

Supporting Information:

**A Totally Phosphine-Free Synthesis of Metal Telluride
Nanocrystals by Employing Alkylamides to Replace
Alkylphosphines for Preparing Highly Reactive
Tellurium Precursors**

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Experimental Materials. Cadmium chloride dihydrate ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), mercury chloride dihydrate ($\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), silver nitrate (AgNO_3 , 99%), lead chloride (PbCl_2 , 99%), chloroform (99%), ethanol (99.5%) and sodium borohydride (NaBH_4 , 96%), were purchased from Beijing Chemical Reagent Ltd., China. *N,N*-dimethylformamide (DMF, 99.5%), *N,N*-dimethylacetamide (DMAC, 99%), *N,N*-diethylpropionamide (DEP, 98%), tellurium powder (100 mesh, 99.5%) , oleylamine (OLA, technical grade, 70%) and poly(3-hexylthiophene-2,5-diyl) (P3HT) were purchased from Aldrich.

Synthesis of CdTe NCs. A typical procedure for synthesizing CdTe NCs was briefly described below. First, 0.032 g (0.25 mmol) Te powder, 0.01 g (0.26 mmol) NaBH_4 and 2 ml DEP were deposited in a flask, cycled between vacuum and nitrogen three times, and then kept at 80 °C under nitrogen atmosphere for about 30 min. When the Te powder was completely dissolved to form a dark purple solution, the solution was cooled down to room temperature. This solution was marked solution A. 1 mmol $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and 8 ml OLA were mixed in a four-neck flask at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 80 °C for 30 min and then heated to a specific temperature in the range of 120 to 200 °C. The solution was labeled as solution B. Under vigorous stirring, 2 ml solution A was injected into solution B. The reaction was maintained for specific duration to produce the CdTe NCs with different diameters. To terminate the reaction, the flask was cooled down to room temperature with an icy rag.

Synthesis of HgTe and PbTe NCs. Following a similar method, except using 0.136 g

(0.5 mmol) $\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ rather than $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, HgTe was synthesized with a rejection temperature of 120 °C. For the synthesis of PbTe , 0.139 g (0.5 mmol) PbCl_2 and 8 ml OLA were used as solution B. Solution A was injected into solution B at 140 °C to produce the NCs.

Synthesis of Ag_7Te_4 NCs. A typical synthetic procedure of Ag_7Te_4 was briefly described below. First, 2 ml DMAC, 0.5 mmol Te powder, 0.5 mmol NaBH_4 were deposited in a flask, cycled between vacuum and nitrogen three times, and then kept at 80 °C under nitrogen atmosphere for about 30 min. When the Te powder was completely dissolved to form a clear dark purple solution, the solution was cooled down to room temperature. The solution was labeled as solution A. 0.5 mmol AgNO_3 and 8 ml OLA were mixed at room temperature and cycled between vacuum and nitrogen three times. Afterward, the mixture was kept at 80 °C for 30 min and then heated to 100 °C. The solution was marked as solution B. Solution A was injected into solution B by vigorous stirring. The solution immediately turned brown with the temperature dropped to ~90 °C. The growth temperature was allowed to recover to 100 °C and maintained for 5 min. Finally, the flask was rapidly cooled to room temperature to produce the NCs.

Purification. 5 ml chloroform was firstly added into a 10 ml NC product and the mixture was centrifugated at 3000 rpm for 3 min to discard the precipitates. 15 ml ethanol was added into the supernatant, and followed by centrifugation at 8000 rpm for 5 min to discard the unreacted precursors. The precipitates were collected and redispersed in 10 ml chloroform.

Device fabrication. A CdTe:P3HT photovoltaic device was fabricated from the as-synthesized CdTe NCs with the average diameter of 10.8 nm following the device structure shown in Fig. S10. ITO-coated glasses first underwent ultrasonic treatment in chloroform, acetone, isopropanol, then were rinsed by deionized water before drying in N₂ flow. After oxygen plasma treatment for 5 min, the TiO₂ layer was spin-coated at 3000 rpm for 1 min and followed by annealing at 350 °C for 15 min. The CdTe layer formed by spin-coating 15 mg/ml toluene solution of 10.8 nm CdTe NCs at 2000 rpm for 1 min and followed by annealing at 300 °C for 1 h. Following a similar method, except annealing at 150 °C for 15 min, the P3HT layer was spin-coated on the CdTe layer. A 5 nm MoO₃ film was further evaporated on the active layer. Finally, Au electrode was evaporated with a 4 mm² mask to produce the device.

