materials proceedings

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Proceeding Paper

Study of Phosphine Tellurides as Precursors in the Synthesis of HgTe CQDs for IR Applications †

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† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net.

Abstract: In this work, we report the study of several phosphine tellurides in the preparation of HgTe CQDs. The efficient synthesis and characterization of HgTe CQDs were developed for the first time by applying Tris(dimethylamino)phosphine telluride in THF (TDMAPTe/THF) and mercury chloride ($HgCl_2$) precursors. The preparation was conducted by organometallic hot – injection route. Transmission electron microscopy (TEM), SAED analysis, X-ray photoelectron spectroscopy, UV-Vis-NIR spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), and Raman spectroscopy were employed in the characterization of obtained nanocrystals. The comparison between TDMAPTe/THF and TOPTe precursors revealed that the first one has a higher chemical reactivity. The band edge peak of the prepared nanocrystals using TDMAPTe/THF was at 1297 nm after 15 min of reaction time with narrow size distribution (FWHM~214 nm). The first absorption peak red-shifted to ~1336 nm after 60 min and no significant red-shift was observed far ahead.

Keywords: mercury telluride; colloidal quantum dots; Tris(dimethylamino)phosphine telluride (TDMAPTe); Tri-octylphosphine telluride (TOPTe)

Citation: Mardini, A.A.; Shuklov, I.A.; Razumov, V.F. Study of Phosphine Tellurides as Precursors in the Synthesis of HgTe CQDs for IR Applications. *Mater. Proc.* **2023**, *5*, x. https://doi.org/10.3390/xxxxx

Published: 5 May 2023

1. Introduction

Mercury telluride colloidal quantum dots are considered the ideal nanomaterial for infrared applications [1]. The nearly zero band gap energy of bulk mercury telluride and the quantum confinement effect allowed us to prepare HgTe CQDs with absorption that covers all infrared windows [2]. The importance of infrared technology was observed in several applications, such as medical imaging, infrared lasers, sensors, and detectors [2–4]. Tri-octylphosphine telluride (TOPTe) is the most common precursor used in the synthesis of HgTe colloidal quantum dots (CQDs) [5]. The weak stability of TOPTe towards dissociation compared to TOPS and TOPSe motivated scientists to explore new tellurium precursors [6]. Tris(dimethylamino)phosphine telluride $(Me_2N)_3PTe$ is a new tellurium precursor that was used in the synthesis of CdTe nanocrystals [6]. In this work, three new tellurium precursors which are $(Me_2N)_3PTe$, methyldiphenylphosphine telluride $Me(Ph)_2PTe$ and dimethylphenylphosphine telluride $(Me)_2PhPTe$ were examined in the synthesis of HgTe CQDs. Only TDMAPTe/THF succeeded. The efficiency of the prepared precursor was studied based on the comparison of its chemical reactivity with TOPTe. The position of the first excitonic peak and the mean size distribution of the obtained HgTe nanocrystals from both precursors were investigated as well.

2. Materials and Methods

2.1. Materials

Te (Sigma-Aldrich, St. Louis, MO, USA, 99.999%, pieces), Trioctylphosphine (ACROS, Pasadena, CA, USA, technical grade 90%), Tris(dimethylamino)phosphine (Sigma-Aldrich, 97%), Tetrahydrofuran (Sigma-Aldrich, ≥99.9%, anhydrous), Mercury (II) chloride (Honeywell/Fluka, ≥99.5%), 1-Dodecanethiol (Sigma-Aldrich, ≥98%), Tetrachloroethylene (Sigma-Aldrich, HPLC grade ≥ 99.9%), Methanol (Chimmed, Moscow, Russia, HPLC grade), Acetonitrile (MACRON, Paris, France, HPLC grade ≥ 99.8%). All chemicals were used as received. Oleylamine (ACROS, approximate C_{18} content 80–90%) was purified under vacuum at 70 °C for two hours to remove water and absorbed CO_2.

