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PbTe colloidal nanocrystals: Synthesis, mechanism and infrared optical characteristics

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ABSTRACT

We report a rapid injection solution-phase synthesis route for the preparation of rock salt structure monodispered PbTe nanocrystals (NCs) in a non-coordinating solvent. In order to obtain uniform and monodispersed PbTe NCs, we rapidly inject an amount of 1-octadecene (ODE) to decrease the reactant temperature abruptly and separate the NC nucleation and growth efficiently. PbTe NCs are characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), and optical characteristics. PbTe NCs show large absorption tunability (>400 nm) by employing time-based strategies because of the strong quantum confinement. PbTe NCs also exhibit strong PL emission. The uniformity and characteristics of these PbTe NCs make them the material for IR devices.

1. Introduction

Due largely to their size-tunable optical properties that result from three-dimensional quantum confinement, colloidal semiconductor nanocrystals (NCs) have attracted significant attention in the past decades. The reason is as follows: research on nanodevices that make use of these properties can be divided into two distinct classes: point-contact devices that utilize a countable number of NCs, or large-area devices that utilize great numbers of NCs [1]. In both cases, the devices require highly tunable monodispersed NCs whose properties may be rationally designed. Therefore, it is critical to synthesize and study materials existing in the limit of strong-quantum confinement. Compared with many traditional II–VI and III–V materials, the IV–VI lead chalcogenide NCs have smaller band gaps and larger Bohr radius. Their band gaps can vary with size of NCs in the range from almost zero to 0.3 eV. The lead chalcogenide NCs enable unique optical, electrical and chemical properties, presenting this family of materials as a good candidate for potential application in solar cells, thermoelectric (TE) devices, telecommunication, field effect transistors (FET), photodetectors and photovoltaics [2–8].

PbTe NCs, with a larger Bohr radius ($\sim$46 nm) and lighter e^- and h^+ masses (0.22 and $0.24m_0$, respectively) than PbSe, have more potential applications in novel photoelectric devices because of their inter-band transitions in the IR region and multiple exciton generation [9,10]. In contrast to the many reports on the synthesis and characterization of PbS [2,4,8,11] and PbSe [12–15], PbTe NCs have received much less attention.

The solution-phase synthetic route utilizing organometallic precursors enables facile and reliable size tuning of monodispersed NCs by employing time-based strategies. Urban et al. [9] and Murphy et al. [10] have demonstrated in solution-phase synthesis of PbTe NCs respectively. Compared with their works, we consider that the nucleation and growth of PbTe NCs are effectively separated by swiftly decreasing reactive temperature and reducing solution concentration, which can be easily controlled and widely used to get monodispersed NCs conveniently.

This manuscript reports a rapid injection solution-phase synthesis route for the preparation of highly luminescent monodispersed PbTe NCs that have band gaps tunable throughout the near-infrared (NIR) by employing time-based strategies. We add an amount of the non-coordinating solvent (1-octadecene, ODE) and decrease the reactant temperature abruptly, which separates the NC nucleation and growth efficiently. This unique process of the ODE injection ensures uniform and monodispersed PbTe NCs. Specifically, this study also reports the absorption spectra, and photoluminescence (PL).

2. Experimental details

The synthesis of PbTe NCs includes preparation of precursors, nucleation, growth, isolation, and purification. The lead oleate precursor was synthesized in a single, three-neck flask. PbO (0.221 g) and oleic acid (0.878 mL) were dissolved

