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Electroluminescence from Nanocrystals above 2 μm

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Abstract: Visible nanocrystal-based light emitting diodes (LEDs) are about to become commercially available. However, their infrared counterparts suffer from two key limitations. First, III-V semiconductor technologies are strong competitors. Second, their potential for operation beyond 1.7 μm remains unexplored. The range from 1.5 to 4 μm corresponds to a technological gap: the efficiency of interband quantum-well-based devices vanishes and quantum cascade lasers are not efficient enough. Powerful infrared LEDs in this range are needed for applications such as active imaging, organic molecule sensing and airfield lighting. In this work, we report the design of a HgTe nanocrystal-based LED with a luminescence between 2 and 2.3 μm . With a 0.3% EQE and a radiance up to 3 W Sr⁻¹ m⁻², these HgTe LEDs already present a competitive performance for emission above 2 μm .

Keywords: narrow band-gap nanocrystals, HgTe, electroluminescence, short wave infrared.

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Introduction

The bright and spectrally tunable emission of nanocrystals (NCs) is certainly their most striking property which has led to their integration as light downconverters for displays.¹ The desire of reducing the device electrical consumption and enhancing the light contrast has driven the development of NC-based light emitting diodes (LEDs).^{2,3} In the visible, such LEDs have almost reached a commercial status. Using narrower band-gap nanocrystals, such as PbS^{4,5} or Ag₂S,⁶ near infrared (IR) LEDs presenting bright and tunable emissions, up to 1700 nm, have also been reported. In this range of wavelengths, corresponding to telecom applications, NC-based LEDs suffer from the competition with III–V epitaxially-grown quantum well structures, that achieve high power-conversion and fast light modulation. Nevertheless, NCs still offer an easier spectral tunability in comparison with III–V semiconductors, by suppressing the constrain of an epitaxial growth onto a substrate.

Beyond telecom wavelengths ($\lambda > 1.55 \mu\text{m}$), a technological gap currently exists for which powerful sources are lacking. Organic LEDs are ineffective due to the strong coupling between the exciton and the molecular vibrations, limiting the light emission below 1 μm .⁷ Indium based III–V semiconductors, used for emission in the 1.3–1.5 μm range, present a too wide a band-gap to reach longer emission wavelengths. In the mid-IR, quantum cascade lasers⁸ (QCLs) have been the most successful solid-state sources for the past decade. Those devices represent the success of wavefunction engineering. However, their power-conversion efficiency remains weak due to voltage biases above 10 V (for an emission around $\approx 250 \text{ meV}$) and large current thresholds ($> 0.5 \text{ A}$). Whereas mid- and far-infrared are addressed by GaAs/AlGaAs technology, the range from 1.5 to 4 μm is only reached by a few technologies, such as Sb-containing lasers,⁹ interband QCLs,^{10,11} and GeSn^{12,13} presenting once again high current thresholds.

Nevertheless, such short-wave infrared sources are needed. CO₂, NH₃ and alkanes¹⁴ present strong absorption bands between 2 and 2.5 μm . Thus, low-cost light sources, operating in this range of wavelengths, are of utmost interest to monitor leaks in methane tankers or to follow green-house effect, for example. Airfield lighting is also a typical application requiring IR emission. Historically, light bulbs emitting in both visible (for pilot guiding) and IR ranges for instrument guiding were used. To reduce the electrical consumption and increase the device lifetime, light bulbs have been replaced with visible LEDs, losing the IR guiding light.

In this paper, we explore the design of NC-based LEDs with emission above 2 μm . Compared with epitaxially-grown semiconductors, NC-based LEDs present a much lower optical index ($n \approx 2.3$ typically,¹⁵ while $n > 4$ for most Sb-based semiconductors), easing the light extraction toward free space. Here, we report the fabrication of a NC-based LED presenting a tunable emission in the 2–2.3 μm range, with a turn-on voltage close to the band-gap energy, a low threshold current (15 $\text{mA}\cdot\text{cm}^{-2}$), and an external quantum efficiency (EQE) comparable to state-of-the-art Sb-based epitaxially-grown LEDs.