2.2. Methods

2.2.1. Preparation of Tellurium Precursors

A 1 M solution of Te dissolved in TOP was prepared by solvating 0.635 g (5 mmol) of Te powder in 5 mL (11 mmol) of TOP (M_w = 370.64 g/mol, d = 0.831 g/cm^3) at 90 °C. A yellow solution of TOPTe (2:1) was obtained [1,4,7,8]. In order to prepare a 0.5 M solution of Te solvated in TDMAP/THF, 0.3175 g (2.5 mmol) of Te powder and 0.7 mL (3.75 mmol) of tris(dimethylamino)phosphine TDMAP (M_w = 163.20 g/mol, d = 0.898 g/cm^3) were added to 4.3 mL of tetrahydrofuran (THF) into a Schlenk tube at 50 °C. A light yellow solution of TDMAPTe (1.5:1) in THF was synthesized.

2.2.2. Characterization of Tellurium Precursors

The characterization of TDMAPTe and TOPTe was performed using ^{31}P NMR spectroscopy. In the case of TOPTe, one signal at $\delta = -23.77$ ppm (solvent, C_6D_6) was observed, Figure 1a. It indicated that the precursor solution consisted of a mixture of TOPTe and TOP. The ability to detect the pattern of pure TOPTe in the existence of unreacted TOP was not available [5]. A signal for TOPO at $\delta = 43.8$ ppm (solvent, C_6D_6) was not shown [9]. For TDMAPTe, one pattern was shown at $\delta = 21.48$ ppm (solvent, C_6D_6) agreeing with the formation of TDMAPTe/TDMAP mixture in THF. No signals for pure TDMAPTe at $\delta = 58.8$ ppm (solvent, C_6H_6) or pure TDMAP at $\delta = 123$ ppm (solvent, C_6H_6) were detected [6,10], Figure 1b.

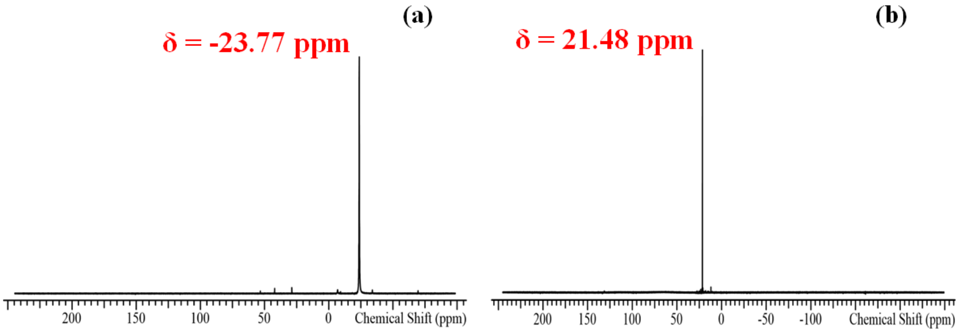

Figure 1. ^{31}P spectra of (**a**) 1 M TOPTe/TOP, (**b**) 0.5 M TDMAPTe/THF precursors in C_6D_6.

2.2.3. Synthesis of Mercury Telluride Colloidal Quantum Dots

HgTe colloidal quantum dots (QDs) were prepared using the procedure mentioned in the references [1,4,7,8,11,12] with a slight modification. The samples were synthesized using the hot-injection route at 60 °C. The synthesis included using oleylamine solutions of mercury and tellurium precursors. 0.2 mmol of $HgCl_2$ dissolved in 6 mL of oleylamine at 100 °C for 1 h (solution A). 0.2 mmol of tellurium precursor resolved in 2 mL of oleylamine at 100 °C for 1 h (solution B). When the solutions cooled to 60 °C, reagent B was speedily inserted by syringe into solution A under Ar flow. At a specific time of reaction, a quenching solution consisting of 16 mL tetrachloroethylene (TCE), 3.1 mL 1-dodecanethiol (DDT), and 1.5 mL Tri-n-octylphosphine (TOP), was added to the previous solution and cooled to the room temperature using an ice bath.

