Infrared narrow band gap nanocrystals: recent progresses relative to imaging and active detection

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ABSTRACT:

Current technologies for infrared detection have been based on epitaxially grown semiconductors. Here we review some of the recent developments relative to colloidal nanocrystals and their use as building blocks for the design of low-cost infrared sensors. We focus on HgTe nanocrystals which appear as the only material leading to infrared photoconductivity and ultra-broad spectral tunability: from the visible to the long-wave infrared. We review some of the important results which demonstrated that colloidal nanocrystals can be compatible with air stable operations, fast detection, and strong absorption. We discuss the recent progresses relative to multipixel devices and show results obtained by coupling short-wave infrared nanoparticles with CMOS circuits to achieve video rate VGA format imaging. In particular we present that nanocrystals are a promising material for long range (>150 m) active detection in both continuous wave and pulsed mode with a time resolution down to 10 ns.

INTRODUCTION

Current technologies for infrared (IR) sensing are driven by epitaxially grown semiconductors. The high maturity of technologies such as InGaAs, InSb, HgCdTe, or type II superlattices [1] has led to exceptional performances which include high signal-to-noise ratio, large format focal plane arrays (FPAs), and fast detection. However, the prospect of costs reduction is extremely limited. This makes that IR sensing is mostly limited to two niche markets, including the defense and astronomy.

Thermal detectors such as pyrometers and bolometers offer room temperature operation and reduced fabrication costs, but signal-to-noise ratio is lower and time response is slower compared with epitaxially grown detectors. Among these technologies, the bolometer is certainly the one achieving the best imaging performances however, it operates in the long wave infrared (LWIR) which let both short-wave IR (SWIR) and mid-wave IR (MWIR) without real low-cost alternative. Extremely cheap (a few hundred euros) focal plane arrays (FPAs) are available but the number of pixels and the frame rate are restricted, leading to low quality images.

There is an alternative technology if the latter can combine the efficiency of quantum sensors (speed and spectral tunability) with the low costs of thermal detectors. Such detector might be useful for applications in night driving, industrial vision for fast sorting, and LIDAR detection. All these applications require a cost break down by at least a factor of 5 compared to current IR sensors. When it comes to low cost, organic-electronic materials are often seen as a possible candidate, but they are ineffective beyond 1 µm.

Several materials have been proposed as alternative candidates such as graphene [2,3] or black phosphorus [4,5]. However, colloidal nanocrystals are particularly those for which most of the efforts have been continuously developed over the past 10 years: switching from the proof of concept for mid IR detection [6] to a high performance versatile platform for IR optoelectronics [7,8]. Their interest has first been raised by their ability to emit light. This has led to their integration into displays as narrow green and red sources. Combining the broad range of materials that can be synthesized under colloidal form with quantum confinement it is possible to
extend the optical spectrum of such nanocrystals from the UV to the THz range [9].

In the IR range, nanocrystals have drawn tremendous attention for the design of solar cells to collect the near IR part of the solar spectrum. In particular the observation of a low energy threshold for multie exciton generation in nanocrystals offered a path to overcome Shockley Queisser limitation, compared to the bulk [10,11]. This is only later (~2005) that the use of nanocrystals for IR sensing have begun to attract interest [12,13]. Nanocrystals combine reasonably low fabrication costs and benefit from the processability of organic electronics. They can be spin-coated or ink-jet printed, which is of utmost interest to address the complex and expensive hybridization step to the read-out circuit.

In this paper we review some of the recent developments relative to the integration of colloidal nanocrystals for IR sensing [14–18]. We chose to focus on mercury chalcogenides [8,19,20] which currently appear as the only material allowing all IR ranges from SWIR to the THz. We try to cover every aspect from the material growth, to concepts introduced to push performance at the single pixel level and finally recent demonstrations relative to image sensing.

**DISCUSSION**

The first colloidal nanocrystals with interband absorption that were developed where based on lead chalcogenides. They are well suited to be used as solar cell absorbers thanks to their tunable band gap around 1.2 eV [21,22]. However, because of their bulk band gap, lead chalcogenides are not appropriate to explore wavelengths above 4 µm [23] at least under colloidal form [24]. Narrower band gap materials or semimetals appear to be better suited to explore longer wavelengths. By far, the colloidal synthesis of nanocrystals has been focused on II–VI semiconductors and especially CdSe [25]. Consequently, semimetals consisting of II–VI materials where looking the most promising to reach the IR taking advantage of the chemical knowledge previously developed. This was pledging for the development of mercury chalcogenide compounds [13,26,27], which was further reinforced by their past extensive use in the IR detection field.