Results

Spectroscopic properties of HgTe nanocrystals

We start with the growth of HgTe nanocrystals¹⁶ with a photoluminescence (PL) above 2 μm . The procedure is taken from Keuleyan *et al.*¹⁷ Transmission Electron Microscopy (TEM, see **Figure 1c** and Supplementary method and note 1) reveals a clearly branched aspect for these particles. Despite their poor shape control, these branched HgTe NCs present a narrower band-edge feature compared to spherical NCs.^{18,19} These HgTe NCs are photoluminescent, see **Figure 1a-b**. The PL signal is red shifted by 120 nm from the absorption maximum due to Stokes' shift. The PL presents a peak at 2 μm , and the full width at half maximum (FWHM) is around 280 nm, corresponding to a $\lambda/\Delta\lambda \approx 7.2$. The PL efficiency of this material was previously found to be around 1% for an emission at 2 μm .²⁰ Increasing the temperature during the growth leads to larger NCs, inducing a reshift of the PL peak, **Figure 1b**. Here, we focus on particles emitting in the 2–2.3 μm range.

For HgTe NCs with a band-edge at around 2 μm , the carrier relaxation exhibits a long component (around 2 ns) attributed to the exciton relaxation²⁰, and a faster contribution (50 ps) associated to Auger relaxation.^{20–22} However, for this material, the ultrafast relaxation (<10 ps) which drives Auger non-radiative relaxations, remains unexplored, while LED performance is known to be limited by such mechanism. To explore such short time scales, we used a pump-probe transient reflectivity spectroscopy with a time resolution as short as 35 fs.²³ The pump-probe is set in a non-degenerated configuration with pump centered at 1.55 eV while the probe is centered at the band edge (of 0.62 eV).

In the first picoseconds, two different behaviors can be depicted: a first sharp rise (**Figure 1e**, regime I) is followed by a smoother increase (regime II) of the transient reflectivity. In HgTe the effective mass asymmetry between holes and electrons makes that the valence band behaves as a continuum, while the density of states is sparse close to the conduction band edge and only hot conduction band states can be assimilated to a continuum. The sharp rise is due to the action of the pump, which empties partially the valence bands by promoting the electrons into the conduction band states (called CB_H in **Figure 1f**), located ≈ 0.9 eV above the band-edge. Therefore, the probed states are no longer the same that at equilibrium, and involves intraband transitions within CB_H (figure 1f, regime I). These electrons thermalize into the empty conduction states, at a time scale of around 250 fs. The hot conduction-band states (CB_H), being quite high in energy, are delocalized. In consequence, their dynamics are strongly affected by a change in their environment. In particular, we show later that the introduction of ZnO in the vicinity of HgTe NCs (like in the emitting layer of our LED) alters the ratio of those two processes. Subsequently, over the next 3 ps, the transient reflectivity is dominated by the relaxation of these photoexcited electrons into conduction band ground state CB_G (**Figure 1f**, regime II). Hereafter, the long decay tail (5–30 ps range, **Figure 1d**) corresponds to the relaxation of the electrons down to their initial valance states (regime III). The decay time is clearly affected by the pump fluence (see **Figure 1d** and Supplementary note 2): this behavior matches the Auger relaxation observed from transient PL measurements.^{20,21,24,25} Then only at longer time scale the decay resulting from the neutral exciton is expected to occurs with a 2 ns characteristic relaxation.^{20,26}

Performance of a HgTe nanocrystal-based LED

To design a LED based on HgTe NCs, emitting at 2 μm and above, we use the LED structure proposed by Pradan *et al.*⁵ This LED design is inspired from III–V based heterostructures used for near-IR emission. In such devices, a quantum well is located within the *p-n* junction as a recombination center. Pradan *et al.*⁵ proposed a colloidal equivalent to this structure starting from a solar cell²⁷ in which narrow band-gap IR emitting NCs are encapsulated between the electron and hole extractors. In their work, they used PbS NCs as emitters, leading to difficulties to explore light emission above telecom wavelengths, due to the large particle size required to reach narrower band-gaps. HgTe²⁸ being a semimetal under the bulk form,^{29,30} its optical band-gap is the result of quantum confinement only.^{31–33} Thus, it allows to reach narrower band-gaps. Similarly to PbS, the emission properties of HgTe have been investigated in the near-IR^{34,35}, including the demonstration of stimulated emission²⁴ and the control of the emission using light resonators.³⁶ However, the effort dedicated to the electroluminescence of HgTe NCs remains limited.^{19,26,37–39} While in our previous work^{19,26}, we demonstrated electroluminescence from HgTe at 1300 nm, shifting the emission spectral above 2 μm requires to reconsider the LED design and operation.

