# NARROW BAND GAP NANOCRYSTALS FOR INFRARED COST-EFFECTIVE OPTOELECTRONICS

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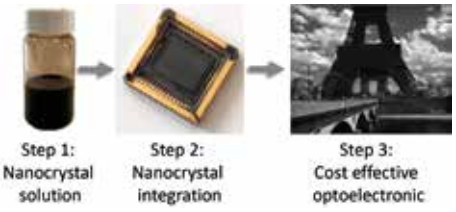


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**Infrared optoelectronics is driven by epitaxially grown semiconductors and the introduction of alternative materials is often viewed with some suspicion until the newcomer has demonstrated a high degree of viability. Infrared nanocrystals have certainly reached this degree of maturity switching from the demonstration of absorption by chemists to their integration into increasingly complex systems. Here, we review some of the recent developments relative to the integration of nanocrystal devices in the 1-5 µm range.**

The spectral properties of a semiconductor are mostly driven by the band gap energy. Thus, the most obvious strategy to achieve spectral tunability is to alloy two semiconductors to obtain intermediate properties. However, this approach tends to be limited by metallurgic considerations and in particular the difference in lattice parameter. Since the late 70's, quantum confinement appears as an alternative approach to increase the band gap of a semiconductor. When the size of a semiconductor is reduced below its Bohr radius (7 nm in CdSe and around 40 nm in HgTe), its optical properties start to deviate from the bulk material and the band gap energy is increased (i.e. the spectrum blue shifts), see Figure 1b. Such quantum confined semiconductors are now widely spread. For exemple, semiconductor quantum wells are used in TV remotes and the quantum cascade laser is certainly one of the greatest outputs of quantum engineering. Initially this strategy has been applied to semiconductor thin films and quantum dots obtained through high vacuum epitaxial growth. However, this approach quickly reached its limits in terms of volume production and thus alternative growth methods for such quantum confined semiconductors have been developed using chemical approaches. Since the early 90s, it has become possible to grow semiconductor nanoparticles (the so-called nanocrystals or colloidal quantum dots) in solution from a basic glassware setup as depicted in Figure 1a. Using wide band gap materials such as CdSe or InP the whole visible spectrum can be covered, see Figure 1c.

Over time the colloidal synthesis has gained maturity and which has allowed to grow a broader range of materials, to achieve atomic scale control of the size and also to synthetize colloidal heterostructures. By growing core shell structures, the wave functions are pushed away from the surface where surface traps prevent radiative recombination. This has led the growth of nanoparticles with a high photoluminescence quantum yield that are now integrated as green and red sources for display.

While early efforts have mostly been focused on the visible spectral range, a significant effort has been later dedicated to narrower band gap materials (PbS or HgTe). The first motivation for infrared absorbing nanocrystals was their use as optimal absorbers for solar cells. However,

