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Article

Size- and Shape-Controlled Synthesis of CdTe and PbTe Nanocrystals Using Tellurium Dioxide as the Tellurium Precursor

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We have developed a new method for the synthesis of CdTe and PbTe nanocrystals by using TeO_2 with trioctylphosphine oxide as Te precursor. Using this method, uniform-sized CdTe nanocrystals are successfully synthesized without the use of any air-sensitive alkylphosphine. The monodispersity, size, and shape of as-synthesized CdTe nanocrystals are well-controlled using “green” chemicals at elevated temperatures; the photoluminescence emission of CdTe nanocrystals covers a wide range from 510 to 750 nm. Oleic acid has been chosen as the only ligand to achieve controllable synthesis of CdTe nanocrystals with not only different sizes covering from green to red emissions but also different crystal structures (wurtzite and zinc blende) and shapes (including spherical, tetrapod, dendrimer, and flower) by simply adjusting the injection and/or growth temperatures. PbTe nanocrystals with spherical and cubic shapes have also been synthesized successfully with this new tellurium precursor and they can easily self-assemble into two-dimensional ordered structures. Special attention has also been paid to the studies of the new molecular mechanisms involved in the formation of metal telluride nanocrystals.

Introduction

As important II−VI and IV−VI semiconductor materials, CdTe and PbTe attract increasing interest for both fundamental studies and various promising applications in the fields of biolabeling/bioimaging, solar cells, photonic crystals, and electroluminescent devices.[1−11] However, up to now, the widely used nonaqueous methods to synthesize high-quality metal tellurium nanocrystals have had to rely on air-free “glove box” manipulations because of the use of the following air-sensitive compounds as tellurium precursors: alkylphosphine (such as trioctylphosphine (TOP) and tributylphosphine (TBP)) with tellurium powder.[1−11] Such air-free manipulations substantially increase the complexity as well as the cost of the synthesis of metal-telluride nanocrystals.

Most recently, the Zou[12] and Mulvaney[13] groups reported the “green approach” phosphine-free (i.e., no TOP and TBP) synthesis of CdSe using elemental selenium as the chalcogenide precursor dispersed in paraffin liquid or 1-octadecene (ODE). More and more researchers are now integrating green chemistry principles into their synthetic approaches for green nanoproducts by using green starting materials. But all these works are still limited to the synthesis of phosphine-free metal selenide nanocrystals including CdSe[12−20] and ZnSe,[21,22] there is still no report on the phosphine-free synthesis of metal telluride nanocrystals due to limited solubility of Te in noncoordinating

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solvents. The demand for high-quality, low-cost CdTe and PbTe nanocrystals has been increased and inspired researchers to develop various new synthesis routes by both aqueous and nonaqueous procedures.

Herein, we report a simple innovative method to synthesize high-quality metal telluride (CdTe and PbTe) nanocrystals using TeO_2 with trioctylphosphine oxide (TOPO) as tellurium precursor (see Scheme S1 in the Supporting Information). To the best of our knowledge, this is the first time not only for the use of TeO_2 as tellurium precursor but also for the elimination of TBP or TOP as solvent to make tellurium precursor. Even though Te and Se have similar chemical reactivity, it has been found that Te powder can not be dissolved using similar method to dissolve Se in ODE.[13,19] As an alternate route, TOPO was chosen to make Te precursor directly. Therefore, this method is much greener than the phosphine related synthesis of metal telluride. "Greener" here means the elimination of TBP or TOP in the entire reaction. We found indeed that Te precursor could be prepared by directly heating a mixture of TeO_2 and TOPO (90% purity) at elevated temperature, which was then used as the reaction solution for the synthesis of CdTe and PbTe nanocrystals. As-synthesized CdTe nanocrystals have reached the same high quality level compared with the method using Te-TBP or Te-TOP as precursors.[2,5] The parameter window was found to be much broader, highly monodisperse CdTe nanocrystals were synthesized successfully even when the reaction temperature was set to as low as 180 °C. During the entire reaction, photoluminescence (PL) emission was between 510 and 750 nm and PL full width at half-maximum (fwhm) was well-controlled between 28 and 35 nm. And different from previous methods, oleic acid was used as the only ligand for the synthesis of CdTe nanocrystals. The resulting nanocrystals exhibit not only different sizes with optical emission spectra covering from green to red, but also different crystal structures (wurtzite and zinc blende) and shapes (e.g., spherical, tetrapod, dendrimer, and flower) by simply adjusting the injection and/or growth temperatures. PbTe nanocrystals have also been synthesized successfully with this new tellurium precursor and they can easily self-assemble into two-dimensional ordered structures.