The LED is made of a glass/ITO/ZnO/ZnO:HgTe/PbS/Au stack, see **Figure 2a**. In this structure ZnO is used as electron injector, while the short-thiol capped PbS NCs are used as hole injector. The emitting layer is made of a ZnO and HgTe mixture. The role of the ZnO will be further discussed in the discussion. ZnO are capped with butylamine to be soluble in chloroform a solvent where they can mix with HgTe NCs. The ligands of the active layer are exchanged for mercaptopropionic acid which maintain some PL signal while making the layer conductive. The band alignment

corresponding to this structure is determined using photoemission measurements (Supplementary note 3) and shown in **Figure 2b**.

Shifting the emission wavelength requires updates compared to the LEDs emitting in the telecom range (1.3–1.55 μm). In the visible and near-IR, the ITO layer is generally chosen to be thick (>150 nm) to minimize the electrode resistance.⁴⁰ However, in the short-wave infrared, ITO absorption becomes problematic (see Supplementary note 4): the IR transmission is less than 15 % for 180 nm thick layer. Thus, a compromise between contact resistance and light extraction has to be addressed. A 35-nm thick layer of ITO, with $\approx 70\%$ transmission of light, has improved the EQE of the 2.15 μm emitting device, while increasing the device resistance by a factor of around 10, see Supplementary note 4.

Using an infrared camera (active layer made of InSb, with $\approx 5.5 \mu\text{m}$ cut-off wavelength), it is possible to observe the electroluminescence of the LED, see **Figure 2c**. The LED presents a low turn-on voltage of around 0.6 V, close to the emitting material band-gap (0.62 eV), see **Figure 2d**. The EQE is strongly correlated to the ZnO content in the emissive layer and the best performances are obtained from 50% volume ratio. The latter corresponds to 4 ZnO per HgTe particle, see Supplementary note 5–6. For emission at 2 μm , typical EQEs are around 0.1% (up to 0.3% for the best device, see **Figure 2e**). This value drops by a factor of two as the emission wavelength is shifted from 2 to 2.3 μm , see Supplementary note 7. Since EQEs above 10% have been reported in the telecom range,^{5,6,41} these EQEs may look modest for NC-based LEDs. However, the PLQY is strongly reduced it is redshifted, and the achieved EQE are already competitive with the ones reported for light sources in this spectral range (Supplementary note 10). The latter are mostly based on epitaxially grown III–V semiconductors, presenting EQEs in the 0.1 to 1% range while, for some of them, requiring cryogenic operation. The NC-based device lifetime is determined to be 10 h for continuous operation starting at 1 W $\text{Sr}^{-1} \text{m}^{-2}$, see **Figure 2f**.

Spectral properties of the HgTe NC-based LED

We have then measured the electroluminescence spectrum of the LED, see **Erreur ! Source du renvoi introuvable.a-b**. EL signal mostly overlaps the PL spectrum from HgTe, with a small redshift and broadening compared to the PL. the latter is attributed to the ligand exchange procedure to make the film conductive. Furthermore, no signal is observed around 1100 nm, the wavelength at which the PL of PbS NC is expected to occur, also see Supplementary note 9. We can thus confirm that HgTe is the optically active material of the device. It is equally important to exclude, the possibility of an emission induced by a blackbody radiation resulting from Joule effect as current flows through the device. Under operation the surface of the LED is found to be around 33°C, see Supplementary note 8. The EL spectrum (**Erreur ! Source du renvoi introuvable.b**) appears to be much narrower and clearly blueshifted with respect to the blackbody emission corresponding to the temperature of the device operation (Supplementary note 9). This allows us to conclude that light emission is effectively due to EL and not from blackbody radiation.

Discussion

We have successfully fabricated and operated a LED above 2 μm , and then we aim to reveal the working mechanisms and in particular the role of ZnO NCs within the emissive layer. In the case of Pradhan *et al.*⁵, PbS was the emitting layer and ZnO was introduced as a surface passivation agent to limit the amount of surface traps and to stabilize PbS NCs.