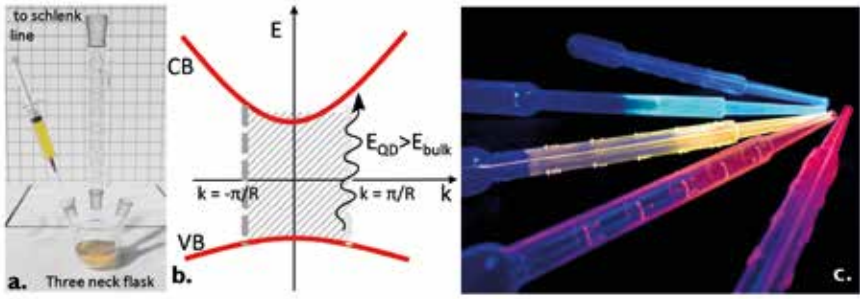


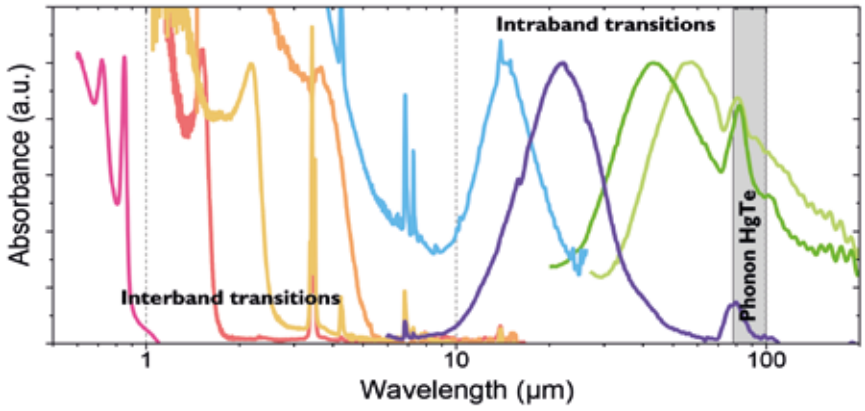

**Figure 1.** a. Schematic of a setup dedicated to nanocrystal synthesis. b. Schematic band structure of a semiconductor highlighting that the finite particle size makes the central part of the energy diagram unavailable and thus increases the optical band gap compared to the bulk material. c. Image of a pipette coated with nanocrystals of various sizes.

over the recent years, these materials have been strongly challenged by the emergence of perovskite materials which offer higher power conversion efficiency thanks to the defect tolerance of their electronic structure. On the other hand, the perovskite band gap remains large preventing the use of these materials for truly infrared applications. HgTe for example offers an exceptionally large spectral tunability since its band gap can be tuned from 1 to 100 µm, as shown in Figure 2. This exceptional spectral tunability together with a reduced fabrication cost make narrower band gap materials promising candidates for the design of infrared optoelectronic devices. Indeed, infrared optoelectronics suffers from a low production volume which makes the cost of devices generally prohibitive. A short-wave infrared camera easily costs 10 k€ and its mid infrared counterpart almost 10 times more. In addition, organic electronics, due to the strong vibration between the excitons and the lattice vibration, is ineffective above 1 µm. Thus, narrow band gap nanocrystals, with few emerging 2D materials (black phosphor, graphene, $PtSe_2$), generate interest as possible alternatives to traditional III-V and II-VI semiconductors usually used in this spectral window. This paper reviews some of the recent development relative to the integration of infrared nanocrystals as a new active material for optoelectronic devices dedicated to the detection and emission of light.

## EXPECTED CONTENTS

Because they appear broadly tunable in the infrared range and their absorption is robust (i.e. weakly affected by photobleaching), infrared nanocrystals are natural candidates to be used as photodetectors. In this case a conductive film must be fabricated. Grown nanocrystals are usually capped with long capping ligands. The latter ensure the colloidal stability of the particle but also ensure the electronic surface passivation of the surface dangling bond. However, these long ligands (alkyl chain with 12 to 18 carbons typically) are insulating by nature so a nanoparticle • • •

**Figure 2.** Absorbance spectra for HgTe nanocrystals of various sizes. The confined size ranges from 1.2 nm for the highest energy curve to above 100 nm for the lowest energy spectrum.