Experimental Section

Chemicals. Cadmium oxide (CdO, 99.998%), cadmium acetate ($Cd(Ac)_2 \cdot 2H_2O$, 99.999%), tri-*n*-octylphosphine oxide (TOPO, 90% (batch S47373, product 223301) and 99% (batch 04028DJ, product 346178)), Tellurium dioxide (TeO_2, 99.995%), decanoic acid (DA, 99%), oleic acid (OA, 90%), octadecylamine (ODA), and oleylamine (OAm, 70%) were purchased from Aldrich. 2,4-Pentanedione (98%), triethylamine (99%), hexanes (analytical grade), methanol (analytical grade), ethanol (analytical grade), lead chlorides ($PbCl_2$, analytical reagent), and paraffin oil (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China. All reagents were used as received without further experimental purification.

Synthesis of Lead Acetylacetonates [$Pb(acac)_2$]. In a typical synthesis, 20 mmol of $PbCl_2$ was dissolved in 10 mL of deionized water. Under magnetic stirring, 2,4-pentanedione (5 mL, 50 mmol) was added and kept stirring for 15 min. $Pb(acac)_2$ was precipitated after appropriate amount of triethylamine was added in the solution. $Pb(acac)_2$ was then washed several times with ethanol and water and finally was dried in vacuum at 50 °C for further use.

Stock Solutions for Cd and Te Precursors. Solution for Cd precursor I: A mixture (10 mL) of CdO (0.256 g, 2 mmol), oleic acid (8 mmol, 2.256 g), and 7.5 mL paraffin oil was loaded in a 25 mL three-necked flask and heated to 240 °C under nitrogen to obtain a colorless clear solution. Solution for Cd precursor II: A mixture (10 mL) of CdO (0.256 g, 2 mmol), decanoic acid (8 mmol, 1.378 g), and 8.5 mL paraffin oil was loaded in a 25 mL three-necked flask and heated to 240 °C under nitrogen to obtain a colorless clear solution. Te precursor: TeO_2 (0.3192 g, 2 mmol) and 40 g of TOPO (90% purity) were loaded in a 100 mL three-necked flask and degassed for 30 min; the mixture was heated to 280 °C under nitrogen, and then maintained for 30 min and subsequently heated to 380 °C for another 5 h. During this time, the color of the mixture changed from dark to light yellow (see Figure S6 in the Supporting Information). The temperature of Te precursor was then maintained at 60 °C for future use.

Syntheses of CdTe and PbTe Nanocrystals. *Synthesis of Spherical-Shaped CdTe Nanocrystals at 280 °C.* Four grams of Te precursor and 2 g of paraffin oil was heated to 280 °C under nitrogen flow in a 25 mL flask. Next, 1 mL Cd precursor I (0.2 mmol) stock solution was injected and temperature was lowered to 260 °C for nanocrystal growth. At 10 min of reaction time, the second injection solution (a mixture of 2 g of Te precursor and 1 mL of Cd precursor I) was slowly injected into the reaction flask dropwise. At 30 min, the third injection solution (a mixture of 4 g of Te precursor and 2 mL of Cd precursor I) was slowly injected into the reaction flask dropwise again.

Synthesis of Spherical-Shaped CdTe Nanocrystals with ODA at 180 °C. Four grams of Te precursor, 2 g of paraffin oil, and 0.5 g of ODA were heated to 180 °C under nitrogen flow in a 25 mL flask. Next, 1 mL of Cd precursor II (0.2 mmol) stock solution was injected and the temperature was maintained at 180 °C for nanocrystal growth.

Synthesis of Tetrapod-Shaped CdTe Nanocrystals at 320 °C. Four grams of Te precursor and 2 g of paraffin oil were heated to 320 °C under nitrogen flow in a 25 mL flask. Next, 1 mL of Cd precursor I (0.2 mmol) stock solution was injected and the temperature was maintained at 300 °C for nanocrystal growth.