*In the case of HgTe NCs, it has been observed that the presence of ZnO within the emissive layer strongly impacts the transport properties.²⁶ HgTe, with PL peak above 2 μm , presents an ambipolar conduction, as shown in the transfer curves (**Figure 3 Revealing spectral properties of the LED: (a) Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. (b)***

Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4c) obtained from an electrolyte gated field-effect transistor. A scheme of this transistor is provided in **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4a. For all films made of a ZnO:HgTe mixture with different volume ratio, we observe that this ambipolar nature is preserved, see Supplementary note 11. In this sense, the transport is fully driven by the HgTe NC array. This behavior contrasts with the one previously observed by Qu et al.,²⁶ using the same LED structure but based on wider band-gap HgTe NCs (electroluminescence peak at 1300 nm). In this case, a bulk heterojunction is formed, and the hole and electron conduction are ensured respectively by HgTe (only p-type) and by the ZnO NCs (only n-type, see **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4b).

As the emission wavelength is shifted above 2 μm , the effect of ZnO becomes more subtle. Even if the ambipolar transport coming from HgTe is preserved after ZnO is introduced (see Supplementary note 10), a shift of the neutrality point toward higher positive gate biases is observed, **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4d. Simultaneously, the ratio of the electron mobility over the hole mobility drops. These two behaviors suggest that electrons are transferred from HgTe NCs to ZnO NCs, tuning then the carrier density in the conductive HgTe array.

To further confirm this charge transfer, we follow the transient reflectivity signal for the mixture **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4e. In this HgTe:ZnO mixture, it appears that the carrier relaxation at long time scale is barely affected by the addition of ZnO, see **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4e (left insert). On the other hand, the rising time (linked to intra-conduction band relaxation) appears to depend on the ZnO presence. In particular, the relative magnitude of the fast component is reduced by the introduction of ZnO, see arrows **Figure 3 Revealing spectral properties of the LED: (a)** Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. **(b)** Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4e (right insert). As shown in the **Figure 1e-f** regime I, this fast component is related to hot states, ≈ 0.9 eV above the conduction band, which partly delocalize in the surrounding environment. Thus, the hot electrons generated in HgTe can easily get transferred to the ZnO. As a result of this

charge transfer, electrons no longer relax toward the conduction band edge and the relative weight of this component gets reduced. Finally, X-ray photoemission (XPS) also confirms this charge transfer. XPS overview spectrum show contribution from both HgTe and ZnO, as well as their thiol (S atoms) surface chemistry, see **Figure 5a**. The Hg 4f core levels include two contributions that are attributed to Hg bound to Te in the NC core (binding energy (Hg 4f_{7/2}) =100.39 eV) and to Hg bound to sulfur via surface thiols (binding energy (Hg 4f_{7/2}) =100.97 eV), see **Figure 5b**. Compared to pristine HgTe, the introduction of ZnO leads to a 50 meV shift of the Hg 4f binding energy towards higher values (Supplementary note 11). For ZnO, a shift of the Zn 3d core level toward lower binding energies is observed when HgTe is added. This observation further supports an electron transfer from HgTe to ZnO.

In the last part of the paper, time resolved photoemission (TrXPS) is performed to follow the light-induced shift of the core level binding energy after laser excitation. This method is a pump-probe approach, for which a 1.55 eV pulsed laser is used to excite the system and the synchrotron beam is used as a probe. A schematic of this experiment is given in **Figure 5c**. While transient reflectivity gives insight on intraparticle relaxations, TrXPS provides device-oriented insights^{42,43}. In particular, the method can be used to reveal the nature of the majority carriers without inducing charge injection as it is done in field effect transistors.^{44,45} In the case of HgTe:ZnO films, we observe a change of sign of the surface photovoltage signal with the increase of ZnO content, see **Figure 5d**. At high HgTe contents (>50%), the binding energy shift of Hg 4f is negative, consistent with a p-type interface band bending. When the amount of ZnO is larger (*i.e.* 25% of HgTe content), the Hg 4f binding energy shift becomes positive, revealing an overall n-type nature for the film. Last, it is also interesting to follow the TrXPS of the Zn 3d state. In the absence of HgTe, no signal is observed due to the large band-gap nature of ZnO, which cannot be excited by the 800-nm laser source, see Supplementary note 12. However, in the presence of HgTe, the Zn 3d appears to be light-sensitive and presents a strong light-induced shift, see **Figure 5e**: beyond the charge transfer occurring in the dark, these two materials are electrostatically coupled and rigidly shift together.

Combining electronic transport and TrXPS, we can draw the following conclusion for the role of ZnO within the active layer. For this given emitting wavelength (2–2.3 μm), transport occurs only within the HgTe NC array which ensure both the electron and hole conduction. ZnO controls the carrier density and can switch the conduction of the HgTe:ZnO film from electrons to holes. As the ZnO content tunes the majority carrier nature, it also modifies the charge injection balance. We can then connect the ZnO ratio at which the TrXPS signals changes its sign to the emissive layer composition that maximizes the LED EQE (Supplementary note 5–6).