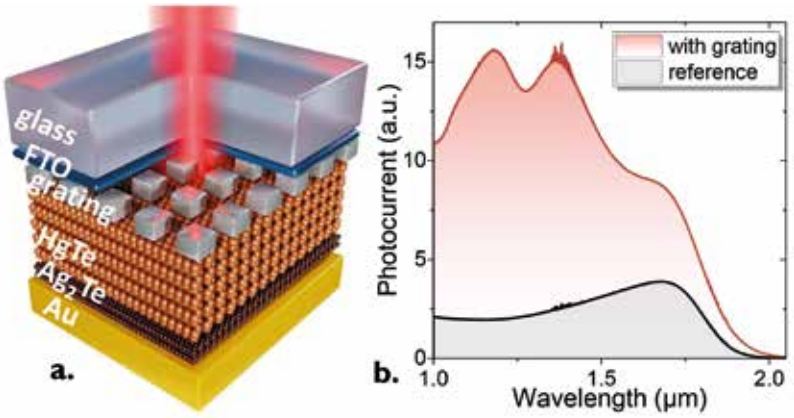


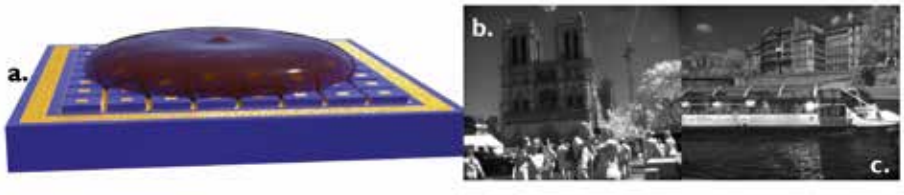

**Figure 3.** a. Schematic of an infrared diode stack coupled to a light resonator which role is to enhance the absorption of a thin film. b. Spectrum of the diode stack with and without the light resonator. Figure is adapted with permission Advanced Optical Materials **9**, 2002066. Copyright {2021} John Wiley and Sons.

array is neither conductive nor photoconductive without post synthesis treatment. Much of the effort dedicated to the integration of colloidal nanocrystals into devices has actually focused on the modification of the surface chemistry to make it compatible with charge conduction. During the ligand exchange step, the initial ligands are replaced by short ones in order to increase interparticle coupling. Macroscopically this leads to an increase in the carrier mobility which starts from very low values ($<10^{-6}$ $cm^2.V^{-1}s^{-1}$) to values in the $10^{-2}$ -10 $cm^2.V^{-1}s^{-1}$ range. Even larger values can be obtained but this generally comes at the prize of a loss of quantum confinement and thus with a dramatic broadening of the optical features. Once the film can be fabricated it can be integrated into various geometries starting from a basic photoconductor to a phototransistor to obtain carrier density control or to a photodiode to supress part of the dark current. An example of a photodiode stack is depicted in Figure 3a. This type of photodiode is obtained by successively depositing layers generally by spin/spray/dip coating. Nanocrystal based light sensors face a trade-off between absorption and conduction. The modest mobility means that charge collection is only efficient over a short distance typically 100 nm, while the absorption depth of such nanocrystal films is generally greater than 1 µm in the infrared. Thus, without a light management strategy the photocharge collection is generally low, this is why an important effort is now dedicated to the introduction of photonic cavities to absorb most of the incident light. For sake of illustration, the diode depicted in Figure 3a can have an increased absorption from 10 % to around 50 % while a metallic grating array can form an optical mode where several light passes though the film are possible. As pointed in Figure 3b this can increase the absorption magnitude but also reshape the absorption spectrum. For a long time, the absorption of nanocrystal-based devices has been dictated by the particle size. The introduction of photonic cavities offers a new degree of freedom to shift the spectral response while keeping the absorbing material unchanged.

As nanocrystal-based devices improve, their performance has also been strongly increased. In the short-wave infrared responsivities in the 0.1 to 1 $A.W^{-1}$ are now commonly achieved and correspond to an external quantum efficiency from 10 to 50 %. At 1.4 µm the detectivity (ie the signal to noise ratio) can reach $10^{12}$ jones at room temperature and this level of performance can be preserved for 2 µm cut-off at the prize of mild cooling (200 K operation). In the mid wave infrared to date most operations are performed at cryogenic temperature but the detectivity remains above $10^{10}$ jones. Moreover, hopping conduction is inherent to the polycrystalline nature of the nanocrystal film and could have been an obstacle to fast time response. It is nevertheless not the case and response times as short as a few ns are typical with planar geometry devices and sub µs times are also achieved using a diode stack.

