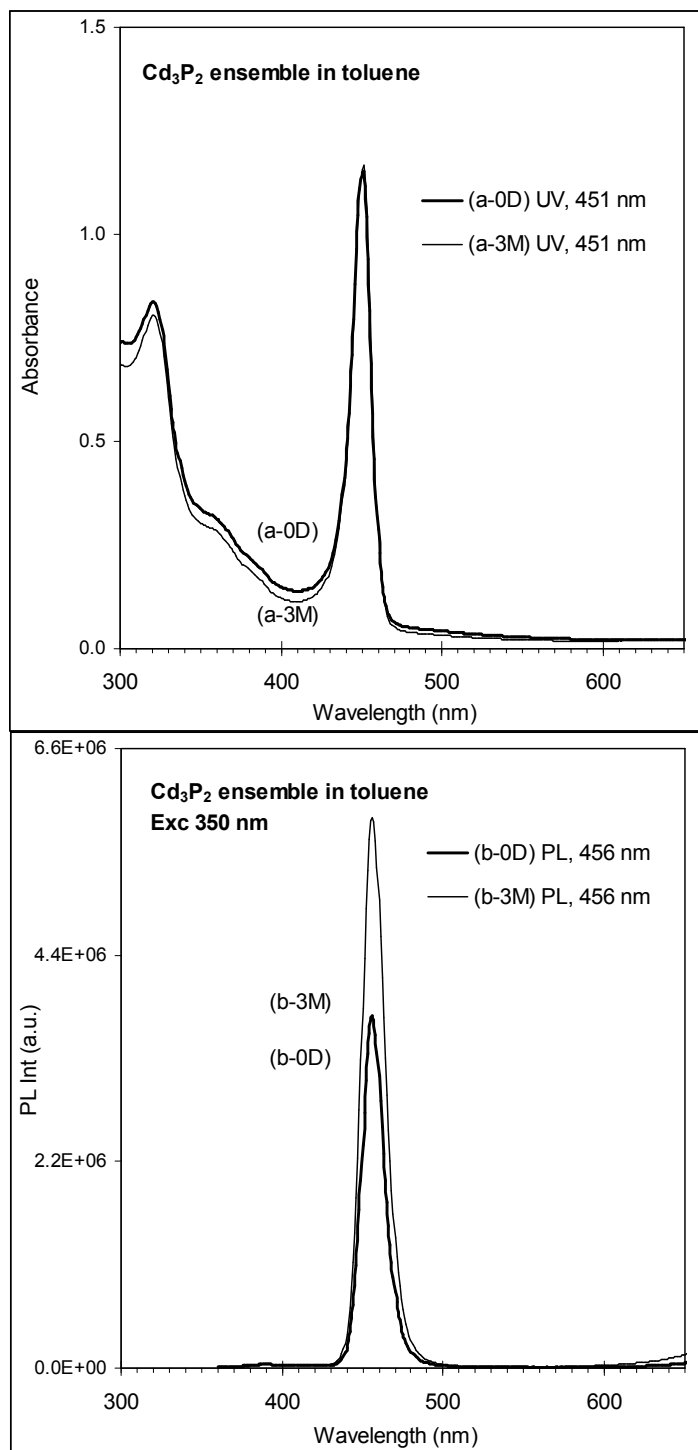
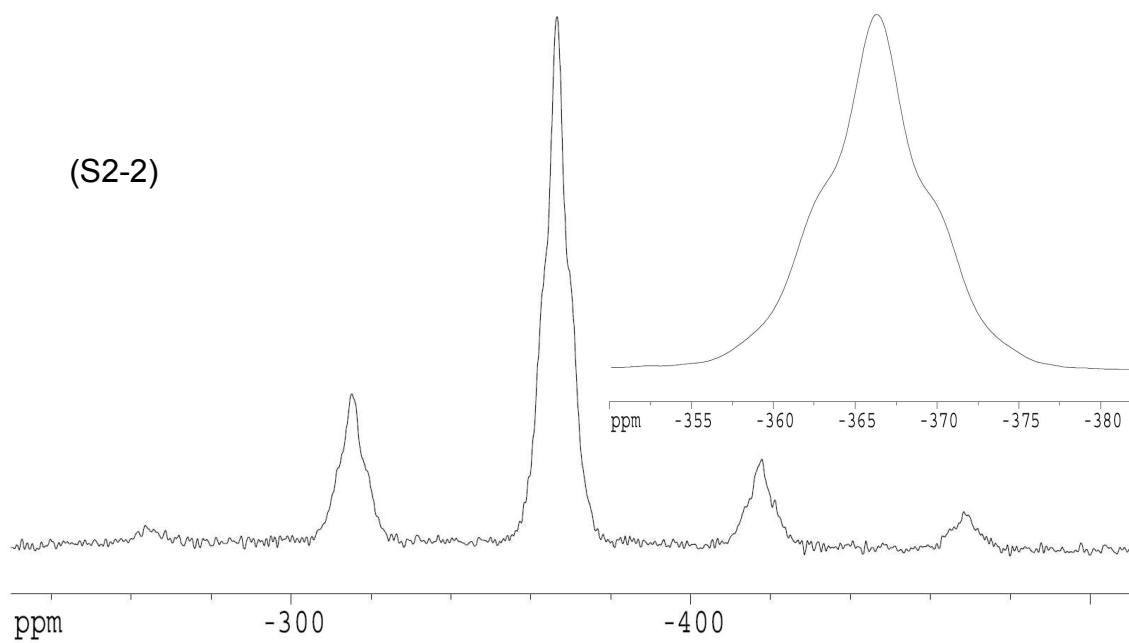
