



Electroluminescence from nanocrystals above 2 μm

Junling Qu¹, Mateusz Weis², Eva Izquierdo¹, Simon Gwénaél Mizrahi², Audrey Chu¹, Corentin Dabard^{1,3}, Charlie Gréboval¹, Erwan Bossavit¹, Yoann Prado¹, Emmanuel Péronne², Sandrine Ithurria³, Gilles Patriarche⁴, Mathieu G. Silly⁵, Grégory Vincent⁶, Davide Boschetto² and Emmanuel Lhuillier¹✉

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 in which 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. Here we report the design of a HgTe nanocrystal-based LED with luminescence between 2 and 2.3 μm . With an external quantum efficiency of 0.3% and radiance up to 3 W Sr^{−1} m^{−2}, these HgTe LEDs already present a competitive performance for emission above 2 μm .

The bright and spectrally tunable emission of nanocrystals (NCs) is certainly their most striking property and has led to their integration as light downconverters for displays¹. The desire to reduce device electrical consumption and enhance the light contrast has driven the development of NC-based light-emitting diodes (LEDs)^{2,3}. In the visible, such LEDs have almost reached commercial status. Using narrower-bandgap NCs, such as PbS (refs. ^{4,5}) or Ag₂S (ref. ⁶), near-infrared LEDs presenting bright and tunable emission up to 1,700 nm have also been reported.

In this range of wavelengths, corresponding to telecom applications, NC-based LEDs suffer from competition with III–V epitaxially grown quantum-well structures, which 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 constraint of requiring 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 because of the strong coupling between the exciton and molecular vibrations, limiting light emission to wavelengths below 1 μm (ref. ⁷). Indium-based III–V semiconductors, used for emission in the 1.3–1.5 μm range, present a too wide bandgap to reach longer emission wavelengths. In the mid-infrared, quantum cascade lasers (QCLs) have been the most successful solid-state sources for the past decade, representing the success of wavefunction engineering. However, their power conversion efficiencies remain weak due to voltage biases above 10 V (for emission around ~ 250 meV) and large current thresholds (> 0.5 A). Although the mid- and far-infrared regimes 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 lasers⁸, interband QCLs^{10,11} and GeSn^{12,13}, which again present 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 . Low-cost light sources, operating in this range of

wavelengths, are of utmost interest to monitor leaks in methane tankers or to follow greenhouse effects, for example. Airfield lighting is also a typical application requiring infrared emission. Historically, light bulbs emitting in both visible (for pilot guiding) and infrared ranges have been used for instrument guiding. To reduce electrical consumption and increase device lifetimes, light bulbs have been replaced with visible LEDs, thus losing the infrared guiding light.

In this Article 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 ($n \approx 2.3$ typically¹⁵, but $n > 4$ for most Sb-based semiconductors), easing light extraction towards free space. We also report the fabrication of an NC-based LED presenting tunable emission in the 2–2.3 μm range, with a turn-on voltage close to the bandgap energy and a low threshold current (20 mA cm^{−2}) and an external quantum efficiency (EQE) comparable to those of state-of-the-art Sb-based epitaxially grown LEDs.

Results

Spectroscopic properties of HgTe NCs. We began with the growth of HgTe NCs¹⁶ with photoluminescence (PL) above 2 μm . The procedure is taken from ref. ¹⁷. Transmission electron microscopy (TEM) investigations (Fig. 1c, Supplementary Methods and Supplementary Note 1) show a clearly branched aspect for these particles. Despite their poor shape control, these branched HgTe NCs present a narrower band-edge feature than spherical NCs^{18,19}. These HgTe NCs are photoluminescent (Fig. 1a,b), with the PL signal redshifted by 120 nm from the absorption maximum due to the Stokes' shift. The PL presents a peak at 2 μm and the full-width at half-maximum (FWHM) is around 280 nm, corresponding to $\lambda/\Delta\lambda \approx 7.2$. The PL efficiency of this material was previously found to be around 1% for emission at 2 μm (ref. ²⁰). Increasing the temperature during growth leads to larger NCs, inducing a redshift of the PL peak (Fig. 1b). In this Article we focus on particles emitting in the 2–2.3 μm range.