Synthesis of Dendrimer-Shaped CdTe Nanocrystals at 350 °C. Four gram Te precursor and 2 g of paraffin oil was heated to 350 °C under nitrogen flow in a 25 mL flask. Next, 1 mL of Cd precursor I (0.2 mmol) stock solution was injected and temperature was maintained at 320 °C for nanocrystal growth.

Synthesis of Flower-Shaped CdTe Nanocrystals at 220 °C. Four gram Te precursor 4 and 2 g paraffin oil was heated to 220 °C under nitrogen flow in a 25 mL flask. Next, 1 mL Cd precursor I (0.2 mmol) stock solution was injected and temperature maintained at 200 °C for nanocrystal growth.

Synthesis of Spherical-Shaped PbTe Nanocrystals. $Pb(acac)_2$ (0.081 g, 0.2 mmol), 0.2 mL OA, 0.6 mL OAm and 4 mL Te precursor were combined in paraffin oil (5.2 mL) and heated to 150 °C under a nitrogen flow. The reaction was stopped after 1 h and spherical-shaped PbTe nanocrystals were synthesized.

Synthesis of Cubic-Shaped PbTe Nanocrystals. $Pb(acac)_2$ (0.081 g, 0.2 mmol), 0.2 mL OA, 0.2 mL OAm and 4 mL Te precursor were combined in paraffin oil (5.2 mL) and heated to 180 °C under a nitrogen flow. The reaction was stopped after 1 h, and cubic-shaped PbTe nanocrystals were synthesized.

Characterization. UV−vis absorption and PL spectra were recorded using an Ocean Optics spectrophotometer (mode PC2000-ISA). PL spectra were taken using an excitation wavelength of 365 nm. PL quantum yields (QYs) of nanocrystals were measured relative to coumarin 540 (QY = 78% in ethanol) and Rhodamine 6G (QY = 95% in methanol). All the QY data of nanocrystals and dyes were collected through SPEX F212. The optical density (OD) values of the nanocrystal samples at the excitation wavelength were in the range of 0.02−0.05. The nanocrystal PL QYs were calculated using the following formula

$$QY_{NC} = QY_{dye}\left(\frac{I_{NC}}{I_{dye}}\right)\left(\frac{n_{NC}}{n_{dye}}\right)^{2}\left(\frac{1-10^{-OD_{dye}}}{1-10^{-OD_{NC}}}\right)$$

where I was the spectrally integrated emission intensity, n was the refractive index, and OD was the optical density of the nanocrystal (NC) or the dye sample (indicated by a subscript).[23] X-ray diffraction (XRD) studies of nanocrystals were carried out with a Philips X' Pert Pro X-ray diffractometer using Cu Kα radiation (wavelength = 0.154 nm). The specimens were prepared as follows: about 20 mg of the purified nanocrystals was dissolved in 0.5 mL of toluene and dropped on a low-scattering quartz sample-holder, it was then dried in air and kept overnight in a vacuum desiccator. To get a better signal-to-noise ratio, we collected the XRD data at a scan rate of 16 s with 0.2° per step. Transmission electron microscopy (TEM) studies were performed using a JEOL-100 CX II microscope operating at 100 kV and JEOL JEM-2010 electron microscope operating at 200 kV. A Bruker AVANCE 400 MHz spectrometer was used to do ^{31}P NMR analysis and identify the chemical composition of Te precursors. For standard measurement, about 50 mg of sample (TOPO, 99% purity, TOPO 90% purity, or TOPO-Te complex) was dissolved in $CDCl_3$ (~ 0.8 mL) to collect ^{31}P NMR spectra.

Results and Discussion

Even though Te and Se have similar chemical reactivity, it has been found that Te can not be dissolved using similar method to dissolve Se in ODE.[22] Thereby, as an alternate route, TOPO has been chosen to test whether it can be used to make Te precursor directly without the use of air-sensitive TOP or TBP. We discover a new method in which Te precursor can be prepared by directly heating a mixture of TeO_2 and TOPO. In this new method, TeO_2 powder was directly dissolved in 90% purity TOPO at elevated temperature, which was then used as the reaction solution for the synthesis of CdTe.