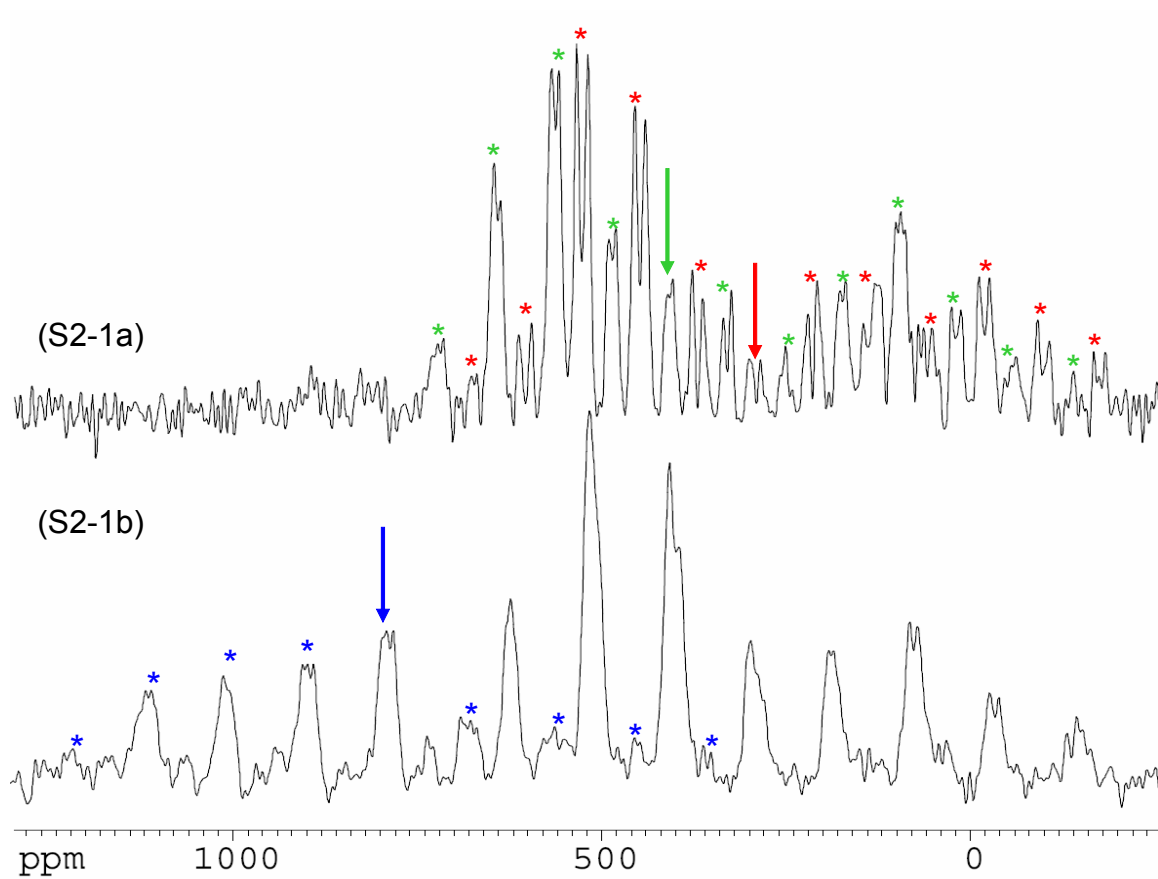