The purification procedure was conducted as follows: 8 mL of methanol was added to 12 mL of the quantum dots solution. The mixture was centrifuged to isolate the precipitate. The obtained precipitate was re-dispersed in 4 mL of tetrachloroethylene (TCE) and 4 mL of acetonitrile was added. The centrifugate product was dried under Ar flow, re-dispersed, filtered using a 0.22 µm hydrophobic polytetrafluoroethylene syringe filter, and diluted to 2 mL using tetrachloroethylene (TCE).

2.2.4. Characterization of HgTe CQDs

The characterization of the obtained HgTe NCs was performed using UV-Vis-NIR spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The quantum confinement effect was observed in the N-IR spectra, Figure 2a,b, of prepared NCs through the red-shifting of the first excitonic peak to a longer wavelength when size increases [4,13,14]. In addition, infrared spectra of HgTe CQDs in TCE demonstrated that the chemical reactivity of TDMAPTe/THF is higher than that for TOPTe/TOP. The first excitonic peak of the synthesized quantum dots was ~1297 nm after 15 min of reaction time with narrow size distribution (FWHM~214 nm). A red-shifting occurred to ~1336 nm after 60 min but no considerable one was shown later, Table 1.

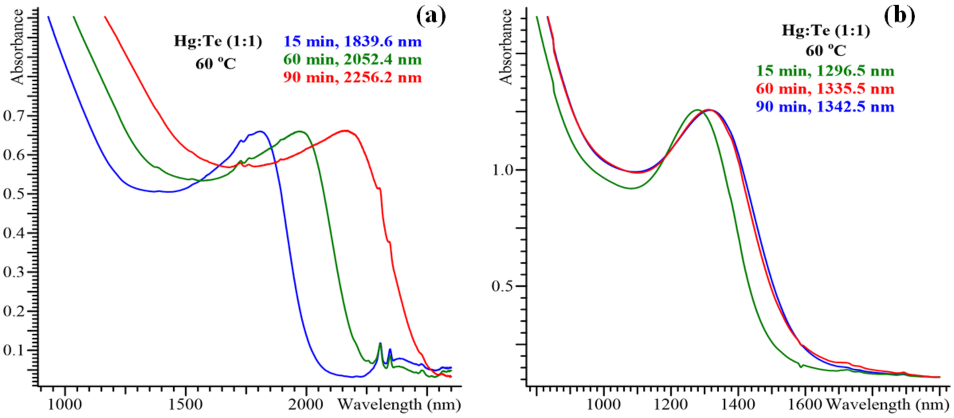

Figure 2. N-IR spectra of HgTe CQDs prepared using (**a**) 1 M TOPTe/TOP, (**b**) 0.5 M TDMAPTe/THF precursors.

Table 1. Investigation the chemical reactivity of tellurium precursors.

Precursor	**15 min**	**FWHM**	**60 min**	**FWHM**	**90 min**	**FWHM**
TDMAPTe/THF	1297	214	1334	241	1342	253
TOPTe/TOP	1840	335	2052	375	2256	425