Characterization. UV-visible absorption spectra were obtained using a Shimadzu 3600 UV-VIS-NIR spectrophotometer. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. The excitation wavelength was 400 nm. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. High-resolution TEM (HRTEM) imaging was implemented by a JEM-2100F electron microscope at 200 kV. X-ray powder diffraction (XRD) investigation was carried out using a Siemens D5005 diffractometer. An energy-dispersive X-ray spectroscopy (EDX) detector coupled with SEM (XL 30 ESEM FEG Scanning Electron Microscope, FEI Company) was used for elemental analysis. ¹³C NMR was recorded

on a Bruker Ultra Shield 500 MHz spectrometer in D₂O. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg K α excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. The current density-voltage (J-V) characterization of the photovoltaic devices under white-light illumination from an SCIENCETECH 500-W solar simulator (AM 1.5 illumination, 100 mW cm⁻²) was carried out on computer-controlled Keithley 2601 Source Meter measurement system in a glove box filled with nitrogen atmosphere.

Fig. S1 The ^{13}C NMR spectra of DMAC (in D_2O) with (a) and without (b) NaBH_4 . The mixture of DMAC and NaBH_4 are processed following a same procedure as described in Te precursor preparation except no Te powder is added. The NMR data clearly show no amine forms.

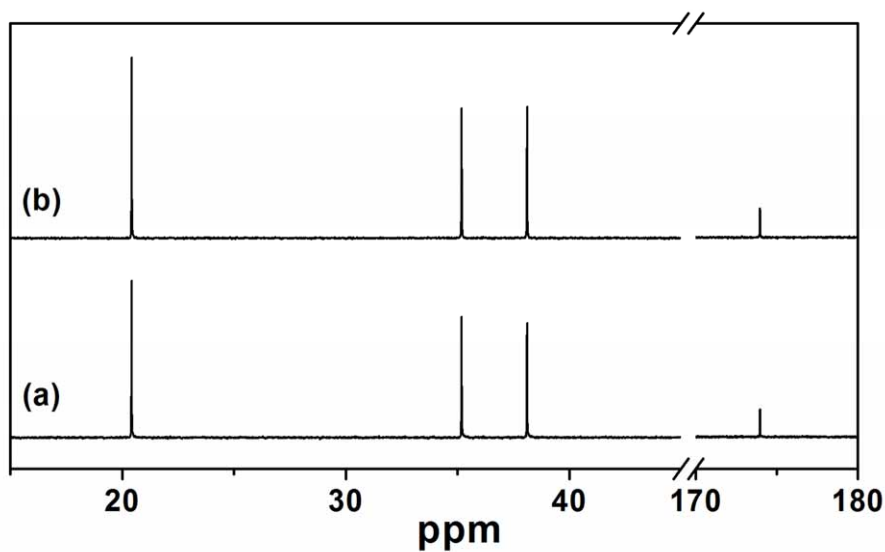


Fig. S2 XPS Cd3d (a) and Te3d (b) spectra of the as-synthesized CdTe NCs.

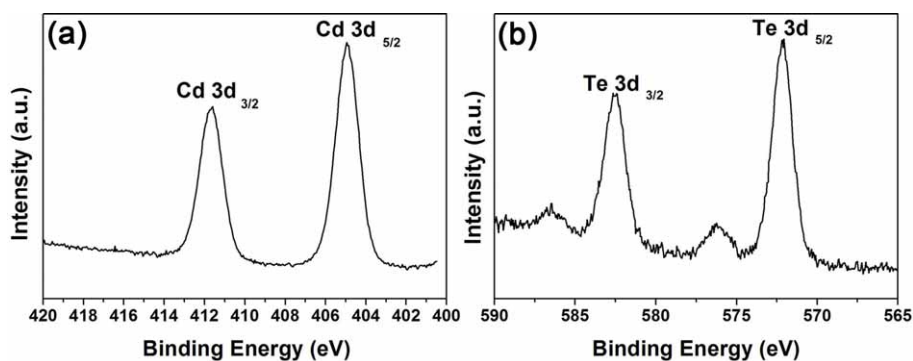


Fig. S3 EDX spectrum of the CdTe NCs shown in Figure 2. The relative elemental molar ratio for Cd/Te is 3.6/1.0.