Figure S1. Storage stability of the 140 °C-growth Cd_3P_2 ensemble (shown in Figures 1 and 2 and 3), monitored by the absorbance (top) and emission (bottom). The storage was 3 months in a fridge (~ -20 °C).



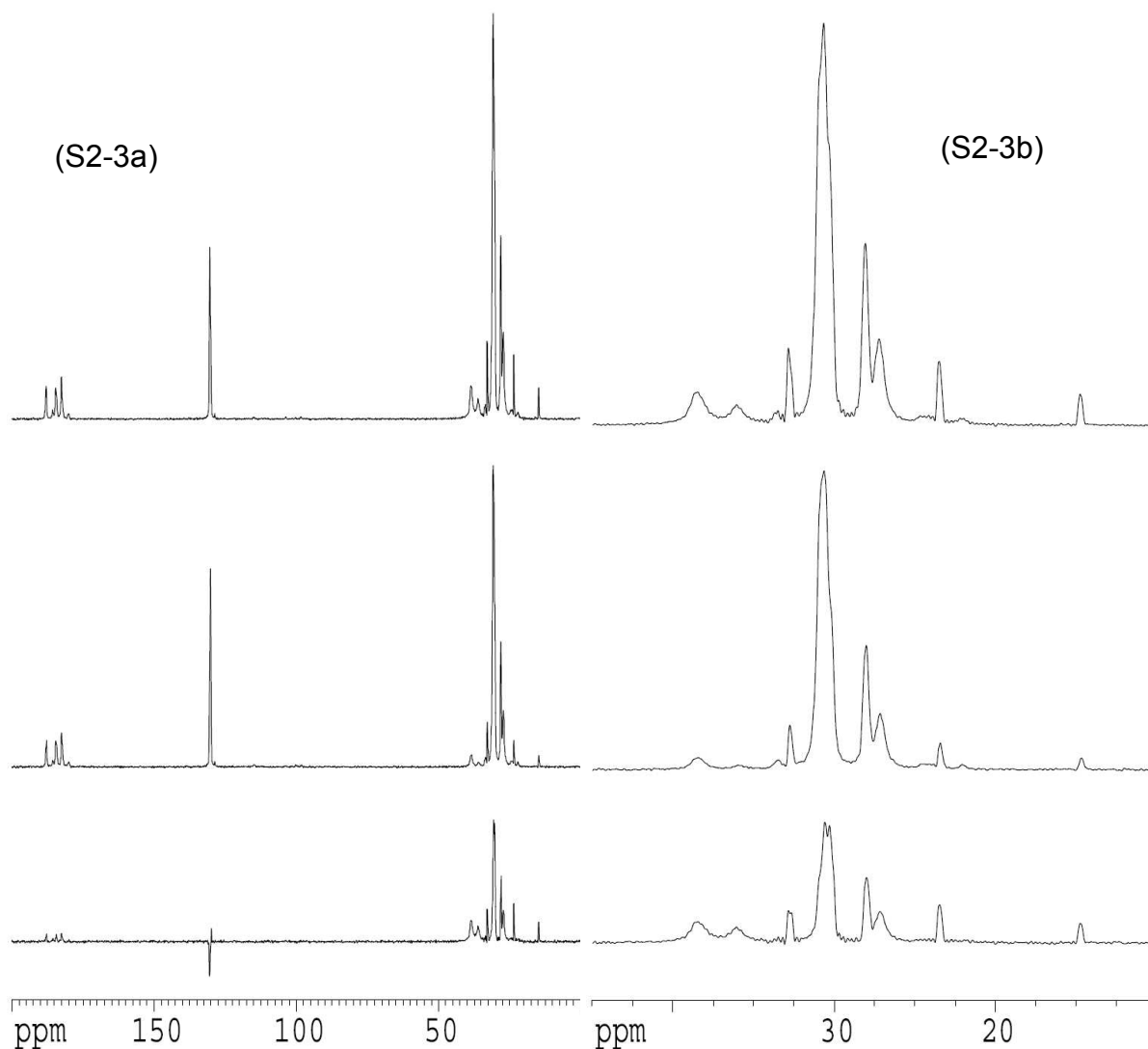


Figure S2. ^{113}Cd (S2-1), ^{31}P (S2-2), and ^{13}C (S2-3) MAS NMR spectra.

The NMR spectra were obtained on a Bruker AMX300 spectrometer and a Doty Scientific Inc. 5mm MAS probe using silicon nitride rotors. ^{113}Cd spectra were referenced to $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ^{31}P to 85 wt% phosphoric acid solution, and ^{13}C to TMS using hexamethylbenzene as external solid reference. The nanoparticle sample was from a large-scale reaction under the same reaction formula and conditions shown in Figures 1 and 2.

^{113}Cd spectra (S2-1a and S2-1b) required very long collection times (4-5 days), both with and without cross-polarization (CP), respectively. The CP/MAS spectrum (S2-1a) show two principal Cd resonances with large chemical shift anisotropies (csa) indicated by many spinning side

bands (ssb, labeled as red and green *). The isotropic lines centred at ~ 292 ppm (indicated with a red arrow) and ~ 407 ppm (indicated with a green arrow) are both split into doublets (or possibly quartets), and these presumably arise from J-coupling to ^{31}P . Without CP but still with high power ^1H decoupling (HPDEC, S2-1b), an additional line, again with a large csa appears with isotropic shift at ~ 790 ppm (indicated with a blue arrow). The spin-rate in the HPDEC spectrum is such that the ssbs of the two surface Cd lines overlap with each other – so the spectrum “appears” accidentally to be simpler. We assign this line to core Cd, since it does not appear with any significant intensity in the CP spectrum, and the two other lines to surface Cds (c.f. our previous assignments of core and surface Cd in CdSe and CdTe nanoparticles^{10d-g}).