Since HgTe CQDs are sensitive materials to the oxygen of the air, X-ray photoelectron spectroscopy (XPS) was used to determine the chemical structure of the prepared nanocrystals. The XPS spectrum, Figure 3a,b, revealed two spectral lines of $4f_{7/2}$, and $4f_{5/2}$ for Hg in HgTe at 100, 104 eV of binding energies. Another two peaks of $3d_{5/2}$, and $3d_{3/2}$ for Te in HgTe at binding energies of 573, 583 eV were observed [12,15]. No signals attributed to the heavy oxidation of Te^{-2} to Te^{+4} such as $HgTeO_3$ or TeO_2 (paratellurite) were shown. Raman spectroscopy was also used in order to identify the obtained nanocrystals. A thin film of mercury telluride CQDs on a glass substrate was prepared by employing a drop-cast route. The measurement was between 50–500 cm^{-1}. The observed phonon lines were as follows: A phonon of longitudinal acoustic (LA) at 88.31 cm^{-1}, A phonon of transverse optic (TO) at 116 cm^{-1}, two phonons of longitudinal optic (LO) at 136 cm^{-1} and at 259 cm^{-1} as a weak signal, Figure 3c. This result agreed well with the reference [7]. The investigation of the shell was conducted using Fourier-transform infrared spectroscopy (FT-IR). The measured FT-IR spectrum, Figure 3d in the 5000–1000 cm^{-1} revealed C–H stretching of methylene and methyl groups at 2955 cm^{-1}, 2922 cm^{-1}, and 2852 cm^{-1}. Methylene groups bending at 1467 cm^{-1}. No band of free thiol at 2595 cm^{-1} was observed [16].

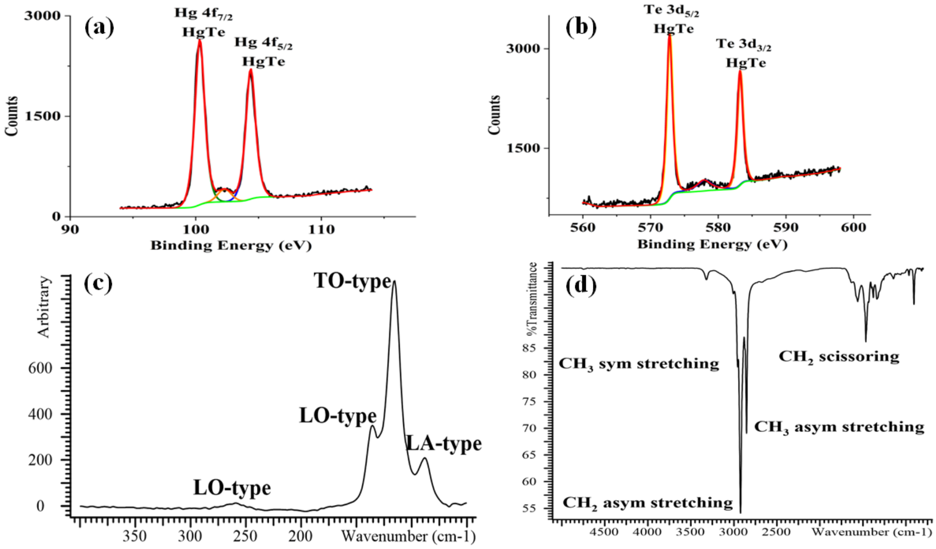

Figure 3. XPS (**a**,**b**), Raman (**c**) and FTIR (**d**) spectra of HgTe CQDs obtained using 0.5 M TDMAPTe/THF precursors.

The TEM image revealed that the synthesized HgTe CQDs have a sphere-shaped with mean size distribution of ~3 nm, Figure 4a,b. The analysis of selected-area electron diffraction (SAED) showed that the prepared HgTe nanocrystals have a tetragonal crystal structure with lattice planes of (020), (031) and (112) that matched well with Miller indices of HgTe (COD No. 96-152-3885) [17].

