

## *Electronic Supplementary Information*

### A Solution-phase Approach to Cd<sub>3</sub>P<sub>2</sub> Nanowires: Synthesis and Characterization

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## Experimental Section

### Chemicals

Cadmium oxide (CdO, 99.998%, alfa), oleic acid (OA, 99%, alfa), 1-octadecene (ODE, 90%, alfa), and tris-trimethylsilyl phosphine ((TMSi)<sub>3</sub>P, ≥98.0 %) were used without further purification. Solvents such as hexane, isopropanol were purchased from various sources and used without purification.

### Synthesis of Bi Nanoparticles

Bi catalyst nanoparticles were prepared according to a modified literature method,<sup>1</sup> and detailed syntheses of nanoparticles over a range of sizes will be reported elsewhere.

### Synthesis of Cd<sub>3</sub>P<sub>2</sub> nanowires

In a typical synthesis, 77.1 mg (0.6 mmol) of CdO, 579 μL OA and 5 mL ODE were loaded into a 50 mL three-necked flask. The flask was degassed by a vacuum pump for 30 min to remove water and other low-boiling point impurities at 120 °C and heated to 290 °C under Ar flow. Then the mixed solution of the 1.2 μmol Bi precursors, 28.7 μL (0.1 mmol) (TMSi)<sub>3</sub>P and 200 μL ODE was quickly injected into the flask. Subsequently, the growth of Cd<sub>3</sub>P<sub>2</sub> nanowires was set at 290 °C for 2 min. After that, the colloidal solution was cooled to room temperature naturally and then precipitated with isopropanol and centrifuged at 8000 rpm for 5 min. A hexane/ isopropanol mixture (1:2) was then added to the solution and the nanowires were isolated by centrifuging. The nanowires were additionally purified thrice by re-dispersing them in hexane and precipitating with isopropanol. The dispersed nanowires were drop-casted into a carbon-coated Transmission Electron Microscopy (TEM) grid for further characterizations.

**Ligand exchange.** The OA ligands capped around nanowires were exchanged by with hydrazine hydrate. The purified nanowires were suspended in a mixture of hydrazine hydrate (≥ 80%) and hexane with a volume ratio of 1:1, and concussed for 12 hours at room temperature. This process was repeated for 3~4 times until the nanocrystals got in to the hydrazine hydrate phase, then the upper clear hexane was removed and isopropanol was added into hydrazine hydrate. The nanowires were then collected through centrifugation and dried under vacuum for hot pressing for photodetector devices.

### Fabrication of Photodetector Devices

To construct photodetectors based on the Cd<sub>3</sub>P<sub>2</sub> nanowire network, the nanowires were directly dispersed on pre-prepared Au electrode pairs (50 nm thick) on SiO<sub>2</sub> (300 nm)/Si substrate. The electrode pairs had a channel length of 8 μm and were fabricated by photolithography (MJB4, SUSS

MicroTec) and sequentially electron beam deposition (PVD 75, Kurt J. Lesker Company). After that, the device was annealed at 250 °C for 1 h under Ar flow to improve the electrical contact.

### **Structural characterization**

X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max- 2500 powder diffraction system using Cu K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ) operating at 40 kV and 200 mA. Samples for the low- and high-resolution transmission electron microscopy (TEM) were prepared by dropping a dilute hexane solution of NWs onto ultrathin carbon coated copper grids and left to evaporate at room temperature. TEM images were obtained using a FEI TECNAI G2 Spirit microscope, operating at an accelerating voltage of 120 kV. HRTEM images were obtained with a FEI TECNAI F30 microscope operating at 300 kV. Element analysis as an ensemble measurement was conducted on FEI Quanta 200F scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDX) detector. UV-Vis-NIR absorption spectra of nanowires suspensions in hexane were acquired in 1 cm path length quartz cuvettes using a Cary 5000 spectrophotometer. Photocurrent measurements were conducted in a quartz cell in aqueous 0.01 M Eu(NO<sub>3</sub>)<sub>3</sub> /0.1 M KCl illuminated under a Xenon lamp. The pseudo-reference electrode was Calomel electrode and a Pt electrode was the counter electrode. The nanowires film was sprayed-cast onto FTO. The current-voltage characteristics were measured at room temperature in air using a Zahner IM6ex electrochemical workstation. The photoresponse properties of the photodetector were characterized using a semiconductor characterization system (4200-SCS, Keithley) assisted by a probe station (M150, Cascade). A Xenon lamp (CEL-HXF300) was used as the light source, which was then filtered to generate monochromatic light with wavelength from 400-800 nm by using different optical filters.

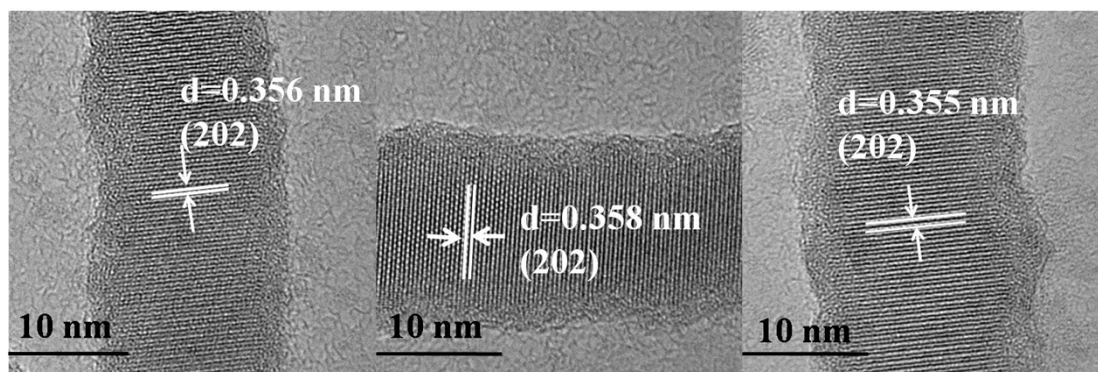


Fig. S1. HRTEM images three different  $\text{Cd}_3\text{P}_2$  NWs.