The ^{31}P spectrum (S2-2) shows only one main resonance line centred at ~ 366.3 ppm which also has a significant csa apparent from the ssb; an expansion of the isotropic line is emphasized. Curiously the spectrum obtained without CP is virtually identical to that with CP except for a very weak resonance at ~ 11 ppm, which is most probably a trace of an oxygen-bearing-P impurity. Thus core and surface P centres are not distinguished. This may indicate that there are no core P atoms. The shift of the line itself is unusual and quite unlike that of bulk tetragonal Cd_3P_2 , which shows three P resonances with isotropic shifts at -140, -162 and -178 ppm (Adolphi, N.L.; Stoddard, R.D.; Goel, S.C.; Buhro, W.E.; Gibbons, P.C.; Conradi, M.S. *J. Phys. Chem. Solids* **1992**, 53, 1275-1278). The shift is towards that of materials with P-P bonds, e.g. P_4 in CD_2Cl_2 solution is at -526.9 ppm (Ehse, M.; Romerosa, A.; Peruzzini, M. *Topics in Current Chemistry*, **2002**, 220, 107-140). The line also shows a multiplet structure (possibly quintet) with an odd intensity pattern that does not correspond to a simple J-coupled pattern, which may arise from both $J(^{31}\text{P}-^{31}\text{P})$ and $J(^{111,113}\text{Cd}-^{31}\text{P})$. Though the exact interpretation of this spectrum is still uncertain, nevertheless it does confirm the PXRD result that the nanomaterial does not have the structure of bulk tetragonal Cd_3P_2 .