Figure 1a shows the absorption and PL spectra of as-synthesized CdTe nanocrystals when injection and growth temperatures were kept at 280 and 260 °C, respectively. The PL peak positions cover from 510 to 750 nm in the entire reaction. Without any size sorting, all UV−vis and PL spectra of as-synthesized CdTe nanocrystals as shown in Figure 1a are comparable to the best optical spectra of CdTe nanocrystals that were obtained through alternative methods by using Te-TBP or Te-TOP as Te precursors.[2,5] Typical PL FWHMs of these as-synthesized CdTe nanocrystals are between 28 and 35 nm and the absorption spectra have up to four absorption peaks from nucleation to the end of the reaction, indicating the narrow size distributions. Indeed, transmission electron microscopy (TEM) studies show that these nanocrystals have a size deviation of approximately 5% (Figure 1b−d). Based on this method, high quality CdTe nanocrystals with an approximate size range of 3−8 nm can be synthesized. The absorption peak position and the average sizes of as-synthesized samples are illustrated in the Supporting Information (Figure S1). The typical PL QYs of these nanocrystals range from 20 to 70%. The QYs are generally lower if CdTe nanocrystals are ultrasmall (3 nm) or large (7.2 nm). The highest PL QYs of those CdTe nanocrystals are obtained in the middle of the reaction (Figure 2).

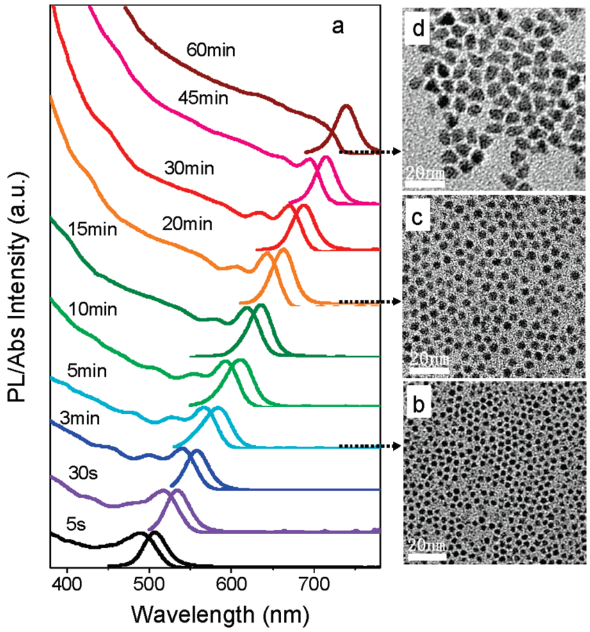

Figure 1. (a) Temporal evolution of the UV−vis absorption and photoluminescence spectra of as-synthesized CdTe nanocrystals. TEM images of CdTe nanocrystals with an average diameter of: (b) 3.4 , (c) 4.5, and (d) 8.6 nm. The relative standard deviation of particle size is ca. 5% and the corresponding optical spectra are indicated by dashed arrows.

Note that the above Cd injection method is different from traditional injection method (i.e., the solution with Cd precursor usually acts as the reaction solution), so this method is termed as "inverse injection method".[20] The reason to use this "inverse injection method" is because the solubility of TeO_2 in TOPO is generally not as high as $Cd(OA)_2$ complex in paraffin oil. But the amount of Cd precursors injected into the reaction solution can be highly concentrated to a small volume. Using such "inverse injection method", large scale synthesis of momodisperse CdTe nanocrystals can be conducted successfully by injecting small volume of concentrated Cd precursor into large volume of solution containing a large amount of Te precursor. This work may provide an essential process for a simple and large production of size- and shape-controlled CdTe nanocrystals.