To summarize, we have designed a LED presenting an emission in the extended SWIR (2–2.3 μm range) using HgTe NCs as emissive material. The diode stack is based on glass/ITO/ZnO/HgTe/ZnO/PbS/gold layers. Compared to their counterparts at shorter wavelengths (1.6 μm and less), the LED structure requires updates and, in particular, a compromise between the resistance and the transparency of the bottom electrode. Best EQE reaches 0.3%, which already matches the performance of emitters at similar wavelength based on III–V semiconductors. In spite of being clearly inspired by the structure operated in the telecommunication range, the LED operation mechanisms strongly differ. Transport is only driven by the HgTe NCs, and ZnO is introduced to tune the nature of the majority carriers, as consistently revealed by the transport, transient reflectivity and time resolved photoemission measurements. By tuning the doping of HgTe NCs, the ZnO is used to obtain better charge balance and to maximize the EQE. Future works will have to focus on the lifetime improvement (currently around 10 h) and pulsed operation may be useful to reduce heat-induced damages.

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Author contributions statement

E.L. designed the project. J.Q. and Y.P. grew the nanocrystals with the support of E.I and S.I. G.P. conducted TEM imaging. J.Q. fabricated the diode with the support of E.B. J.Q. and E.B. characterized the diode with the support of A.C. and G.V. for infrared camera imaging. D.B., M.W., S.G.M., E.B. measured the EL spectrum. Synchrotron measurements have been done by C.G., C.D. and M.G.S. M.W., S.G.M., E.P. and D.B. conducted the transient reflectivity measurements. All authors discussed the results; E.L. wrote the manuscript with input from all other authors.

COMPETING INTEREST Statement

The authors declare no competing interests.

Figure Legends

Figure 1 Spectroscopic properties of 2 μm emitting HgTe NCs: **a** Absorption and photoluminescence (PL) spectra of HgTe NCs for which the PL occurs at 2 μm . **b** PL spectra for three different sizes of HgTe NCs: PL maxima occur at 2, 2.15 and 2.3 μm respectively. **c** STEM-HAADF image of HgTe nanocrystals presenting a PL maximum at 2 μm . Scale bar is 50 nm. **d** Transient reflectivity measurements in a two-color pump-probe configuration for several pump fluences. An 800 nm pump pulse and a 2 μm probe pulse are used. **e** Early time scale transient reflectivity signal as depicted in part d for a fluence of 60 $\mu\text{J cm}^{-2}$. **f** Simplified scheme of the transitions involved in the pump and probe processes. VB, CB_G and CB_H stand for valence band, conduction band ground state and conduction band hot state respectively.

Figure 2 LED design and performance with emission at 2 μm : **a** Schematic of the multilayer stack used for 2 μm emitting LED. **b** Band diagram corresponding to the stack depicted in part a. **c** Infrared image (from InSb camera) of the LED under operation. Scale bar is 1 cm. **d** Current and radiance as a function of the applied bias for the 2 μm emitting LED. **e** EQE and radiance as a function of the applied driving current for the 2 μm emitting LED. **f** Radiance as a function of time

with the 2 μm emitting LED driven under a constant current of 900 mAcm^{-2} (corresponding to an initial radiance of 1 $\text{W Sr}^{-1}\text{m}^{-2}$).

Figure 3 Revealing spectral properties of the LED: (a) Comparison of the PL spectrum and electroluminescence spectrum in the 1-2.5 μm range. (b) Comparison of the PL and EL spectra with the blackbody radiation at 33°C (measured to be the temperature of the device under operation at 7 mA) in the 1 to 10 μm range.

Figure 4 Transport and dynamic properties of HgTe:ZnO film: a Schematic of an electrolyte field effect transistor whose channel is based on HgTe:ZnO film. Transfer curves (drain and gate currents as a function of the applied gate bias) for a thin film of ZnO NCs (b – $V_{\text{DS}}=0.5$ V) and HgTe NCs (c – $V_{\text{DS}}=0.2$ V). d Neutrality gate bias and the ratio of the electron and hole mobilities as a function of the HgTe content for a field effect transistor based on HgTe:ZnO NC channel. e Comparison of the transient reflectivity behavior of two types of samples: pure HgTe and a mixture of HgTe:ZnO (with 50 % of HgTe, this set of data is multiplied by 2 to normalize the signal by the amount of material). The arrows highlight the magnitude of the regime I. Insets show the same data using two different time scale windows.