The ^{13}C CP/MAS spectrum (S2-3a top, normal CP/MAS) shows the carbons of the oleic acid capping material (or more probably oleate ion). The dipolar dephased spectrum (S2-3a middle) shows that many of the protonated carbons are in fact dynamic; their appearance in the dipolar dephased spectrum means that their ^1H - ^{13}C dipolar couplings have been reduced due to motion. However, close inspection of the spectra, including the difference spectrum (S2-3a bottom), shows that some of the resonances in the CH_2 region do not appear in the dephased spectrum. This is consistent with a model where the oleate groups are attached to the surface and the CH_2 groups closest to the $-\text{CO}_2^-$ are effectively static whereas CH_2 further along the chain have increasingly more freedom to move. Note that an expansion of the CH_2/CH_3 region is on the right (S2-3b).

To check on the integrity of the NMR sample, the solid material was redissolved in toluene after the NMR experiments were completed and its absorbance and emission spectra (see Figure S3) were very similar to those shown in Figure S1 above and Figure 2 in main text, in peak position but with higher quantum yield of 7.2% (the fresh sample's quantum yield of 3%).

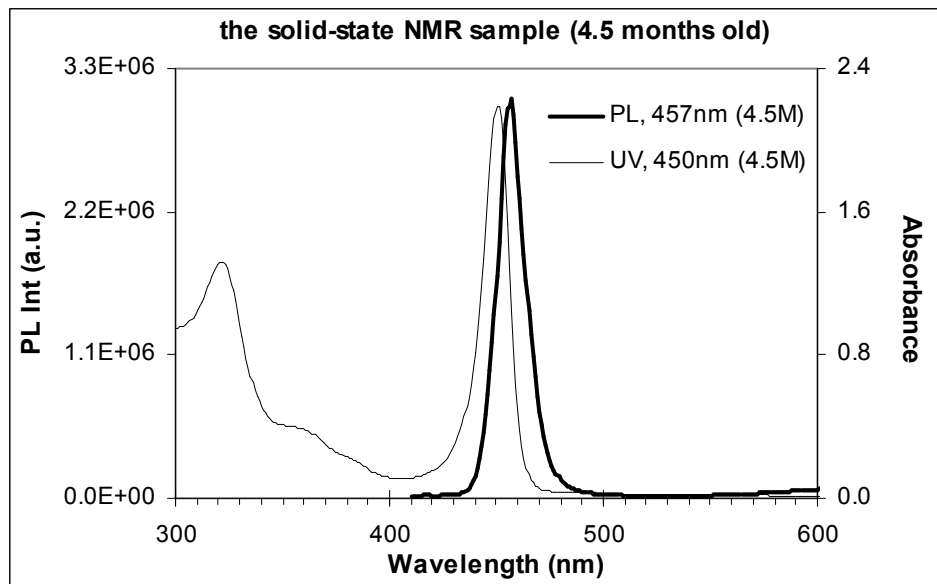


Figure S3. Absorbance (thin line) and emission (thick line) of the solid-state NMR Cd_3P_2 sample (shown in Figure S2) after 4.5-month storage (about 3 months at room temperature and 1.5 months in fridge).