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in ODE (5.98 mL), and the mixture was heated to 130 °C for 0.5 h under Argon to obtain a lead oleate solution. The lead oleate solution was then heated to 180 °C. In the meantime, tellurium powder was dissolved in trioctylphosphine (TOP) at 70 °C to obtain a clear yellow/green solution. The resulting trioctyphosphine telluride (TOPTe) solution (1.00 mL, 0.500 M) was injected swiftly into the lead precursor solution to start nucleation under vigorous stirring. Several seconds later, ODE of equal volume was rapidly injected to end nucleation. The reaction mixture was subsequently maintained at 150 °C for several minutes and then promptly cooled to room temperature using a water bath to assure isolation and purification. When the temperature reached 30–40 °C, the crude solution was successively blended with mixture solvents of chloroform/hexane (1:1 by volume) and acetone/methanol (1:1 by volume) to quench PbTe NCs by centrifugation. The precipitated NCs were next re-dissolved in hexane/chloroform (1:1) and precipitated with acetone/methanol (1:1). Finally, the NCs were re-dispersed in tetrachloroethylene (TCE) for optical studies.

Based on the synthesis process, possible chemical reactions involved in the synthesis of PbTe NCs can be expressed as follows:

$$\mathrm{PbO} + 2\mathrm{CH_3(CH_3)_7CH:CH(CH_3)_7COOH} \rightarrow \mathrm{Pb[CH_3(CH_3)_7CH:CH(CH_3)_7COO]_2} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{C_{24}H_{51}P} + \mathrm{Te} \rightarrow \mathrm{C_{21}H_{51}PTe} \quad (2)$$

$$\mathrm{C_{24}H_{51}PTe} + \mathrm{Pb[CH_3(CH_3)_7CH:CH(CH_3)_7COO]_2} \rightarrow \mathrm{PbTe} + \mathrm{C_{24}H_{51}P} + 2\mathrm{CH_3(CH_3)_7CH:CH(CH_3)_7COO^-} \quad (3)$$

Phase composition of the samples was identified by a Rigaku D/max-2400 X-ray diffraction (XRD) using Cu Kα radiation. Transmission electron microscope (TEM), high-resolution TEM (HRTEM) and Selected area electron diffraction (SAED) images of PbTe NCs were taken using a JEOL JEM-3010 operated at 300 kV. Linear optical absorption spectra were measured by JASCO V-570 UV–vis spectrometer at room temperature. The photoluminescence emitted at a right angle relative to the excitation source was collected at the excitation wavelength (1064 nm) using a KDPL Nd: YAG laser.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD pattern of PbTe NCs prepared by the rapid injection solution-phase synthesis method. It clearly confirms the rock salt structure of PbTe NCs (JCPDS card No. 38-1435). The line broadening of the (2 0 0), (2 2 0) peaks and disappearance of other diffraction peaks indicates that PbTe NCs are small and not well crystallized. The crystalline structure of PbTe NCs obtained from the XRD patterns closely corresponds to the information obtained from the selected area electron diffraction (SAED) pattern with indexing of the main diffraction rings to PbTe.

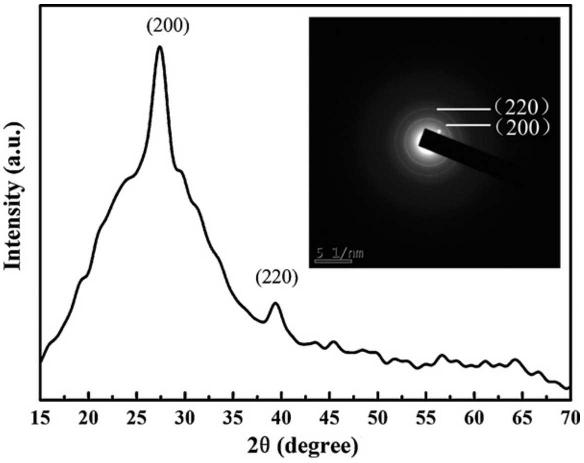

Fig. 1. XRD pattern of PbTe NCs synthesized via the rapid injection solution-phase synthesis method. Inset: the selected area electron diffraction (SAED) pattern of PbTe NCs with indexing of the main diffraction rings to PbTe.