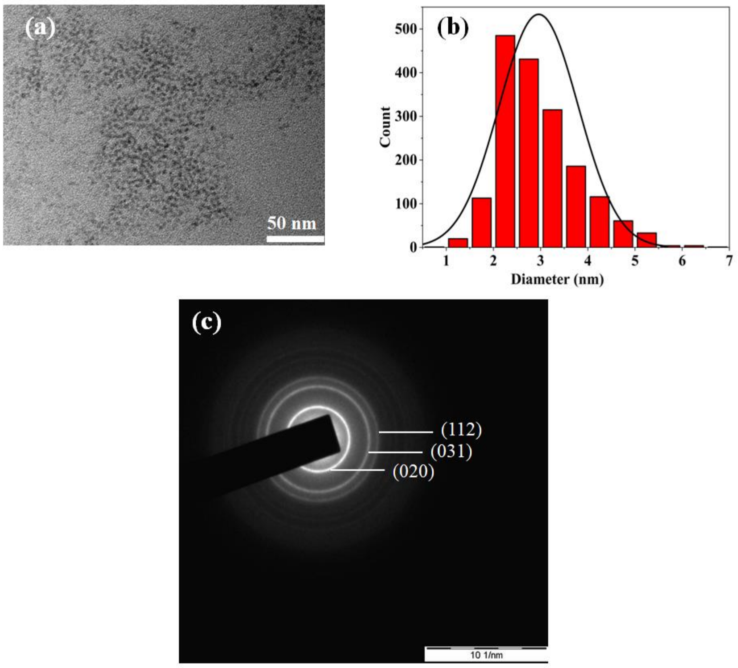

Figure 4. (**a**) TEM image, (**b**) size distribution histogram, (**c**) SAED pattern of HgTe CQDs synthesized using 0.5 M TDMAPTe/THF precursors.

3. Conclusions

The preparation of mercury telluride colloidal quantum dots using new tellurium precursors was presented. Among three phosphine-telluride precursors that were tested, only TDMAPTe/THF prospered. The higher chemical reactivity of TDMAPTe/THF compared to TOPTe allowed us to obtain small sizes of HgTe CQDs at the same empirical conditions. The first excitonic peak of the prepared NCs using TDMAPTe/THF was red-shifted by 50 nm in the N-IR window compared with 416 nm in the SW-IR window for TOPTe between 15–90 min of reaction time and temperature of 60 °C.

Author Contributions: A.A.M.: investigation, writing, review and editing. I.A.S.: methodology, investigation, review and editing. V.F.R.: supervision, review and editing. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data that support the findings of this study are available on request from the corresponding author.

