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# Shape and confinement control in mid and far infrared nanocrystals

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**ABSTRACT** In this paper, we discuss recent progress obtained on infrared nanocrystal based on mercury chalcogenides (HgTe and HgSe). These materials can become some key building blocks for the next generation of infrared optoelectronic devices. To reach this goal, the infrared nanocrystals need to combine fine control on the optical features and efficient electronic transport. Here, we report about (i) the development of HgTe NPL for enhanced optical features (narrower and faster PL) in the near IR and (ii) about the development of self-doped nanocrystals of HgSe to demonstrate tunable intraband absorption up to the THz range.

**KEYWORDS** nanocrystals, narrow band gap, mid and far-infrared, self-doping.

## INTRODUCTION

Colloidal quantum dots (CQD) have been attracting a growing interest over the past few years. Their integration as the next generation of phosphors for display has pushed their use up to the industrial scale. However, in this application, the CQD remain electrically passive and only their photoluminescence (PL) is used. The use of CQD for optoelectronics [1] remains far more challenging because both optical and transport properties need to be addressed.

On the material side, most of the effort has been focused on cadmium chalcogenides because of their visible tunable optical features. Nevertheless, in the visible range, current optoelectronic devices (source and detector) already combine high efficiency and cost effectiveness. This is not the case in the IR where low cost devices are generally associated with lower performances. Since organic electronics are ineffective in the mid IR and that current technologies based on epitaxially grown semiconductors are unlikely to bring a cost disruption, alternative materials still have to be identified. CQD can become the building block of a new generation of infrared devices as long as they can demonstrate competitive device performances [2].

Here, we introduce some of the recently obtained progress on the synthesis of HgTe and HgSe CQD [3,4]. We present early demonstration of mid infrared optical features thanks to the growth of large and poorly confined HgTe CQD. Recently, a next step has been reached on the shape control of HgTe CQD, with the growth of HgTe 2D nanoplatelets [5]. Their anisotropic shape brings enhanced optical features with narrower and faster emission. Finally, we discuss the recent progress obtained with self-doped CQD of HgSe. They present additional optical features resulting from intraband absorption, which is tunable from 3 to 20  $\mu\text{m}$  [6].

## DISCUSSION



So far, the direct synthesis of HgTe NPL has not been reported. Izquierdo *et al* [5] used an indirect path to obtain these NPL. They first synthesized CdTe NPL and in a second step used a cation exchange [18,19,20] procedure to remove the Cd<sup>2+</sup> cations from the NPL and replace them by mercury. The challenge comes from the fact that the 2D shape has to be preserved to avoid either the CQD dissolution or shape reconstruction, see Figure 2b. To do so, a bulky precursor of Hg is prepared by complexing the Hg<sup>2+</sup> ions with long alkane chains. After the cation exchange, the optical features of the CdTe NPL initially in the green shift toward near infrared, see Figure 2a. The obtained materials present a narrow PL of 55 meV for the entire measurement. For the sake of comparison, the other nanocrystal materials (PbS and CuGaInS(e)) emitting in the same range of wavelength present a linewidth of 100 meV, even for single particle measurements. Another striking optical feature resulting from the 2D shape is the fast PL emission of these NPL. The PL decay has been determined to be around 60 ns. Due to the higher binding energy resulting from the 2D shape. The PL decay is typically 50 times faster than what can be obtained with PbS and CIGS,

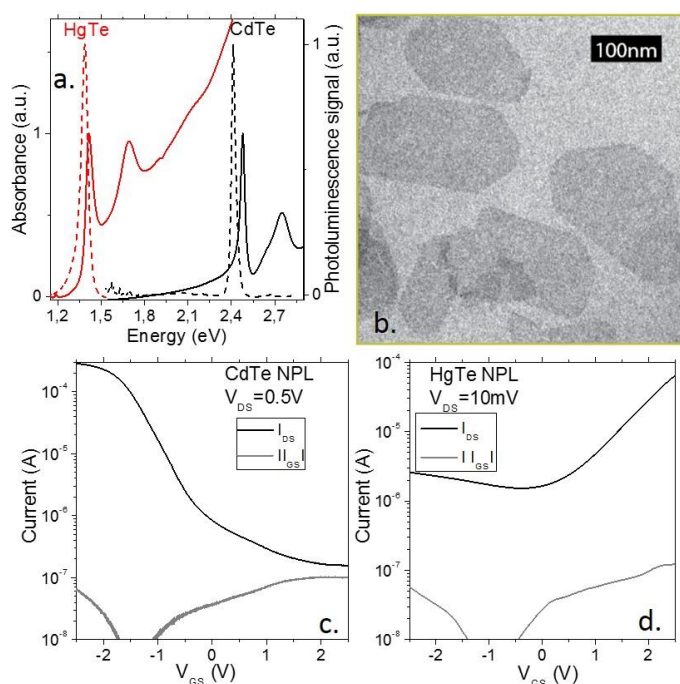


Figure 2 a. Absorption spectra of CdTe and HgTe NPL. b. TEM image of HgTe NPL. c. Transfer curve (drain and gate current as a function of gate bias) for CdTe NPL film measured in an electrolytic transistor configuration at room temperature. d. Transfer curve for a film of HgTe NPL. Adapted from ref [5]

We further investigate the transport properties of these 2D NPL. To do so, we incorporate the NPL into an electrolytic transistor, where the gate is obtained by ion gel gating [21,22]. This geometry allows us to explore large carrier density injection thanks to gate capacitance in the range of some  $\mu\text{F}\cdot\text{cm}^{-2}$  and in volume gating volume [23]. To build the device, we first exchange the NPL ligands. The initial long capping ligands (oleylamine and oleic acid) are replaced by short S<sup>2-</sup> ions [24]. In a second step, the ion gel made of LiClO<sub>4</sub> in PEG is deposited on the top of the film. The initial CdTe NPL present a p-type behavior, see Figure 2c whereas after the cation exchange, the HgTe NPL become n-type, see Figure 2d.