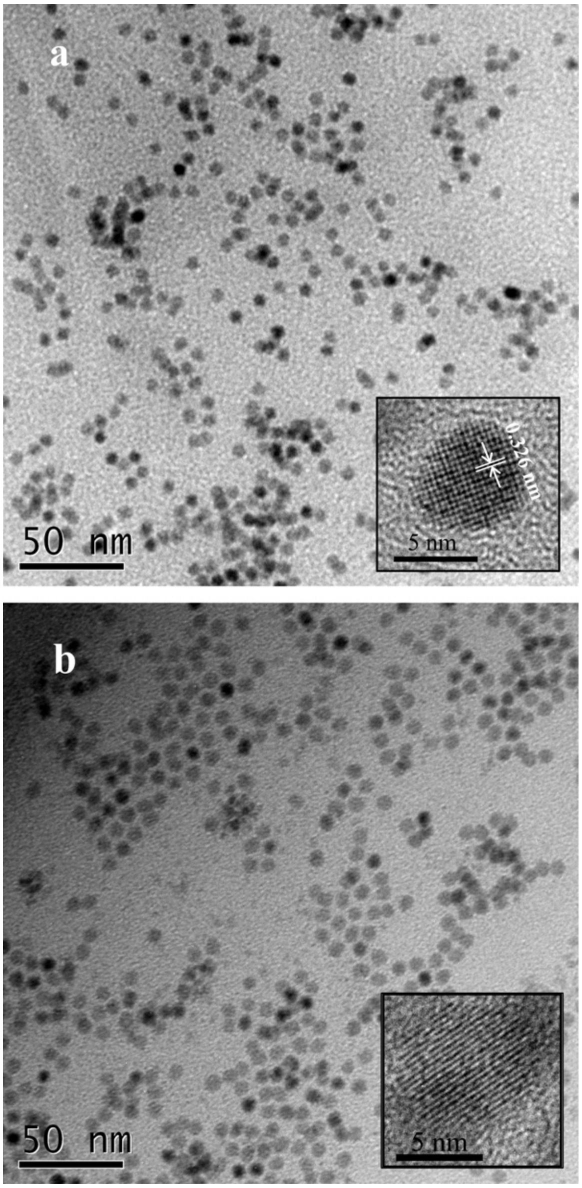

Fig. 2. Low-resolution TEM images of PbTe NCs of different absorption at (a) 1614 nm; (b) 1832 nm. The insets of (a) and (b) show representative high-resolution TEM (HRTEM) images of individual NCs from each of these samples.

3.2. Transmission electron microscope

The lead and tellurium precursors readily react and easily form PbTe NCs in the solution-phase synthesis process. Thus the key to prepare monodispersed PbTe NCs lies in controlling NC nucleation and subsequent growth. Urban et al. [9] and Murphy et al. [10] have found that the reactant temperature, stable ligands and growth solvent are crucial because they influence the reactivity of the monomers and aid in NC synthesis. Besides, we consider that the efficient separation of NC nucleation and growth is also essential to prepare monodispersed PbTe NCs. So we add amount of ODE and decrease the reactant temperature abruptly, which separates the NC nucleation and growth efficiently. This unique process of the ODE injection ensures uniform and monodispersed PbTe NCs.

As-prepared PbTe NCs are monodispersed, confirmed in Fig. 2a and b with TEM micrographs of two different sizes (6.5 and 7.5 nm). The monodispersed PbTe NCs are isolated from the crude product without size-selective precipitation, and those with average diameters of 6.5 and 7.5 nm have first excitonic absorption peaks centered