In this new synthesis, TeO_2 needs to be reduced to an active form, such as Te, before the formation of CdTe nanocrystals. To test this hypothesis, we conducted the reactions between TeO_2 and 90% and 99% purity TOPO. Under N_2, the mixture of TeO_2 and TOPO was heated to

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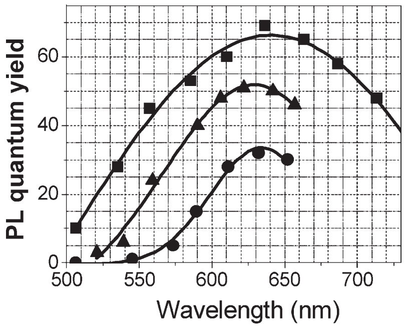

Figure 2. Photoluminescence quantum yield vs the PL peak positions for as-prepared CdTe nanocrystals at different reaction conditions. Including OA as the ligand and injection at 280 °C (squares); DA as the ligand and injection at 180 °C with ODA (triangles); DA as the ligand and injection at 220 °C (dots).

Scheme 1. Proposed Mechanism for the Formation of Te by the Reaction of TOPO with TeO_2

$$2TOPO + TeO_2 \xrightarrow{\Delta} 2ODOP + Te$$

280 °C first and then maintained for 30 min. During this process, the color of the mixture changed from white to black and TeO_2 in TOPO at high-temperature gave simple substance of Te along with *n*-octyl-di-*n*-octylphosphinate (ODOP) (Scheme 1).

The generation of the simple substance of Te was identified by XRD (Supporting Information, Figure S2) and the formation of ODOP was identified by ^{31}P NMR (Figure 3).[24] This is the first example of providing a pure Te source from TeO_2 and it can be used to synthesize CdTe nanocrystals. Subsequently, the solution was heated to 380 °C and maintained for 5 h. The color of the mixture changed from black to light yellow (see the Supporting Information, Figure S3). It was found that the Te generated from TeO_2 was more soluble in a "bad" TOPO (90% purity) in comparison with a "good" TOPO (99% purity). Recently, the impurities in TOPO have been demonstrated to influence the quality, morphology, and growth kinetics of nanocrystals.[24,25] Buhro and co-workers analyzed the impurities present in commercially TOPO and introduced di-*n*-octylphosphinic acid (DOPA) was the essential impurity and ligand for the synthesis of high-quality CdSe quantum wires.[24,25] In the ^{31}P NMR of TeO_2 and 90% purity TOPO, the existence of a high amount of DOPA has been observed. Therefore, such DOPA may be used as ligand to form Te-DOPA complex and caused Te to dissolve in TOPO finally. Because TOPO and TeO_2 have high chemical stability in air, this new method does not require the use of glove box operation.

When using TeO_2 as tellurium source and TOPO as solvent to make Te precursor, the parameter window for the growth of high-quality CdTe nanocrystals is found to be much broader than that to synthesize the corresponding CdTe nanocrystals with the use of Te-TBP/Te-TOP precursors. Absorption and PL spectra are used to assess the quality of CdTe nanocrystals synthesized through reactions with 320 or 240 °C as the injection temperature, respectively (see the Supporting Information, Figure S4). It is clearly indicated that nucleation efficiency at 320 °C is higher than that at 280 °C; the first absorption peak is located at 488 nm when the reaction lasts 5 s and PL fwhm is 32 nm (see the Supporting Information, Figure S4a). The first exitonic absorption peak for sample extracted at the initial 5 s of 320 °C is blue-shifted for about 3 nm compared to which obtained with 280 °C as the injection temperature and this maybe an evidence that more nuclei are formed at 320 °C than at 280 °C. Absorption and PL spectra are red-shifted as the reaction continues and FWHMs decrease further and are kept between 28 and 34 nm throughout the whole reaction as PL covering from 510 to 660 nm (see the Supporting Information, Figure S4a inset). Figure S4b shows the time evolution profile of the absorption and PL spectra of CdTe nanocrystals synthesized at 240 °C, it is noticed that the reaction went slow in the early stage of the reaction. No absorption and PL peaks are observed when the reaction last only 10 s, absorption peak begins to show up at 513 nm after reaction lasts 1 min, but its PL is still weak. Then, absorption and PL turn stronger after 3 min. The absorption peak turns sharper as the reaction lasts longer, the PL covers from 530 to 675 nm and FWHMs are controlled between 30 and 35 nm in the whole reaction (see the Supporting Information, Figure S4b inset). But the QYs of as-synthesized CdTe nanocrystals are very weak, below 10%.