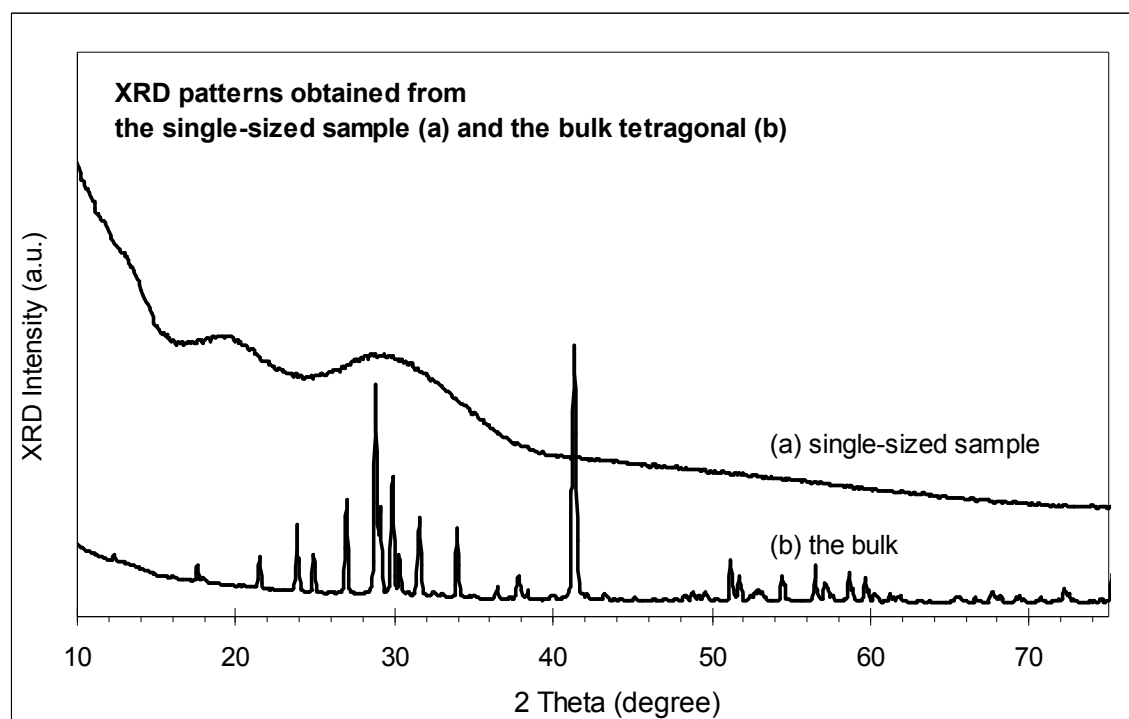


Figure S4. Powder XRD patterns of our Cd_3P_2 sample (a) and the tetragonal bulk Cd_3P_2 materials (purchased from CERAC inc., Milwaukee, WI, USA) (b), without background subtractions.

The PXRD pattern shows only very broad features centred at about 13.5° , 20° and 30° in 2θ . This is inconsistent with the tetragonal structure of bulk Cd_3P_2 . The most recent single crystal structural determination for Cd_3P_2 gives two similar possible structural arrangements²² but simulated powder patterns calculated from either one of these are not compatible with the observed pattern. In particular, both structural models have a very strong line at about 42° in 2θ and other groups of lines at higher angles, yet there is no indication whatsoever of any intensity in the observed pattern above about 36° . In fact the PXRD pattern does not appear to represent a 3D crystalline structure.

Regarding the crystal structure, a reviewer suggested the possibility of alloy formation, which is believed to plague the synthesis of other P-containing nanocrystals.

Table S1. The atomic composition (expressed by atomic percentage) of the Cd₃P₂ nanoparticle sample analyzed by the EDX spectra (shown in Figure 3).

Spectrum	In stats.	P	Cd
Spectrum 1	Yes	36.23	63.77
Spectrum 2	Yes	42.73	57.27
Spectrum 3	Yes	36.80	63.20
Spectrum 4	Yes	38.48	61.52
Spectrum 5	Yes	41.50	58.50
Spectrum 6	Yes	41.42	58.58
Mean		39.53	60.47
Std. deviation		2.72	2.72
Max.		42.73	63.77
Min.		36.23	57.27