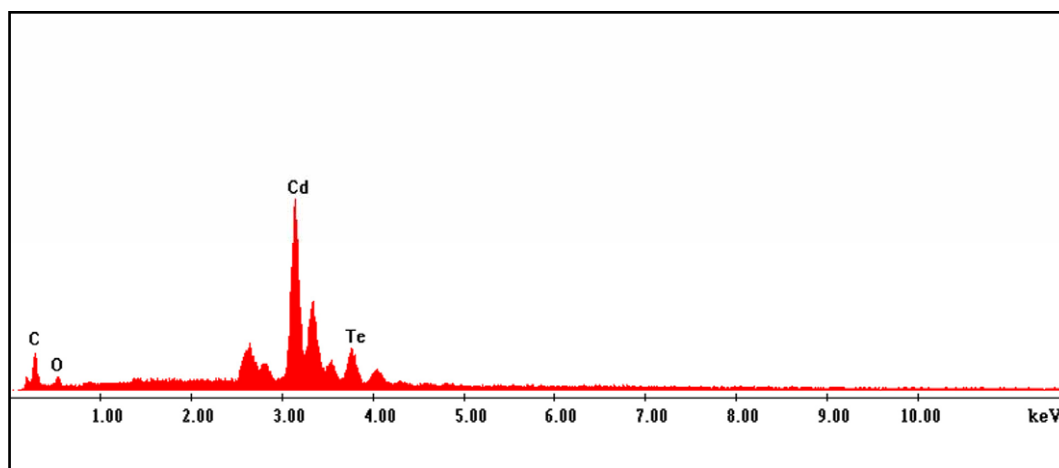


Fig. S4 UV-vis absorption spectrum of the 10.8 nm CdTe NCs shown in Figure 4a.

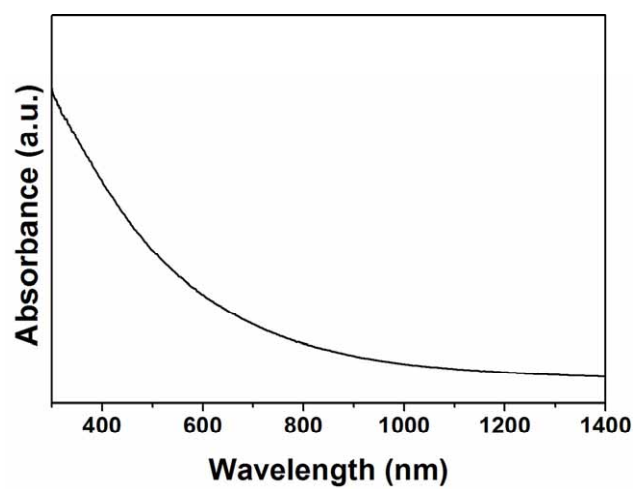


Fig. S5 (a) XRD pattern and (b) UV-vis absorption spectrum of the as-synthesized HgTe NCs shown in Figure 4b.

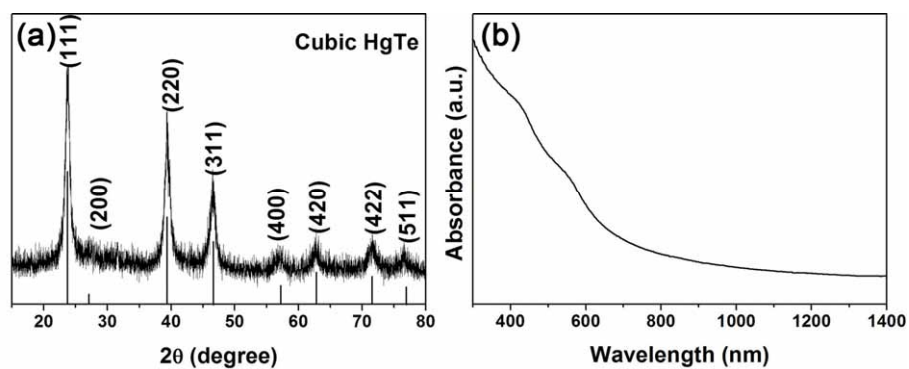


Fig. S6 (a) XRD pattern and (b) UV-vis absorption spectrum of the as-synthesized PbTe NCs shown in Figure 4c.