¹Institut des NanoSciences de Paris, Sorbonne Université, Paris, France. ²Laboratoire d'Optique Appliquée, CNRS, Ecole Polytechnique, ENSTA Paris, Institut Polytechnique de Paris, Palaiseau, France. ³Laboratoire de Physique et d'Etude des Matériaux, ESPCI-Paris, PSL Research University, Sorbonne Université, Paris, France. ⁴Centre de Nanosciences et de Nanotechnologies, Université Paris-Saclay, Palaiseau, France. ⁵Synchrotron-SOLEIL, Saint-Aubin, France.

⁶ONERA – The French Aerospace Lab, Palaiseau, France. ✉e-mail: el@insp.upmc.fr

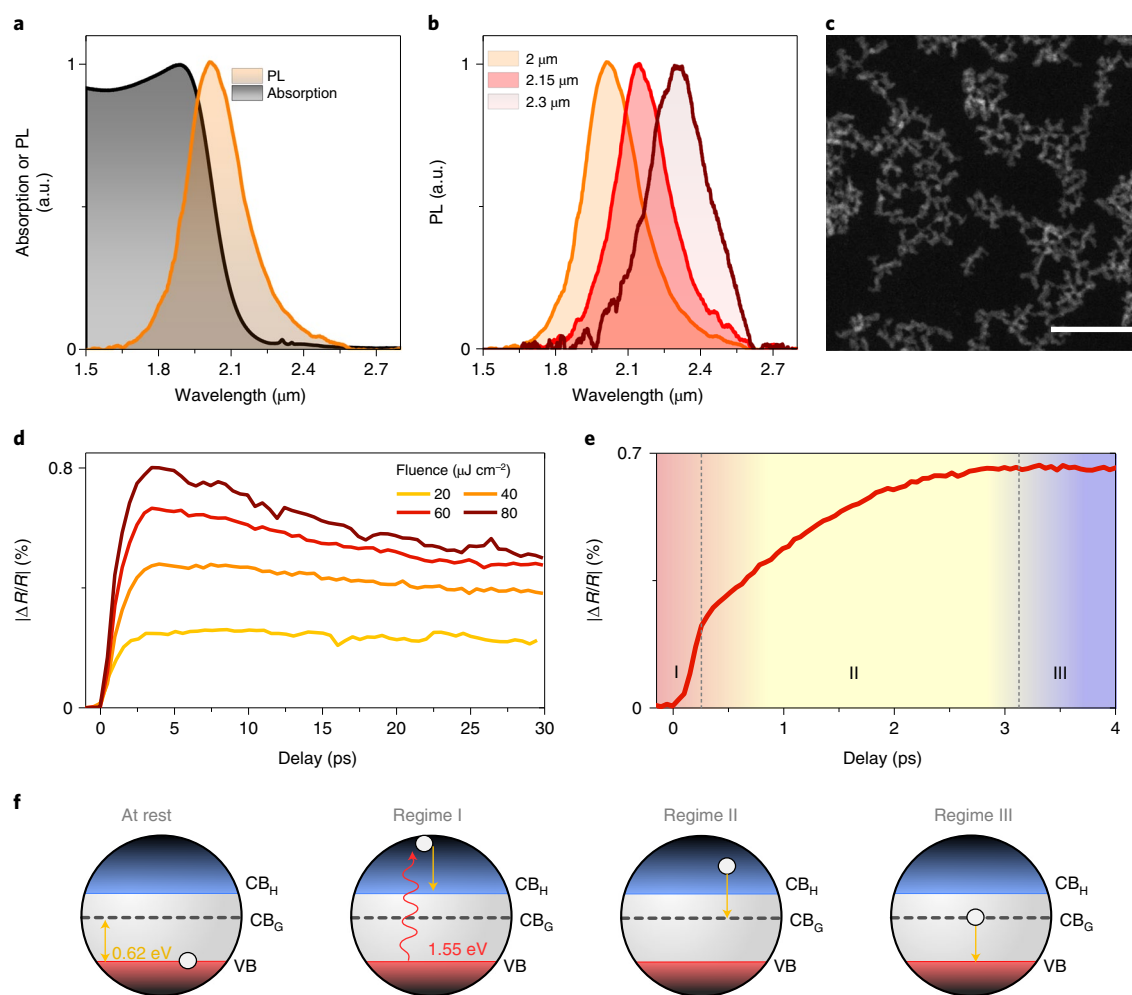


Fig. 1 | Spectroscopic properties of 2- μm -emitting HgTe NCs. **a**, Absorption and PL spectra of HgTe NCs for which the PL occurs at 2 μm . **b**, PL spectra for three different sizes of HgTe NCs, showing PL maxima occurring at 2, 2.15 and 2.3 μm , respectively. **c**, HAADF-STEM image of HgTe NCs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

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

In the first picoseconds, two different behaviours can be observed: a first sharp rise (Fig. 1e, regime I), followed by a smoother increase (regime II) of the transient reflectivity. In HgTe, the effective mass asymmetry between holes and electrons makes the valence band behave as a continuum, while the density of states is sparse close to the conduction band-edge and only hot conduction-band states (CB_H) can be assimilated to a continuum. The sharp rise is due to the action of the pump, which partially empties the valence bands by promoting the electrons into the conduction-band states (CB_H in Fig. 1f), located ~ 0.9 eV above the band-edge. The probed states

are therefore no longer the same as that at equilibrium, and involve intraband transitions within CB_H (Fig. 1f, regime I). These electrons thermalize into the empty conduction states at a timescale of ~ 250 fs. The hot conduction-band states, being quite high in energy, are delocalized. As a 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 the conduction-band ground state, CB_G (Fig. 1f, regime II). Thereafter, the long decay tail (5–30 ps range, Fig. 1d) corresponds to relaxation of the electrons down to their initial valence states (regime III). The decay time is clearly affected by the pump fluence (Fig. 1d and Supplementary Note 2)—this behaviour matches the Auger relaxation observed from transient PL measurements^{20,21,24,25}. Only at a longer timescale is the decay resulting from the neutral exciton expected to occur with a 2-ns characteristic relaxation^{20,26}.

Performance of a HgTe NC-based LED. To design an LED based on HgTe NCs emitting at 2 μm and above, we used the LED structure