Given this already competitive level of performances achieved at the single pixel level, the current technological challenge is now to transfer this technology to the focal plane array level. On paper, nanocrystals coupling to the read-out circuit (ROIC) should offer some promising developments. Historically the coupling between the absorbing layer and the ROIC is obtained by hybridization though small Indium bumps. However, this process has a limited yield that generates costs and becomes more and more challenging as the pixel size is reduced. The nanocrystal solution can be directly deposited on the ROIC surface, as shown in Figure 4a. This eases film deposition and offers the possibility to reduce the pixel size close to the diffraction limit. A recent report in the near infrared using the ROIC initially developed for the visible range finally led to the demonstration of a focal plane array with a pitch size below 2 µm. High quality images and

**Figure 3.** a. Schematic of a CMOS read-out circuit coated with an infrared nanocrystal film. b and c are images acquired from a focal plane array which active layer is made of HgTe nanocrystals.



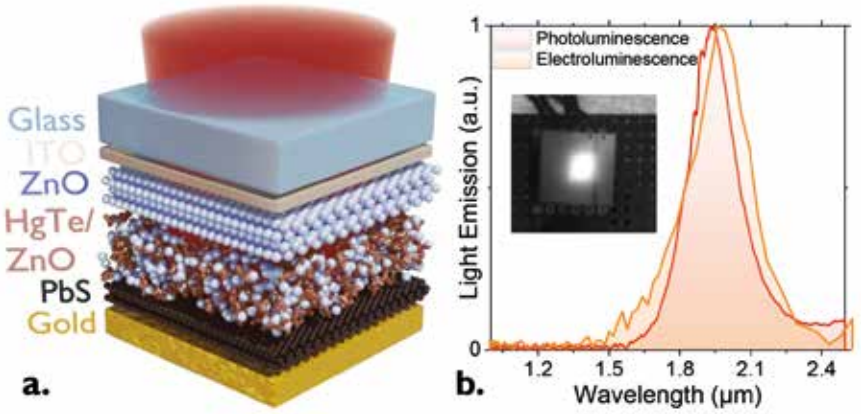



**Figure 5.** a. Schematic of a light emitting diode stack with emission at around 2 µm. b. Electroluminescence and photoluminescence spectra from HgTe nanocrystals. The inset is an infrared image of the LED under operation. Figure is adapted from with permission Nature Photonics **16**, 38. Copyright {2022} Nature springer.

movies can now be reported in the near and short-wave infrared, see Figure 4b.

The promise of infrared nanocrystals is not limited to light absorption for photodetection and they can also be interesting light sources at telecom wavelength and beyond. While the first mass market application was their use as down converters for display, a large effort has also been dedicated to the design of an electrically excited light emitting device based on QLED. Compared to the strategy where the nanocrystals are optically excited the electrical excitation may offer a higher contrast and reduce electrical consumption, which might be an important step toward their integration into smartphone display. In the infrared, the light emission remains largely dominated by III-V epitaxially grown semiconductors. Quantum wells based on III-V heterostructures are massively used at telecom wavelength as a powerful source compatible with fast modulation. Above 4 µm, the quantum cascade laser is also now a well-established source. In the middle from 1.5 to 4 µm, there is a technological gap where only emerging technologies are currently available and where nanocrystals can also be used as an infrared photon source. Pushing the electroluminescence (EL) of nanocrystals in this spectral range remains nevertheless challenging due to the strong near field coupling between the exciton and the vibration of the capping ligands. Such coupling tends to quench the luminescence, making the ligand exchange procedure even more important.

An example of a light emitting diode with an emission above 2 µm is schematized in Figure 5a and its operation is imaged using an infrared camera in the inset of Figure 5b. It should be noted that the emission is not just blackbody radiation due to the passing of current in the stack and that the EL spectrum indeed matches the photoluminescence signal, see Figure 5b.

## CONCLUSION

Infrared nanocrystals have made tremendous progress in recent years enabling their integration into increasingly complex devices including photonic structures, focal plane arrays and light emitting diodes. Future efforts should focus on increasing thermal stability to make the material fully compatible with traditional semiconductor processing. Further understanding of the material electronic structure and its transport properties will also be required to enable the design of complex structures.

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