**Mercury Chalcogenides nanocrystals, the most tunable platform for infrared optoelectronics**

While CdSe nanocrystals have been widely investigated for several years, only a few work have been done on HgTe before 2010 [13]. In 2010, Keuleyan et al.[28] have proposed the first colloidal synthesis facilitating mid-IR absorption in nanocrystals, see Figure 1b. This first material was strongly aggregated as shown transmission electronic microscopy image, see Figure 1a. This aggregation explains the poorly defined and smooth excitonic feature of the absorption spectrum. Later, the synthesis was improved to reduce aggregation of the nanocrystals, see Figure 1c. As objects were better defined, the band edge absorption feature was also sharper, see Figure 1d. Operating the same growth procedure in more dilute conditions decreased polydispersity, see Figure 1e. We obtained, as a result, an “atom-like” spectrum and up to six excitonic transitions can be observed in the absorption spectrum, see Figure 1f.

The synthesis of 2D HgTe colloidal quantum wells [28,29] demonstrated an improved control of the material growth see Figure 1g. The obtained material is often called nanoplatelets (NPLs) [30,31] and offers interesting features: the growth mechanism makes that the only confined direction presents no roughness and thus atomic control is achieved. This gives rise to the narrowest optical feature achieved for nanocrystals due to the lack of inhomogeneous broadening. Currently, the thinnest material is only 3 monolayers thick, which leads to an optical feature in the near IR (800-1000 nm), that can expanded to the short-wave IR by the growth of a shell [32,33]. Because of the semimetal nature of the bulk material, all the energy of the optical transition is due to quantum confinement: this makes HgTe NPLs one of the most confined nanocrystal material with approximately 1.5 eV of confinement.

It is also possible to explore extremely reduced confinement in this material. The Bohr radius of HgTe [34] is around 40 nm, which requires to grow large nanoparticles. This was presented by Goubet et al who have proposed a synthetic method where the size of the nanoparticles can be tuned from 5 nm and up to 1 µm [9], see Figure 1i. The obtained nanoparticles can absorb from long wave IR up to the THz range [9,35] (60 µm for the absorption peak and up to 200 µm for the absorption edge, see Figure 1j).

Last, it is worth also mentioning that heterostructures (core-shell objects) based on
mercury chalcogenides have also been demonstrated [36–38], even though several challenges are remaining to further enhance the luminescence efficiency and decrease the non-radiative decay path of the exciton [18].

The principle of IR absorption in colloidal nanocrystals can be classified by two different mechanisms: interband transition in a narrow band gap/semi metal material or intraband absorption. The latter requires degenerate doping, which has been a synthetic challenge for long. Significant progresses have been realized over the recent years, to obtain doped nanoparticles via introduction of extrinsic impurities within the NCs [39–41] or within the nanocrystal array [42], non-stoichiometry of the material (Cu2-xS [43], (Bi;Sb)2Te3, HgSe [35,44]), metal functionalization [45,46], and functionalization by redox molecules [47,48] or surface dipole functionalization [49–53].

In the case of mercury chalcogenides, the doping magnitude will tune the observed IR transition. When the size of particles is small, confinement reduces the doping and this is mostly interband absorption that is observed, see Figure 2a and d. When confinement is reduced but is still present (typically in the 3-12 µm range), intraband absorption, which is the 0D analog of the intersubband absorption in quantum wells, is observed [44,51,54,55], see Figure 2b and d. When doping is vanishing or doping level is very high, the density of state becomes dense and the optical feature acquires more and more a metallic nature, leading to the observation of plasmonic transitions [9,53,56]. This unique combination with various types of transitions and their tunability thanks to doping and quantum confinement make that mercury chalcogenides are the most tunable nanocrystals. The energy of the first excitonic feature can be tune by almost two orders of magnitude. For sake of comparison, in CdSe, quantum confinement offers not more than 30% of tunability for the energy of the excitonic feature.