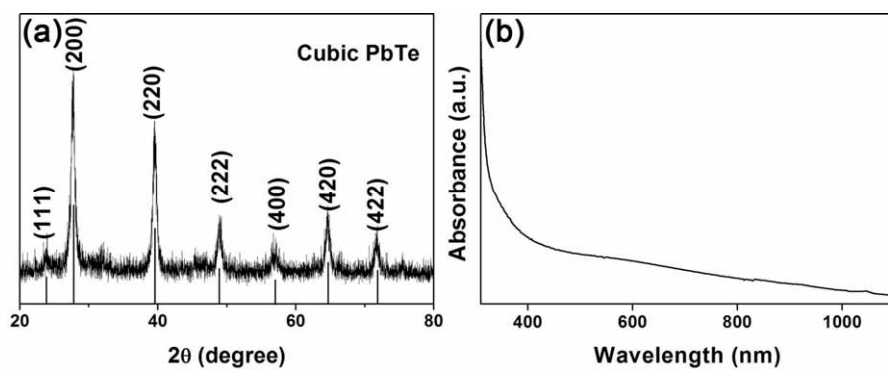


Fig. S7 (a) XRD pattern and (b) UV-vis absorption spectrum of the as-synthesized Ag_7Te_4 NCs shown in Figure 4d.

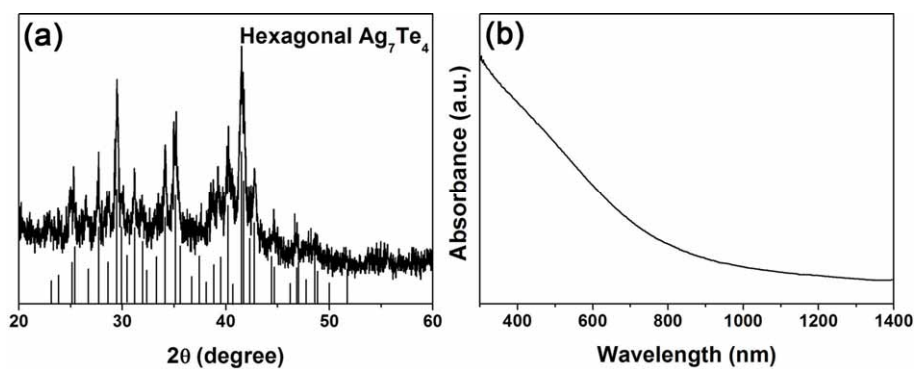


Fig. S8 EDX spectrum of the HgTe NCs shown in Figure 4b. The molar ratio of Hg/Te is 1.9/1.0.

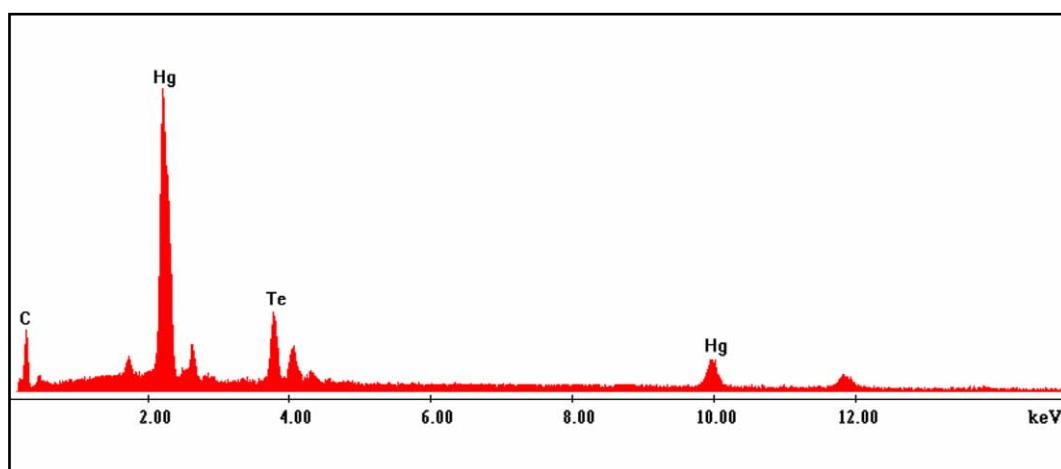


Fig. S9 EDX spectrum of the PbTe NCs shown in Figure 4c. The molar ratio of Pb/Te is 1.3/1.0.