Figure 5 Static and time resolved photoemission for HgTe:ZnO nanocrystals based thin film: a Overview spectrum of HgTe:ZnO nanocrystal-based thin film. b Photoemission spectrum relative to the Hg 4f states from HgTe:ZnO nanocrystal-based thin film. c Schematic of the pump-probe photoemission setup used to perform time resolved photoemission. A 800-nm laser is used as pump, while the soft x-rays from the synchrotron are used as probe. Acquisition is made by focussing on a given core level and following the shift of its binding energy after illumination. d Shifts of the binding energy for the Hg 4f core level after its illumination by a short 800-nm laser pulse obtained from film containing 100, 50 and 25% of HgTe. e Shift of the binding energy for the Zn 3d core level after its illumination by a short 800-nm laser pulse obtained from a film containing 50 % HgTe.

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METHODS

DATA AVAILABILITY

The data that support the findings of this study are available upon reasonable request.

HgTe nanocrystals emitting at 2 μm : In a 100 mL three neck flask, 543 mg of HgCl_2 and 50 mL of oleylamine were degassed under vacuum at 110 °C for 1 h. Meanwhile, 2 mL of TOP:Te (1 M) were extracted from the glove box and mixed with 8 mL of oleylamine. After that the atmosphere was switched to N_2 and the temperature was set as 70 °C. When the temperature stabilized, the TOP:Te solution was quickly injected. After 3 min of reaction, 10 mL of DDT/Toluene (1:9 in volume) solution was injected and a water bath was used to quench the reaction. The nanocrystals were precipitated with methanol and redispersed in CHCl_3 twice. After that, the nanocrystals dispersed in CHCl_3 were centrifugated to remove the unstable phase. The stable phase was precipitated again with methanol and stored in CHCl_3 at a concentration of 30 $\text{mg}\cdot\text{mL}^{-1}$. To shift the emission to 2.15 μm (resp. 2.3 μm), the reaction is conducted at 75 °C (resp. 80 °C).

TEM: A drop of diluted NCs solution was drop-casted onto a copper grid covered with an amorphous carbon film. The grid was degassed overnight under secondary vacuum. Imaging was conducted using a JEOL 2010 transmission electron microscope operated at 200 kV. Complementarily, TEM/STEM observations were made on a Titan Themis 200 microscope (FEI/Thermo Fischer Scientific) equipped with a geometric aberration corrector on the probe. The microscope was also equipped with the "Super-X" systems for EDX analysis with a detection angle of 0.9 steradian. The observations were made at 200 kV with a probe current of about 35 pA and a half-angle of convergence of 17 mrad. HAADF-STEM images were acquired with a camera length of 110 mm (inner/outer collection angles were respectively 69 and 200 mrad).

UV-Vis spectra of nanocrystal solution or thin films were recorded using a JASCO V-730 spectrometer.

Infrared absorption spectroscopy was conducted using a Fisher IS50 Fourier transform Infrared spectrometer. To measure the absorption of the obtained NCs, ATR configuration with a white light source, a CaF_2 beam splitter and DTGS detector was used. Typically, a drop of NC solution was deposited and dried on the diamond cell. Spectra are acquired from 12 000 cm^{-1} to 2100 cm^{-1} with a 4 cm^{-1} resolution while averaging over 32 spectra.

Infrared photoluminescence spectroscopy was obtained again by a Fisher IS50 Fourier transform Infrared spectrometer. The infrared-emitting NCs were drop-casted onto a glass substrate and illuminated by a blue (460 nm) LED. The infrared PL, as an external light source, was fed into the Fisher IS50 Fourier transform Infrared spectrometer, in which the CaF_2 was chosen as the beam splitter, and the extended InGaAs sensor as the detector. Spectra were typically acquired from 8 000 cm^{-1} to 3000 cm^{-1} with a 4 cm^{-1} resolution while averaging over 32 spectra.