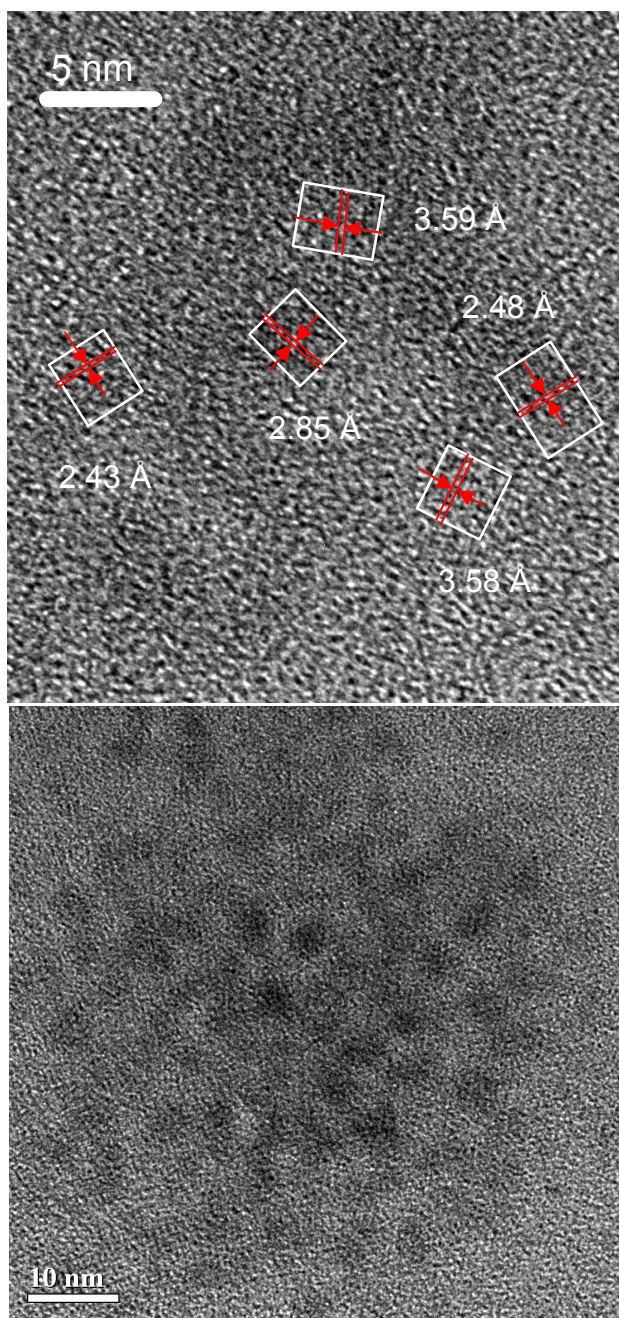


Figure S5. TEM images of the Cd_3P_2 sample (also presented in Figure 4). The measured d-spacing values are individually labeled with the unit of angstrom (\AA) and the measured areas are also indicated with boxes.