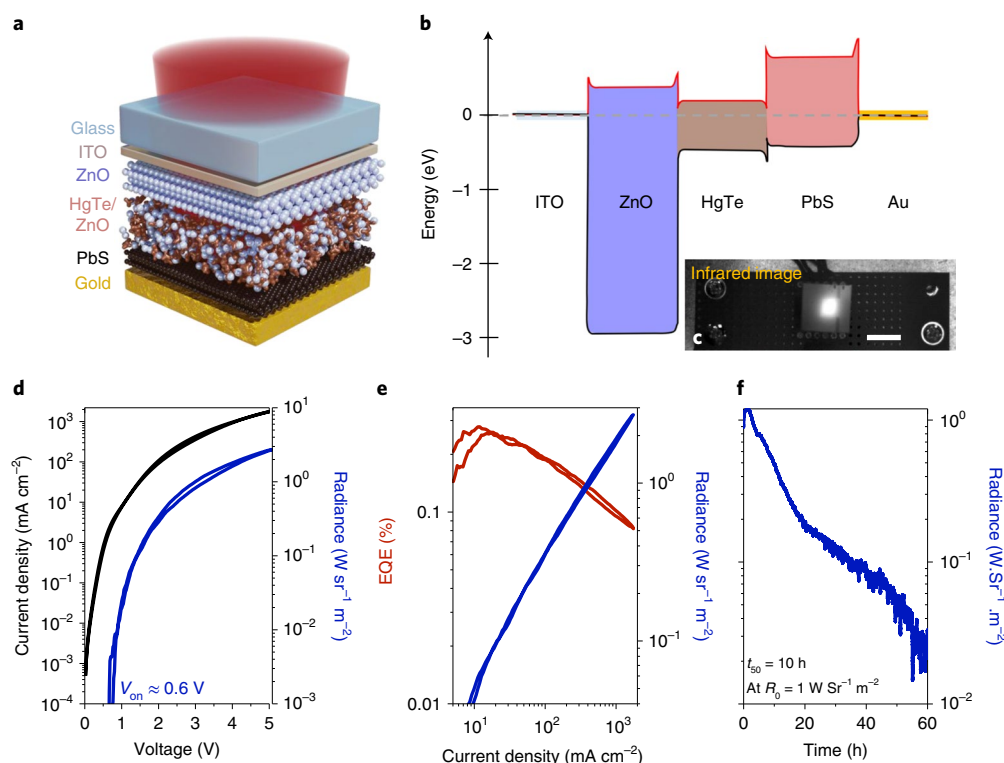


Fig. 2 | LED design and performance with emission at 2 μm . **a**, Schematic of the multilayer stack used for the 2- μm -emitting LED. **b**, Band diagram corresponding to the stack depicted in **a**. **c**, Infrared image (obtained using an InSb camera) of the LED under operation. Scale bar, 1 cm. **d**, Current (black) and radiance (blue) as a function of applied bias for the 2- μm -emitting LED. **e**, EQE (red) and radiance (blue) 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 mA cm^{-2} (corresponding to an initial radiance, R_0 , of 1 $\text{W Sr}^{-1} \text{m}^{-2}$).

proposed by Pradhan and colleagues⁵. This LED design is inspired by the III–V-based heterostructures used for near-infrared emission. In such devices, a quantum well is located within the p–n junction as a recombination centre. Pradhan et al.⁵ proposed a colloidal equivalent to this structure starting from a solar cell²⁷, in which narrow-bandgap infrared-emitting NCs are encapsulated between the electron and hole extractors. In their work, they used PbS NCs as emitters, leading to difficulties in exploring light emission above telecom wavelengths due to the large particle size required to reach narrower bandgaps. In HgTe²⁸, being a semimetal in bulk form^{29,30}, the optical bandgap is the result of quantum confinement only^{31–33}. It thus allows narrower bandgaps to be reached. Similar to PbS, the emission properties of HgTe have been investigated in the near-infrared^{34,35}, including the demonstration of stimulated emission²⁴ and control of the emission using light resonators³⁶. However, the effort dedicated to investigating the electroluminescence (EL) of HgTe NCs remains limited^{19,26,37–39}. Although, in our previous work^{19,26}, we demonstrated EL from HgTe at 1,300 nm, shifting the emission spectra above 2 μm requires reconsideration of the LED design and operation.

Our LED is made of a glass/indium tin oxide (ITO)/ZnO/ZnO:HgTe/PbS/Au stack (Fig. 2a). In this structure, ZnO serves as the electron injector and the short-thiol-capped PbS NCs as the hole injector. The emitting layer is composed of a mixture of ZnO and HgTe. The role of the ZnO will be discussed further in the Discussion. The ZnO is capped with butylamine to be soluble in chloroform (CHCl_3), a solvent where they can mix with HgTe NCs. The ligands of the active layer are exchanged for mercaptopropionic acid (MPA), which maintains some PL signal while making the layer conductive. The band alignment corresponding to this

structure was determined using photoemission measurements (Supplementary Note 3) and is shown in Fig. 2b.

Shifting the emission wavelength requires adjustments to the LEDs emitting in the telecom range (1.3–1.55 μm). In the visible and near-infrared, the ITO layer is generally chosen to be thick (>150 nm) to minimize the electrode resistance⁴⁰. However, in the short-wave infrared, ITO absorption becomes problematic (Supplementary Note 4), as the infrared transmission is <15% for a 180-nm-thick layer. Thus, a compromise between contact resistance and light extraction has to be made. A 35-nm-thick layer of ITO, with ~70% transmission of light, improved the EQE of the 2.15- μm -emitting device while increasing the device resistance by a factor of ~10 (Supplementary Note 4).