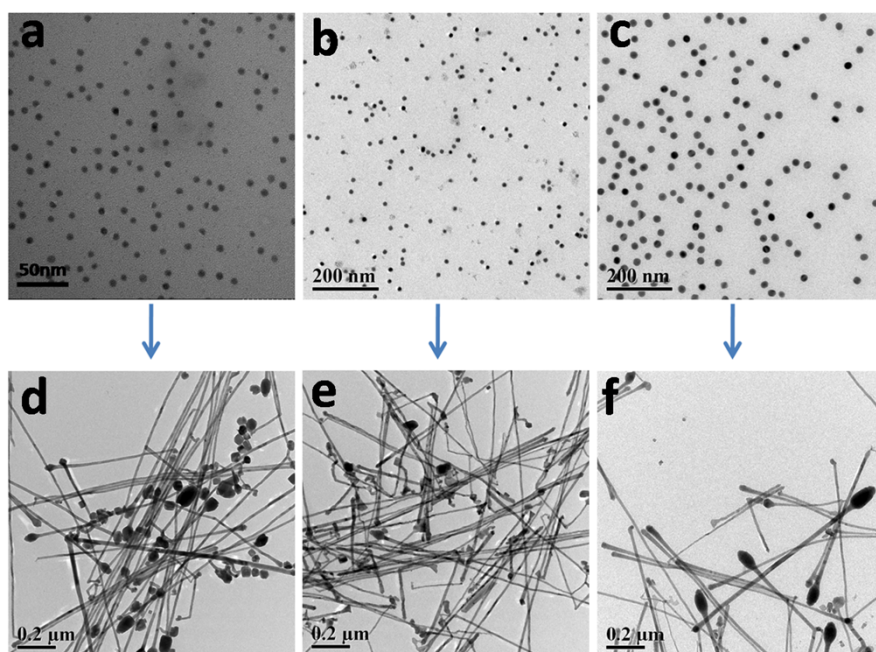
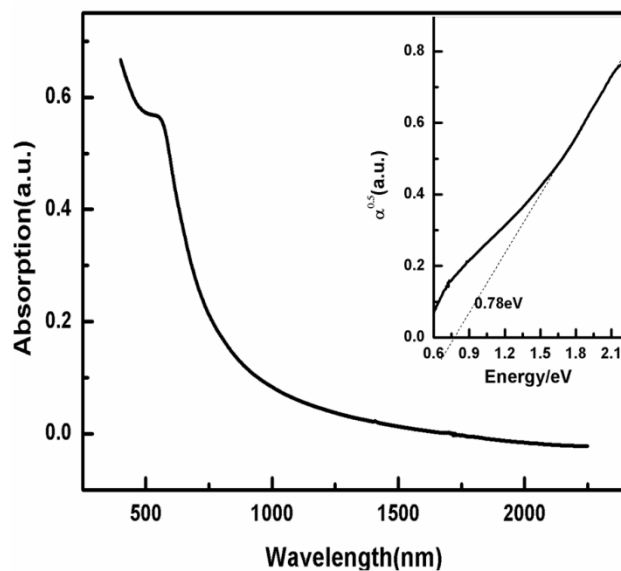
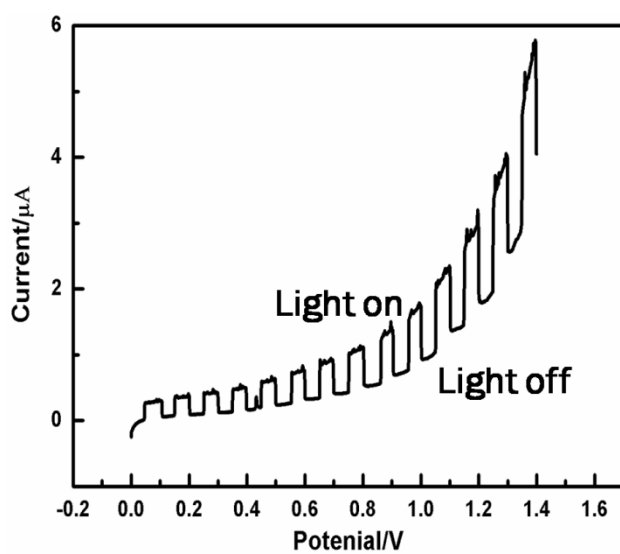


Fig. S2. TEM images of Bi NPs with sizes (a) 7.7 nm, (b) 11.3 nm, (c) 24 nm. (d), (e) and (f) are the TEM images of the  $\text{Cd}_3\text{P}_2$  NWs synthesized from them



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**Fig. S3.** UV-Visible absorption spectra of the  $\text{Cd}_3\text{P}_2$  nanowires dispersed in hexane. The square root of the absorption coefficient plotted as a function of energy (inset) displays a linear trend for an indirect transition.



**Fig. S4.** Transient photocurrent response of the  $\text{Cd}_3\text{P}_2$  nanowires.

## References

- 1 F. D. Wang, E. William, Buhro, *small*, 2010, **6**, 573.