To further explore the infrared properties of CQD and push their absorption toward longer wavelength, an interesting approach is to switch from interband transition in narrow band gap material to intraband transition. To observe intraband transition in CQD, some carrier(s) have to be injected within the conduction band. This can be obtained by optical pumping [25] or electrochemical injection [26]. However, these approaches remain poorly convenient for the design of device. Recently, self-doped CQD presenting mid infrared intraband absorption have been obtained with HgS [27] and HgSe [6,28]. We proposed an improved synthesis for HgSe with a wider range of size [6]. The typical absorption spectrum of the HgSe CQD presents two main contributions. In the near IR, we observe a broad absorption relative to interband absorption and in the mid and far infrared, we observe a peak relative to the intraband transition. Transport measurements, again conducted in an ion gel transistor configuration,

have confirmed this doping and demonstrate its n-type nature (ie electron doping) [6,29]. In this case we rather use  $\text{As}_2\text{S}_3$  as capping ligand because of its low absorption in the mid infrared and also because of the previously demonstrated capability of this ligand to generate high mobility and photoresponsivity [30,31]. We demonstrate the possibility to tune the HgSe CQD size from 4 to 50 nm while tuning the Se precursor (Se complexed with trioctylphosphine or  $\text{SeS}_2$ ), reaction duration and temperature ( $70^\circ\text{C}$ - $120^\circ\text{C}$ ). As a result, the intraband peak energy can be tuned from 3 to 20  $\mu\text{m}$ , see Figure 3b and d. The obtained material presents no aggregation, as shown on the TEM image, see Figure 3c.

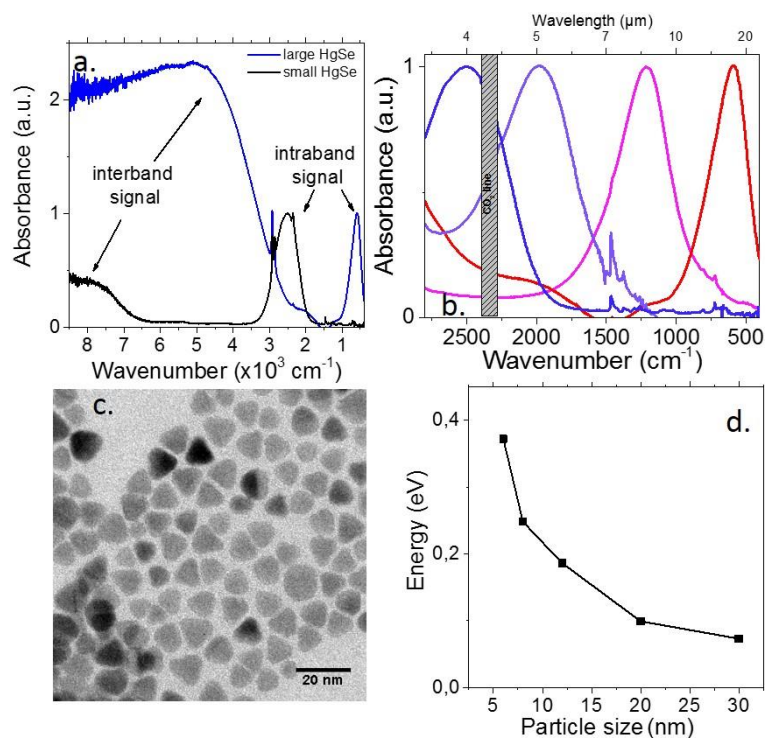


Figure 3 a. Absorption spectrum for two sizes of HgSe CQD. b. Zoom on the intraband contribution of the absorption spectra of HgSe CQD for four sized of HgSe CQD. c. TEM image of HgSe CQD. d. Energy dependence of the intraband transition as a function of the CQD size. Adapted from ref [6].

The origin of the self-doping was attributed to a reduction of the HgSe by its environment because of the large work function of the bulk [32] and limited interband band edge energy. This brings the conduction band below the  $\text{O}_2/\text{H}_2\text{O}$  redox couple and the negatively charged CQD becomes the stable form. We demonstrate that the doping magnitude can be tuned by charging the capping ligands [29], we typically observe that the carrier density can be tuned by a factor 10 from 2 carriers per dot with dodecanethiol capping down to 0.2 carrier per dot with  $\text{S}^{2-}$  capping ions.

## CONCLUSION

Significant progress has been obtained on the synthesis of mercury chalcogenides CQD with infrared optical absorption. Since the early nanocrystals absorbing above 3  $\mu\text{m}$  in 2011, 2D materials have been proposed and synthesized with a strategy to achieve narrower optical features. Compared to previously existing nanocrystals, the 2D NPL of HgTe have enhanced PL performances with PL a narrower, faster and greater efficiency (about 10%).

Concerning the mid infrared absorption, the synthesis of self-doped nanocrystals made of HgS and HgSe, have for the first time allows the observation of intraband features in the mid IR. It addresses the atmospheric transparency window, without the constrain of optical or electrochemical pumping. This interband absorption is tunable up to the THz range. The possibility to use intraband transition opens new possibilities for the design of infrared CQD based device.

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