Using an infrared camera (active layer of InSb, with a cutoff wavelength of ~5.5 μm), it is possible to observe the EL of the LED (Fig. 2c). The LED presents a low turn-on voltage of ~0.6 V, close to the emitting material bandgap (0.62 eV; Fig. 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 four ZnO per HgTe particle (Supplementary Notes 5 and 6). For emission at 2 μm , typical EQEs are around 0.1% (up to 0.3% for the best device; Fig. 2e). This value drops by a factor of two as the emission wavelength is shifted from 2 to 2.3 μm (Supplementary Note 7). Because EQEs above 10% have been reported in the telecom range^{5,6,41}, these EQEs may look modest for NC-based LEDs. However, the PL quantum yield is strongly reduced as it is red-shifted, and the achieved EQE is already competitive with the values 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 0.1–1% range, but with

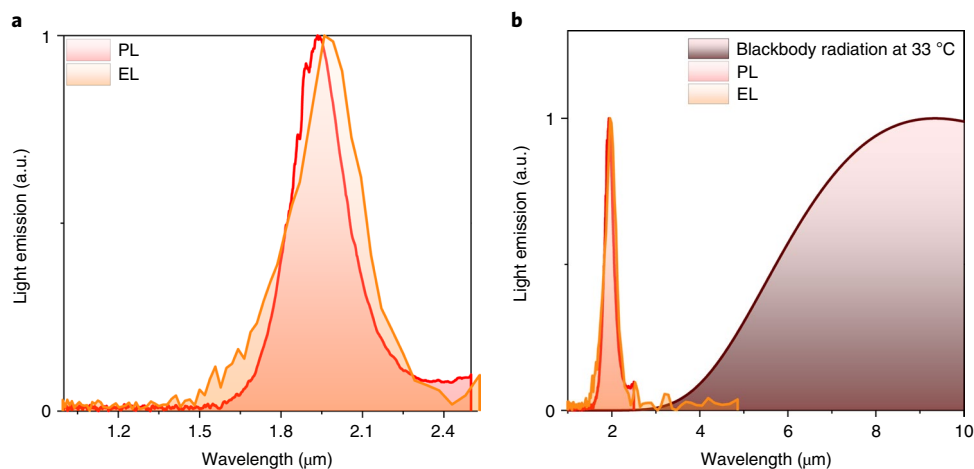


Fig. 3 | Revealing spectral properties of the LED. **a**, Comparison of the PL spectrum and EL spectrum in the 1–2.5 μm range. **b**, Comparison of the PL and EL spectra with the blackbody radiation at 33 °C (measured to be the temperature of the device under operation at 7 mA) in the 1–10 μm range.