The electronic structure of mercury chalcogenides nanocrystals

A critical step for the integration of these nanocrystals into devices, especially for diode type devices, is the determination of their electronic spectrum in absolute energy scale. The band diagram of bulk HgTe is already unusual with an inverted band structure [57] (i.e. the band with a Γ6 symmetry, which is usually the conduction one is below the Fermi level and is deep in the valence band). The other distinction already mentioned is the semi-metal nature of this material which is used...
for THz absorption thanks to vanishing confinement. The optical absorption in this material occurs between the two bands with $\Gamma_8$ symmetry [58,59], see Erreur ! Source du renvoi introuvable.a. Note that quantum confinement in HgTe nanocrystals is used to tune the energy of the absorption cut-off similarly to the Cd content for bulk HgCdTe alloys.

In contrast to the bulk original band structure, HgTe nanocrystals add two other specificities which are the quantum confinement (Erreur ! Source du renvoi introuvable.b) and the dependence on the spectrum with surface chemistry (Erreur ! Source du renvoi introuvable.c). These different effects combined make it is currently impossible to predict a priori the exact energy level of each band for a given nanocrystal. This is why the exact energy has to be measured. Two main methods can be used: electrochemistry [29,53,60–62] or more conventionally for semiconductors: X-ray photoemission spectroscopy. The work function of the material has been found to be 4.6±0.1 eV and poorly depends on the size. It is interesting to notice that surface chemistry can induce p- and n-type nature to a given material and so to a given size. This was for example used in the design of p-n junction [63]. In the case of HgTe, the determination of the electronic spectrum was used to build by design a unipolar barriers used to filter the dark current [60] in a diode geometry.

**Detection-oriented performance**

Integration of nanocrystals into devices to replace historical technologies not only requires achieving
high signal-to-noise ratio, but also imposes to provide similar temporal stabilities and fast time response. For long these issues have not been still addressed.

Recently we started to tackle this issue. HgTe nanocrystal arrays are intrinsically porous which makes the material more exposed to oxidation by the environment. We indeed observe that the conductance of a film stored in air rises by a factor >50 over a week, see Figure 4a. The material is also sensitive to temperature because of its low temperature growth (60 to 120 °C depending on the targeted size). Once exposed to high temperature the nanoparticles sinter, which increases the delocalization length, reduces the optical band gap and increases the dark current. Thus, we proposed a room temperature deposition of a multilayer system which is air (PVA) and water (PMMA and PVDF) repealing. An encapsulated film achieved stable dark current over three months. More work will have to be done in this direction.

Another challenge about the potential use of nanocrystals lies in transport and time response optimization. Transport in nanocrystal arrays occurs via a hopping mechanism, typically a nearest neighbor hopping at room temperature. First, this mechanism requires essentially a ligand exchange procedure. During this process, the native long ligands grafted onto the nanocrystal surface behaving as a tunnel barrier, are stripped and replaced by shorter organic molecules or even inorganic ions [64,65]. Such procedure has been extremely useful to improve the carrier mobility [66] (now around 1cm²·V⁻¹·s⁻¹ [67]). Such long ligands (and tunnel barriers) have presumably prevented fast detection. In addition, for a long time, the time response of mid-IR nanocrystals was probed in a non-appropriate way using high energy pulsed lasers. Fast detection times were observed but may also have been the result of hot electrons cooling. Using a quantum cascade laser resonant with the band edge of MWIR nanocrystals (see the inset of Figure 4b), we have recently demonstrated that the electrical time response of HgTe thin films can be no longer than 20 ns [68], see Figure 4b.

**Photon Management in HgTe**

The previously mentioned low carrier mobility leads to a short carrier diffusion length (below 100 nm), which is typically 1 order of magnitude smaller than the material absorption depth (a few μm) [59]. Consequently, thin nanocrystal films only absorb a limited part of the incident light. As a sake of example, a film of HgTe nanocrystals which is 200 nm thick and with an excitonic feature at 2.5 μm only absorb 12% of the incident light. Building thick films may increase absorption, but the charge collection will not be improved due to this short carrier diffusion length. In 2019, a significant effort has been done to develop a new film deposition method which combines better inter-nanocrystal coupling and allows the deposition of thicker films [66,67]. Films with thicknesses above 500 nm can now be routinely obtained and absorb around 40% of the incident light, see Figure 5a.