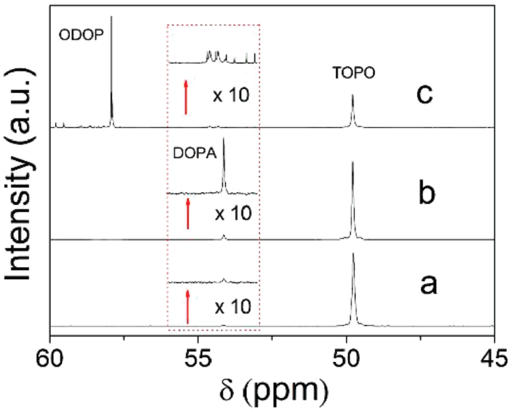

Figure 3. Representative ^{31}P NMR spectra (in $CDCl_3$) of (a) TOPO (99%, Aldrich, batch S47373, product 223301); (b) TOPO (90%, Aldrich, batch 04028DJ, product 346178); and (c) Te-TOPO (90%).

It is well-known that fatty acid with short chain generally has more activity than that with long chain,[26,27] such as decanoic acid (DA) is more active than OA. To further test whether high quality CdTe could be synthesized at a lower temperature, OA was replaced by DA to make Cd precursor ($Cd(DA)_2$). The promising results indicated that monodisperse CdTe nanocrystals still could be synthesized even when the temperature was as low as 220 °C. This could be explained in the terms of the steric repulsion from acid chain. Te precursor generated from TeO_2 easily

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attacked $Cd(DA)_2$ than $Cd(OA)_2$, so CdTe nanocrystals were synthesized successfully even at 220 °C. Because of the slow initial reaction speed, there was almost no detectable PL when the reaction only lasted 5 s (see the Supporting Information, Figure S5a). PL first began to appear after the reaction lasted 10 s, but the overall QYs were still below 30% (Figure 2). It did not show too much QY improvement comparing with the use of $Cd(OA)_2$ precursor, even though the reaction temperature was successfully lowered to 220 °C.

The activation of cadmium or zinc precursor (cadmium or zinc fatty acid salts) by alkylamines is a widely used way to synthesize high-quality CdSe or ZnSe nanocrystals with high QYs.[27,28] Octadecylamine (ODA) has therefore been chosen to aid the synthesis of high QY CdTe nanocrystals at low temperature. By only addition of 0.5 g of ODA, the reaction speed became faster at 220 °C and the reaction solution turned into black sooner. A PL peak at 573 nm has been observed when reaction only lasts 5 s and PL only shifted to 625 nm eventually (see the Supporting Information, Figure S5b). In the presence of alkylamine, it coordinated a good Lewis base than TOP or TOPO,[29] the decarbonylation of $Cd(DA)_2$ was faster through the reaction between alkylamine and Te precursor and the conversion to CdTe nanocrystals happened instantly. So ODA can act a role to activate reaction and more nuclei formed immediately after the injection of Te precursor. By keeping every condition the same and only lower the injection temperature to 180 °C, it was found that the reaction went slow in the early stage of reaction, which was confirmed by very weak absorption and PL spectra of samples underwent only the first 5 s of reaction (see the Supporting Information, Figure S6). Both absorption and PL turned stronger after 30 s of the initial injection. PL went stronger after the reaction lasted several minutes and the QYs increased for about 6 times from 10 s ($QY \approx 6\%$) to 5 min ($QY \approx 40\%$) (Figure 2). The absorption peak turned sharper as the reaction lasted longer and the PL covered from 520 to 660 nm. But if every condition was kept the same and only the injection temperature was increased to 240 °C, tetrapod-shaped CdTe nanocrystals were synthesized (see the Supporting Information, Figure S7).