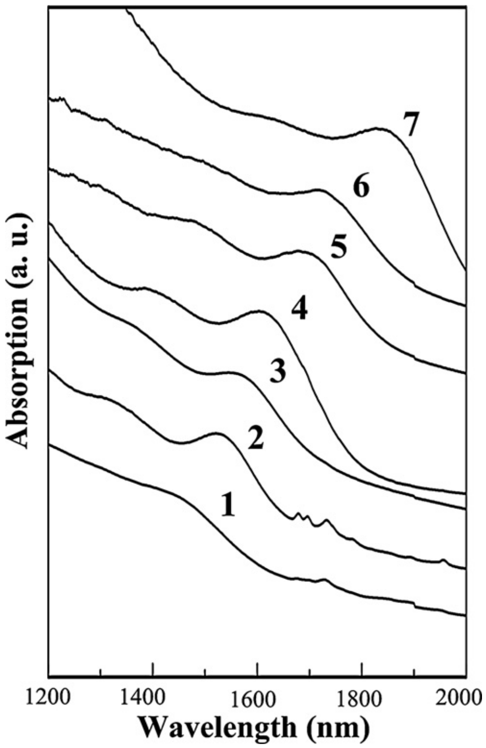

Fig. 3. Optical absorption spectra collected on PbTe NCs of different sizes. Spectra 1–7 are 1440, 1520, 1564, 1610, 1678, 1716, 1840 nm.

at wavelengths of 1614 and 1832 nm, respectively. The lattice spacing in HRTEM images (inset in Fig. 2b) is 0.326 nm, corresponding to the (2 0 0) plane of the crystalline cubic rock salt structure PbTe.

3.3. Absorption spectra

Fig. 3 shows room temperature absorption spectra recorded on seven different sizes of PbTe NCs dispersed in TCE. The first excitonic transition peaks of these samples demonstrate infrared optical characteristics with great blue-shift phenomena. The influence of strong-quantum confinement is evident in Fig. 3, in which large absorption tunability >400 nm is exhibited over small variation in PbTe NC diameters. We find that the first excitonic transition peak is broader in PbTe compared to that of the PbS [16] or PbSe [15]. The broadening is partially due to the large increase in the anisotropy [17]. Another reason may be that PbTe has stronger quantum confinement.

3.4. Photoluminescence spectra

Fig. 4 shows the room temperature absorption and photoluminescence spectra for PbTe NCs having absorption at 1590 nm and photoluminescence at 1610 nm. The shape of the intense PL peak indicates the emission is primarily band-edge. The small Stokes shift of the emission is attributed to surface state-induced trapping [18]. We note that the measured PL characteristic was found to depend on the excitation wavelength, which is related to the NC size distribution.

4. Conclusions

In conclusion, we report a rapid injection solution-phase synthesis route for the preparation of rock salt structure monodispered PbTe NCs in a non-coordinating solvent. Based on TEM observation, we consider that it is propitious to obtain uniform and monodispersed PbTe NCs by rapidly adding ODE which decreases the reactant temperature abruptly and separates the NC nucleation and growth efficiently. PbTe NCs show large absorption tunability (>400 nm) by employing time-based strategies, which means PbTe NCs have band gaps tunable throughout the NIR. NCs also exhibit strong PL emission. The excellent uniformity and characteristics of these PbTe NCs make them the material for IR device applications.

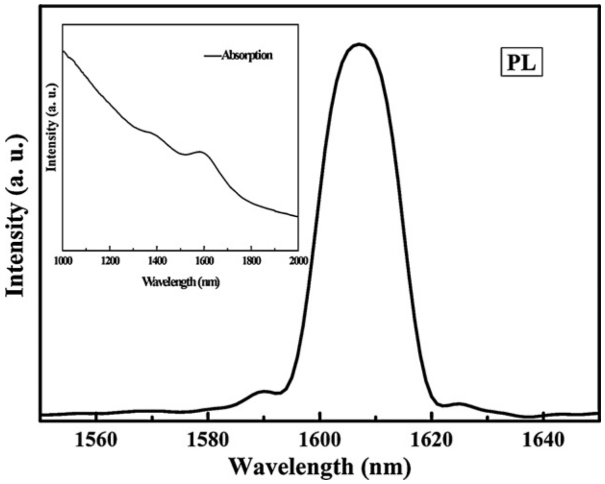

Fig. 4. Optical absorption and PL emission for PbTe NCs having absorption at 1590 nm.

Acknowledgements

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