Acknowledgments: The studies were supported by the Ministry of Science and Education of Russian Federation (Agreement № 075-03-2022-107/10 at 03.11.2022, Project № FSMG-2022-0034).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Keuleyan, S.E.; Guyot-Sionnest, P.; Delerue, C.; Allan, G. Mercury Telluride Colloidal Quantum Dots: Electronic Structure, Size-Dependent Spectra, and Photocurrent Detection up to 12 µm. *ACS Nano* **2014**, *8*, 8676–8682. https://doi.org/10.1021/nn503805h.
2. Kim, S.; Kim, T.; Im, S.H.; Seok, S.I.; Kim, K.W.; Kim, S.; Kim, S.-W. Bandgap engineered monodisperse and stable mercury telluride quantum dots and their application for near-infrared photodetection. *J. Mater. Chem.* **2011**, *21*, 15232–15236. https://doi.org/10.1039/C1JM12436F.
3. Kagan, C.R.; Lifshitz, E.; Sargent, E.H.; Talapin, D.V. Building devices from colloidal quantum dots. *Science* **2016**, *353*, aac5523. https://doi.org/10.1126/science.aac5523.
4. Keuleyan, S.; Kohler, J.; Guyot-Sionnest, P. Photoluminescence of Mid-Infrared HgTe Colloidal Quantum Dots. *J. Phys. Chem. C* **2014**, *118*, 2749–2753. https://doi.org/10.1021/jp409061g.
5. Shuklov, I.A.; Mikhel, I.S.; Nevidimov, A.V.; Birin, K.P.; Dubrovina, N.V.; Lizunova, A.A.; Razumov, V.F. Mechanistic Insights into the Synthesis of Telluride Colloidal Quantum Dots with Trioctylphosphine-Tellurium. *ChemistrySelect* **2020**, *5*, 11896–11900. https://doi.org/10.1002/slct.202002711.
6. Sun, H.; Wang, F.; Buhro, W.E. Tellurium Precursor for Nanocrystal Synthesis: Tris(dimethylamino)phosphine Telluride. *ACS Nano* **2018**, *12*, 12393–12400. https://doi.org/10.1021/acsnano.8b06468.
7. Goubet, N.; Jagtap, A.; Livache, C.; Martinez, B.; Portales, H.; Xu, X.Z.; Lobo, R.; Dubertret, B.; Lhuillier, E. Terahertz HgTe Nanocrystals: Beyond Confinement. *J. Am. Chem. Soc.* **2018**, *140*, 5033–5036. https://doi.org/10.1021/jacs.8b02039.
8. Livache, C.; Martinez, B.; Goubet, N.; Greboval, C.; Qu, J.; Chu, A.; Royer, S.; Ithurria, S.; Silly, M.G.; Dubertret, B.; et al. A colloidal quantum dot infrared photodetector and its use for intraband detection. *Nat. Commun.* **2019**, *10*, 2125. https://doi.org/10.1038/s41467-019-10170-8.
9. Chauzov, V.A.; Kostina, L.P. Alkylation In Situ of Arylphosphines Formed during Thermolysis of Hydrophosphoryl Compounds. *J. Gen. Chem. USSR* **1991**, *61*, 2181–2186.
10. Du Mont, W.W.; Kroth, H.J. Zur Reaktion von Organophosphien mit Chalkogenen und Halogenen Rasche Ubertragung von Tellurund Jod Zwischen Phosphinen. *J. Organomet. Chem.* **1976**, *113*, C35–C37.
11. Chu, A.; Martinez, B.; Ferre, S.; Noguier, V.; Greboval, C.; Livache, C.; Qu, J.; Prado, Y.; Casaretto, N.; Goubet, N.; et al. HgTe Nanocrystals for SWIR Detection and Their Integration up to the Focal Plane Array. *ACS Appl. Mater. Interfaces* **2019**, *11*, 33116–33123. https://doi.org/10.1021/acsami.9b09954.
12. Shen, G.; Chen, M.; Guyot-Sionnest, P. Synthesis of Nonaggregating HgTe Colloidal Quantum Dots and the Emergence of Air-Stable n-Doping. *J. Phys. Chem. Lett.* **2017**, *8*, 2224–2228. https://doi.org/10.1021/acs.jpclett.7b00775.
13. Brichkin, S.B.; Razumov, V.F. Colloidal quantum dots: Synthesis, properties and applications. *Russ. Chem. Rev.* **2016**, *85*, 1297–1312. https://doi.org/10.1070/rcr4656.
14. Im, S.H.; Kim, H.J.; Kim, S.W.; Kim, S.W.; Seok, S.I. Efficient HgTe colloidal quantum dot-sensitized near-infrared photovoltaic cells. *Nanoscale* **2012**, *4*, 1581–1584. https://doi.org/10.1039/c2nr11722c.
15. Kim, S.; Kim, T.; Im, S.H.; Seok, S.I.; Kim, K.W.; Kim, S.; Kim, S.-W. Bandgap engineered monodisperse and stable mercury telluride quantum dots and their application for near-infrared photodetection. *J. Mater. Chem.* **2011**, *21*, 15232–15236. https://doi.org/10.1039/c1jm12436f.
16. Nyquist, R.A. *Interpreting Infrared, Raman, and Nuclear Magnetic Resonance Spectra*; Academic Press: San Diego, CA, USA, 2001; Volume 2, pp. 65–83.

17. Grazulis, S.; Chateigner, D.; Downs, R.T.; Yokochi, A.F.T.; Quiros, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P.; Le Bail, A. Crystallography Open Database—An open-access collection of crystal structures. *J. Appl. Crystallogr.* **2009**, *42*, 726–729. https://doi.org/10.1107/S0021889809016690.