Generally speaking, the final crystal structure of the nanocrystals is intensively dependent on the growth temperature. Higher temperature generally leads to a wurtzite structure.[30] XRD patterns of nanocrystals synthesized at different reaction temperatures are shown in Figure 4 for comparison. It can be seen that zinc blende CdTe (JCPDS, 75−2086) is formed when the temperature is lower than 220 °C, whereas wurtzite CdTe (JCPDS, 19−0193) is formed when the temperature is higher than 280 °C. These results indicated that the temperature was a main factor for the formation of final crystal structure if only fatty acid was used as ligand. The top diffraction pattern shown in Figure 4a is in agreement with those from bulk CdTe with zinc-blende structure. Three obvious diffraction peaks located at 24.0, 39.7, and 46.4 degrees are corresponded to the (111), (220), and (311) planes of zinc blende CdTe. As shown in Figure 4b, it fits well with a wurtzite structure with one stacking fault perpendicular to the *c*-axis. This single stacking fault significantly varies the diffraction pattern of the sample from a standard pattern. For example, the (103) diffraction peak is significantly broader than that of the adjacent (110) and (200) peaks, although the integrated area of (103) matches reasonably well with the expected intensity.[5] In fact, for CdTe, the wurtzite structure is the thermodynamically stable phase, so a high temperature is suitable for its formation and good crystallization.

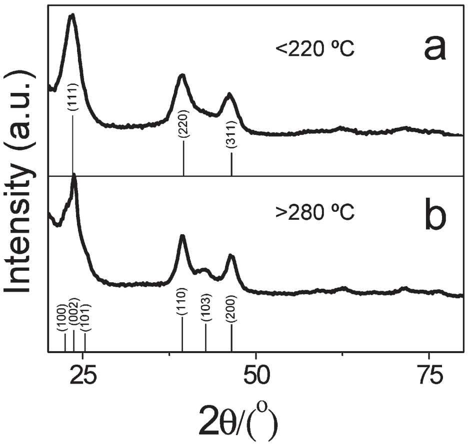

Figure 4. XRD patterns of as-synthesized CdTe nanocrystals formed at different temperatures.

It is well-known that the use of different ligands can play critical roles during the synthesis of nanocrystal and affect nanocrystal's structure, shape, size distribution, and stability.[5−7,31] For instance, octadecylphosphonic acid (ODPA) is a "must-have" ligand for the synthesis of small sized CdTe nanocrystals with green emissions.[5] But by this new method, it is demonstrated that different shaped CdTe nanocrystals can be simply controlled synthesized by adjusting the reaction temperature when only OA is chosen to make Cd precursor. Thereby, this method is demonstrated to be different from all previously reports by which different size or shape of CdTe nanocrystals have to be obtained by selecting different ligands including ODPA, OA, eladic acid (EA), or thioglycolic acid (TGA), etc.[5,7] TEM and HRTEM images of CdTe nanocrystals synthesized under different temperatures are shown in Figure 5. Spherical-shaped CdTe nanocrystals with an average size of 5 nm are obtained at 280 °C. Once the reaction temperature is increased to 320 °C, tetrapod-shaped CdTe nanocrystals are synthesized. Dendrimer-shaped CdTe nanocrystals are observed if the temperature is further increased to 350 °C. If the reaction temperature is

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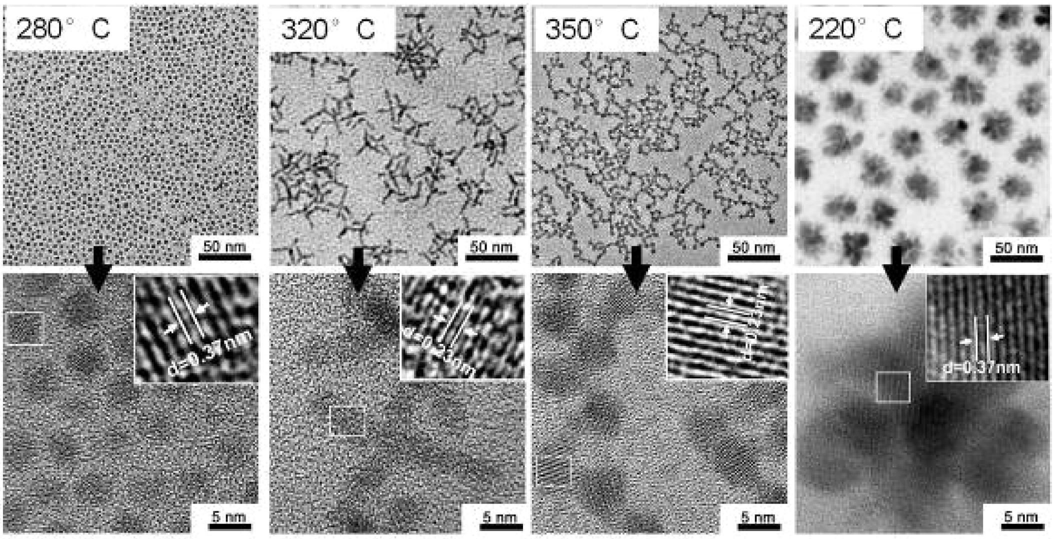