To further enhance the absorption of a nanocrystal film, it has been proposed to introduce plasmonic resonators [69–76]. Our approach to this issue is to modify the plane wave propagation of the incident light to generate a guide mode in the film. To do so a grating which spacing is roughly given by the wavelength divided by the medium dielectric constant is placed below the film. We proposed a device which combines a back-side reflector with

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**Figure 4** (a) Dark current as a function of time spent in air for a HgTe CQD film with and without protective layers. Time zero corresponds to the sample in the air-free glove box. Inset is a scheme of the HgTe CQD film device with protective layers. The figure is adapted with permission from ref [65]. Copyright (2018) American Chemical Society. (b) Typical HgTe nanocrystal film response to a laser-limited 20 ns Quantum Cascade laser pulse at 4.4 μm. The inset is a scheme of the measurement setup with a mid-infrared Quantum Cascade laser. The figure is adapted with permission from ref [66]. Copyright (2018) American Chemical Society.
such guided mode resonator [77]. The back-side mirror is here to generate two passes for the incident light while the grating generates multi-passes of the light as explained on the scheme of Figure 5b-d. The obtained device can absorb 70% of the total incident light and even 100% of the light propagating along the transverse magnetic (TM) mode. In such a device a lot of attention have been paid to locate the absorption within the semiconductor and not in the metal to avoid thermal losses. Here around 80% of the absorption occurs in the semiconductor, this is good enough to enhance absorption but also offers interesting perspectives for future improvements.

**Short Wave Infrared imaging using HgTe nanocrystals**

All previously discussed results were focused on single pixel devices. It is worth pointing that the interest in nanocrystals is not only generated by the reduced fabrication cost but possibly also by their ease to be hybridized to the read-out circuit. Thanks to their solution processability, direct deposition of the nanocrystal film onto the read-out circuit should be possible. There have been several demonstrations of this concept either using PbS nanocrystals in the near IR [78] or using HgTe in the MWIR [79,80]. Here we rather focus on the SWIR as a possible alternative to InGaAs. Our first attempt was very basic and based on a homemade 10x10 pixel array, see Figure 6a and b. The deposition of a HgTe ink leads to photoconductive and strongly absorbing film as described in Figure 5a. This reduced-size focal plane array was then used as an IR laser beam profiler, see Figure 6c.

To achieve a higher image quality, the nanocrystal film was then deposited on a VGA format read-out integrated circuit (ROIC) by New Imaging Technologies. One can follow the recent progresses achieved while coupling such absorbing nanocrystal films to these ROICs in Figure 6c-d. First demonstrator (Figure 6c) was requiring direct illumination by a laser, suggesting a poor external quantum efficiency. It is now possible (Figure 6d) to make passive imaging of a scene in the near IR (i.e. visible part of the sun light is removed by a high pass filter).

**Use of nanocrystals for active detection**
To finish this discussion, we would like to mention another promising result for the use of nanocrystals in active detection. PbS nanocrystals based on solar cells have actually been designed to efficiently absorb the near IR part of the solar spectrum, but they are used as broad-band absorbers in solar cells. We have actually revisited this concept and operated them as sensors for near IR active detection [81]. Such a detector presents a high detectivity above $10^{12}$ Jones at room temperature and a fast time response (10 ns rise time – 1 µs decay time). We demonstrate that they can detect back scattered light between two building spaced by 85 m, see Figure 7a and b. We also show that they can be used for time-of-flight measurements, see Figure 7c. This is promising for their use in LIDAR detection as long as similar performance can be preserved at telecom wavelengths.

CONCLUSION

We have discussed some of the recent developments of IR nanocrystals and their use for IR sensing including for imaging and active detection. 10 years ago, the challenge was to grow nanocrystals absorbing in the IR. Material growth is now mature, and the electronic structure of the material is mostly known. Great progresses have also been obtained for the doping of the nanoparticles which has open the way for the use of intraband absorption. Nanocrystals can achieve air stable (>3 months), fast (down to 20 ns) operation and absorb most (>70%) of the incident light. Large format imaging is also possible with limited dead pixels and edge effect. More sophisticated operation mode based on active detection and time gated operation appears to be also possible.

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Figure 7. (a) Scheme of the long-range active imaging. A light source (10 W/940 nm lamp) enlights a building at 85 m distance. The device detects retrodiffused light from the building. (b) Photocurrent modulation measured at 100 Hz as a function of time in a long range detection configuration (c) Device response at 0 V as a function of the total distance from the source. The bottom black curve corresponds to the silicon photodiode (PD) response used for triggering. Adapted with permission from ref [83]. Copyright (2019) American Chemical Society.
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