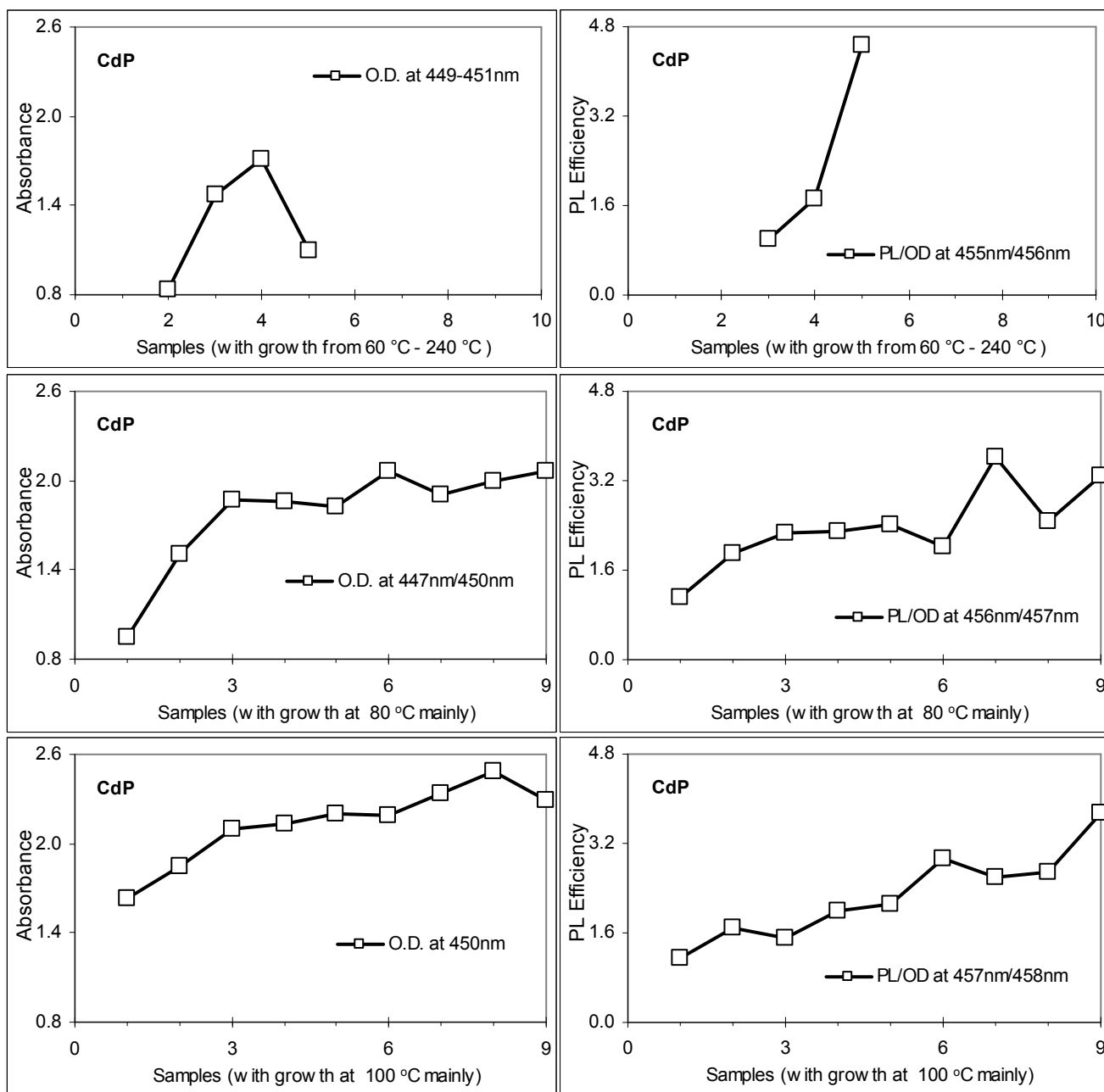


Figure S6. The formation of the single-sized CdP nanoparticles from the three batches (top, middle, and bottom) with the same feed molar ratios of 4OA-4Cd-1P and [P] of 10 mmol/Kg; the growth periods and temperature were

Top batch (0 min): 60 °C (1), 80 °C (2), 100 °C (3), 120 °C (4), 140 °C (5), 160 °C (6), 180 °C (7), 200 °C (8), 220 °C (9), and 240 °C (10). This batch is presented in Fig. 1.

Middle batch: 0 min/60 °C (1), 0 min/80 °C (2), 10 min/80 °C (3), 20 min/80 °C (4), 30 min/80 °C (5), 60 min/80 °C (6), 120 min/80 °C (7), 180 min/80 °C (8), and 240 min/80 °C (9).

Bottom batch: 0 min/80 °C (1), 0 min/100 °C (2), 10 min/100 °C (3), 20 min/100 °C (4), 30 min/100 °C (5), 60 min/100 °C (6), 120 min/100 °C (7), 180 min/100 °C (8), and 240 min/100 °C (9).

The as-synthesized Cd₃P₂ nanoparticle samples from the three synthetic batches were dispersed in toluene, with the concentration of 10 μ L/mL. They exhibited bandgap absorption and emission at \sim 447 nm – 451 nm and at \sim 455 nm – 458 nm, respectively. It is clearly that the synthesis can be carried out at relatively low temperature such as 100 °C with long growth periods and at relatively high temperature such as 140 °C with short growth periods.