Figure 5. TEM and HRTEM images of CdTe nanocrystals synthesized at 280, 320, 350, and 220 °C, respectively.

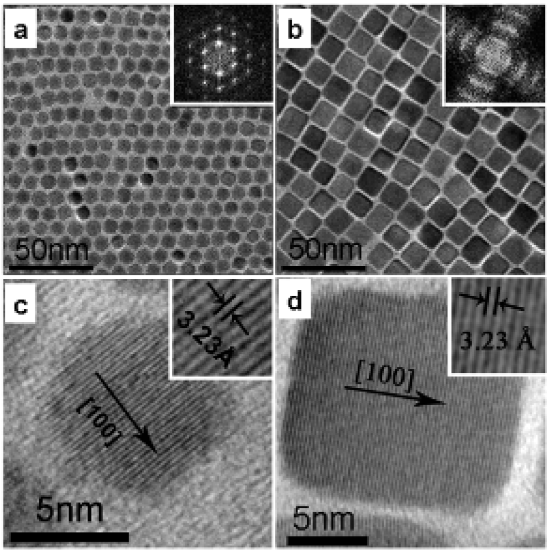

Figure 6. TEM image of (a) 8.2 nm spherical-shaped PbTe nanocrystals and (b) cubic-shaped PbTe nanocrystals with edge length between 14 and 18 nm, inset are corresponding FFTs. Corresponding high-resolution TEM (HRTEM) images of (c) a and (d) b.

decreased to 220 °C, monodisperse flower-shaped CdTe nanocrystals are synthesized.

Furthermore, this Te-TOPO based method has been extended to make PbTe nanocrystals. In the synthesis of PbTe nanocrystals, Pb(acac)$_2$ was used as the lead precursor. The resulting PbTe nanocrystals from a typical synthesis at 180 °C have a spherical morphology with an average diameter of 8.2 nm (Figure 6a). Cubic-shaped PbTe nanocrystals with edge length between 14 and 18 nm have been synthesized once the temperature was increased to 230 °C (Figure 6b). Both the spherical- and cubic-shaped PbTe nanocrystals show a good self-assembly behavior. The corresponding Fast Fourier Transforms (FFTs) are shown as insets in images a and b in Figure 6, respectively. HRTEM images shown in images c and d in Figure 6 indicate that the distances between adjacent lattice fringes are 3.23 Å, in accordance with the interplanar distances of (200) plane of face-centered-cubic (fcc) phase PbTe, and this implies the orientation of a basic [100] direction of these nanocrystals. The well-resolved lattice images represent a uniform particle with a highly ordered crystalline structure. The XRD pattern shown in Figure S8 in the Supporting Information confirms the cubic crystal structure of PbTe.

Conclusions

In summary, we have developed an innovative "green" and simple method for the syntheses of high-quality metal telluride nanocrystals by using TeO$_2$ with trioctylphosphine oxide as Te precursor and oleic acid as the only ligand. Using this method, uniform-sized CdTe and PbTe nanocrystals are successfully synthesized without the use of any air-sensitive alkylphosphine. The monodispersity, size, crystal structures (wurtzite and zinc blende), and shape (spherical, tetrapod, dendrimer, and flower) of as-synthesized CdTe nanocrystals are well-controlled using "green" chemicals through simply adjusting the injection and/or growth temperatures at elevated temperatures. The PL emission of CdTe nanocrystals covers a wide range between 510 and 750 nm. Spherical- and cubic-shaped PbTe nanocrystals have also been synthesized with this new tellurium precursor and they can easily self-assemble into two-dimensional ordered structures.

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Supporting Information Available: UV−vis, PL, TEM, and XRD of CdTe and PbTe nanocrystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.