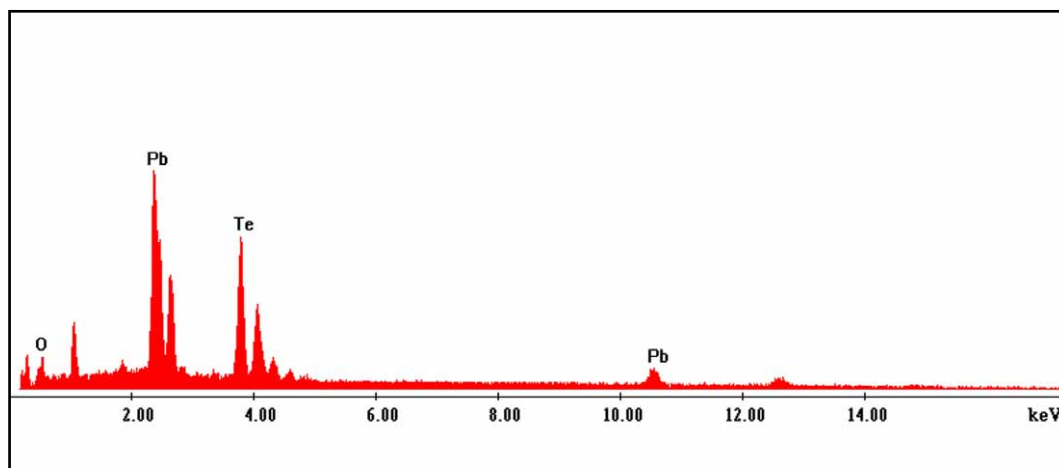


Fig. S10 EDX spectrum of the Ag₇Te₄ NCs shown in Figure 4d. The molar ratio of Ag/Te is 1.5/1.0.

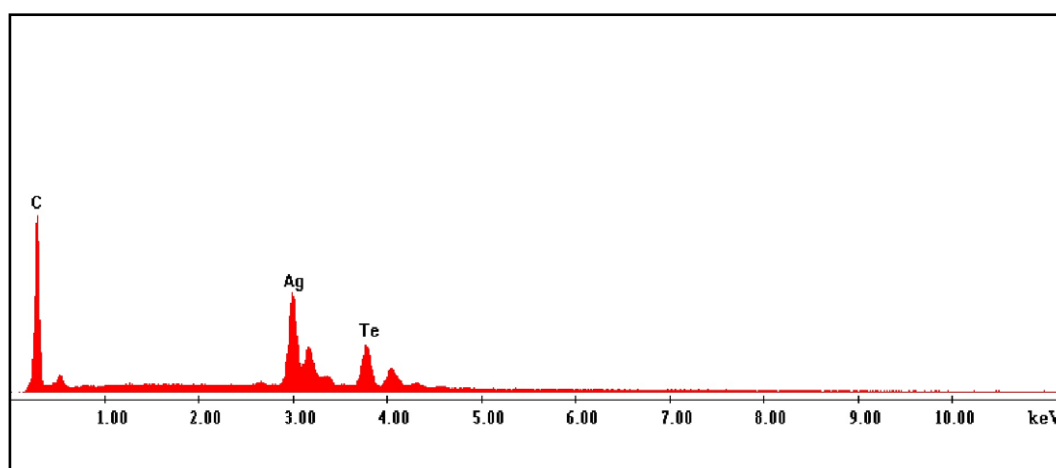


Fig. S11 J-V characteristics of the CdTe:P3HT photovoltaic device. The power conversion efficiency (PCE) is 0.1 %. The inset is the structure of CdTe:P3HT device.