Infrared ultrafast spectroscopy: Time-resolved reflectivity measurements have been performed in a standard pump-probe setup, using a commercial laser system at 1 kHz repetition rate and centered at 800 nm, with $\Delta\tau = 35$ fs pulse duration and 1.5 mJ energy per pulse. The laser pulse is split into two parts, with energy balance of 10%/90%. The time delay between the two pulses is

controlled by a motorized micrometric stepmotor. The highest energy arm is used to pump an optical parametric amplifier (OPA), which allows wavelength tuning from around 1 micron up to around 20 microns. For the experiment presented here, we used the 800 nm pulse as pump and the OPA pulse at 2 μm as probe. The typical fluence is 60 $\mu\text{J}\cdot\text{cm}^{-2}$. Typical focal spot size are around 500 microns for the pump and 250 microns for the probe. Both pump and probe pulses arrive close to the normal incidence on the sample. The pump was chopped mechanically at 0.5 kHz, and the signal was detected using a photodiode connected to a lock-in amplifier. We can neglect the coulombic shift in the analysis of the transient reflectivity since the charging energy of the HgTe NC (≈ 20 meV) is small compared to the pulse broadening (60 and 40 meV for the pump and the probe, respectively).

X-ray photoemission measurements (XPS): For photoemission spectroscopy, we used the Tempo beamline of synchrotron Soleil. Films of nanocrystals were spin-casted onto a gold coated Si substrate (gold layer was 80 nm thick). The ligands of the nanocrystals were exchanged using the same procedure as for the device fabrication to avoid any charging effect during measurements. Samples were introduced in the preparation chamber and degassed until a vacuum below 10^{-9} mbar was reached. Then samples were introduced to the analysis chamber. The signal was acquired by a MBS A-1 photoelectron analyzer equipped with a delay line detector developed by Elettra.⁴⁶ Acquisition was done at constant pass energy (50 eV) within the detector. Photon energy of 150 eV was used for the acquisition of valence band and work function while 600 eV photon energy was used for the analysis of the core levels. A gold substrate was used to calibrate the Fermi energy. The absolute value of the incoming photon energy is determined by measuring the first and second orders of Au4f core level peaks. Then for a given analyzer pass energy, we measure the Fermi edge and set its binding energy as zero. The same shift is applied to all spectra acquired with the same pass energy. To determine the work function, we apply an 18 V bias, whose exact value has been determined by looking at the shift of a Fermi edge.

Time resolved X-ray photoemission measurements (TrXPS): The sample was excited by a 800 nm Ti:sapphire laser (RegA from COHERENT). The pulse duration was around 60 fs. The repetition rate was 284 kHz. 10% of the maximum Laser Power was used to excite the sample. The output equivalent CW power used for the experiment was 100 mW and the beam spot was typically 300 $\mu\text{m}\times 300 \mu\text{m}$ (synchrotron beam) and 400 $\mu\text{m}\times 2 \text{ mm}$ (laser beam). The FWHM of them are at the sample level. The laser beam was spatially aligned to overlap with the synchrotron beam on the sample holder. The pump probe TrXPS was conducted in stroboscopic mode (*i.e.* the detection of the photoelectron analyser was synchronized with the laser pulse excitation) where the temporal resolution was determined by the time response of the high-resolution photoelectron analyzer. The latter was estimated to be 30 ns, limited by the spread of the electrons between the hemispheres. Then, the photoemission spectrum of a given core level was acquired every 10 ns. Each spectrum of the series was fitted by two Gaussians to extract the binding energy of each peak. This procedure enables to follow energy shifts as small as 5 meV. Since the excitation duration (<1 ps) is much shorter than the temporal resolution (30 ns), only the decay of the binding energy after illumination can be followed.

LED fabrication - ITO patterning: ITO substrates (7 Ω/sq) with a thickness of 180 nm were cut into 15 mm \times 15 mm pieces and cleaned by sonication in acetone for 5 min. After sonication, the substrates were rinsed with acetone and isopropanol before dried completely with N_2 flow. The substrates were further cleaned with O_2 plasma for 5 min to remove organic residuals on the surface. After cleaning, TI-Prime and AZ 5214E photoresist were sequentially spin-coated on the surface of

ITO substrates at the rate of 4000 rpm for 30 s and baked at 110 °C for 120 s and 90 s, respectively. In the next stage, a mask aligner was used to expose the substrates to UV light (using a UV lamp generating h-line (405 nm) and i-line (365 nm) with a 15 W.cm⁻² total irradiance) for 20 s through a lithography mask (1 mm width). Photoresist was then developed using AZ 726 developer for 20 s before rinsed with deionized water and dried. After another 5-minute plasma cleaning, the substrates were etched in a 25% HCl (in water) bath for 10 min at 40 °C before they were dipped immediately in deionized water. Finally, the lift-off of photoresist was conducted in an acetone bath.

LED fabrication - *n*-type ZnO layer deposition: On the top of a patterned ITO substrate, ZnO nanoparticles dispersed in Toluene (40 mg.mL⁻¹) were spin coated at a speed of 2000 rpm for 45 s. The film was subsequently annealed at 250 °C for 5 min on a heating plate. The above steps were repeated two more times to obtain a ZnO layer of 100-110 nm.

LED fabrication - Emitting ZnO/HgTe layer deposition: First, HgTe and ZnO solutions in CHCl₃ at the same concentration of 30 mg.mL⁻¹ were prepared. Then, the two solutions were mixed according to the desired ratio, which was defined by the percentage of HgTe volume in the HgTe/ZnO mixture solution, for example, HgTe (50%)/ZnO represents that the HgTe solution takes up 50% of the mixture solution. The mixture solutions were spin coated on the top of ZnO bottom layer at a speed of 4000 rpm. After each layer deposition, ligand exchange was conducted by adding several drops of MPA in methanol (0.05% in volume) on the film and allowed them stay for 10 s before dried by spinning. The excess ligands were rinsed twice with methanol and dried. For each device, three HgTe/ZnO layers were deposited, leading to an emitting layer of around 120 nm.

LED fabrication - *p*-type PbS layer: EDT-capped PbS nanocrystals absorbing at 980 nm were used to build a hole injection layer. Inside a glovebox, a PbS solution (30 mg.mL⁻¹ in toluene) was spin coated at 2500 rpm on the top of MPA-capped HgTe/ZnO emitting layers. EDT in acetonitrile (0.03% in volume) was used for the ligand exchange. The EDT solution in acetonitrile was deposited on the film for 1 min before being dried and rinsed twice with acetonitrile. Three layers of EDT-capped PbS were deposited successively to achieve an overall thickness of around 60 nm.

LED fabrication - Top contact: After the deposition of the PbS nanocrystal layers, the sample was set into a thermal evaporator. 80 nm of Au was deposited at the vacuum below 5x10⁻⁶ mbar through a shadow mask. The pixel size, which is defined as the overlap of the ITO and Au contact, is 1 mm².

Infrared electroluminescence spectroscopy: The electroluminescence spectrum has been measured from the *in-operando* device in the following way. The emitting device was put in the focal point of a golden off-axis parabola with 5 cm focal lens, and overture of 10 cm. This allows to cover a large solid angle, given that the emission is isotropic. The outgoing reflected beam is nearly parallel to the propagation direction. We used two additional off-axis parabolas with 18 cm and 9 cm focal length, respectively, in order to ensure a reduction of the beam size of a factor of 2, which implies a photon density twice as much and therefore improves the signal-to-noise ratio. In the focal spot between these two off-axis parabolas, we put a mechanical modulator (chopper), in order to modulated the continuous emitted beam at an arbitrary selected frequency of 456 Hz. The collimated beam was sent into a FTIR spectrometer (Fischer IS 50 with step scan). The detector was connected to a lock-in amplifier (SR830 Stanford Research Systems), which selectively detects only the signal at the master reference of 456 Hz. In this way, we were able to further increase the sensitivity of the measurement. The spectrums were acquired using the step-scan mode of the FTIR spectrometer.

We acquired the spectrum as function of the current/voltage applied to the device, in order to measure the spectrum corresponding to several emitting conditions, see supplementary note 9.

EQE and radiance. Assuming that the LED emission is Lambertian, the flux leaving the device directly can be described as $P = \int_0^{\pi/2} 2\pi L_0 \cos\theta \sin\theta d\theta = \pi L_0$, with L_0 the flux per solid angle of light leaving the device in the forward direction. The number of photons emitted per second to the forward direction was obtained by $N_p = \frac{P}{h\nu} = \frac{\lambda P}{hc}$, with λ the wavelength of the electroluminescence peak, h the Plank's constant and c the speed of light. The number of electrons injected per second can be obtained by $N_e = \frac{I}{e}$, with I the current flow in the device. Thus, the EQE can be calculated as $\frac{N_p}{N_e} = \frac{\lambda e P}{h c I}$, and the irradiance of the device $R = \frac{L_0}{S_2} = \frac{P}{\pi S_2}$, with S_2 the area of the pixel.