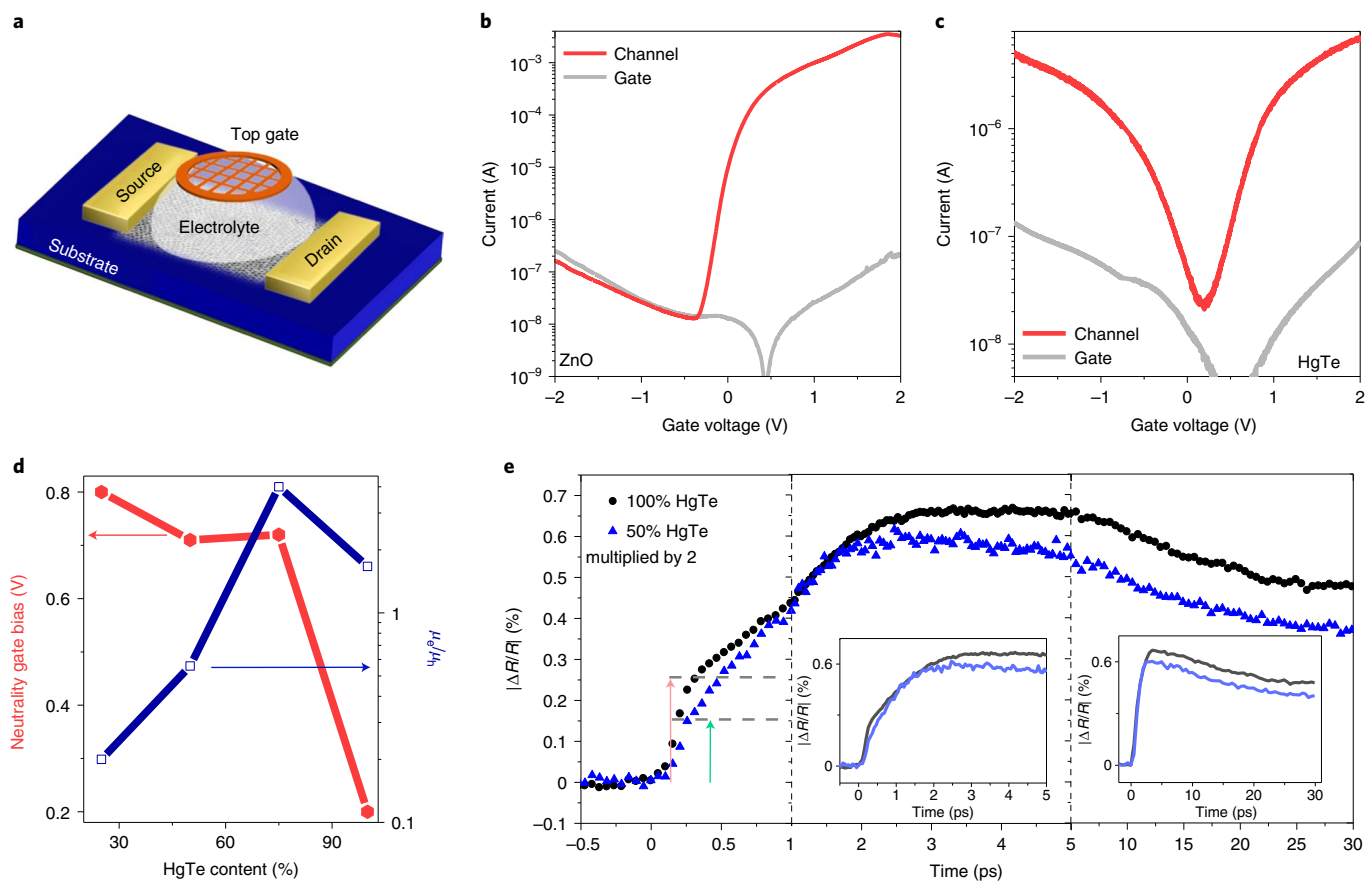


Fig. 4 | Transport and dynamic properties of the HgTe:ZnO film. **a**, Schematic of an electrolyte field-effect transistor with its channel based on HgTe:ZnO film. **b**, **c**, Transfer curves (drain and gate currents as a function of applied gate bias) for a thin film of ZnO NCs (**b**, $V_{DS} = 0.5$ V) and HgTe NCs (**c**, $V_{DS} = 0.2$ 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 the HgTe:ZnO NC channel. **e**, Comparison of the transient reflectivity behaviour of two types of sample: pure HgTe and a mixture of HgTe:ZnO (with 50% of HgTe, this set of data is multiplied by two to normalize the signal by the amount of material). The arrows highlight the magnitude of regime I (red arrow for HgTe only, green arrow for mixture). Insets show the same data using two different timescale windows.

some of them requiring cryogenic operation. The NC-based device lifetime is determined to be 10 h for continuous operation starting at $1 \text{ W Sr}^{-1} \text{ m}^{-2}$ (Fig. 2f).

Spectral properties of the HgTe NC-based LED. We then measured the EL spectrum of the LED (Fig. 3a,b). The EL signal mostly overlaps the PL spectrum from HgTe, with a small redshift and broadening

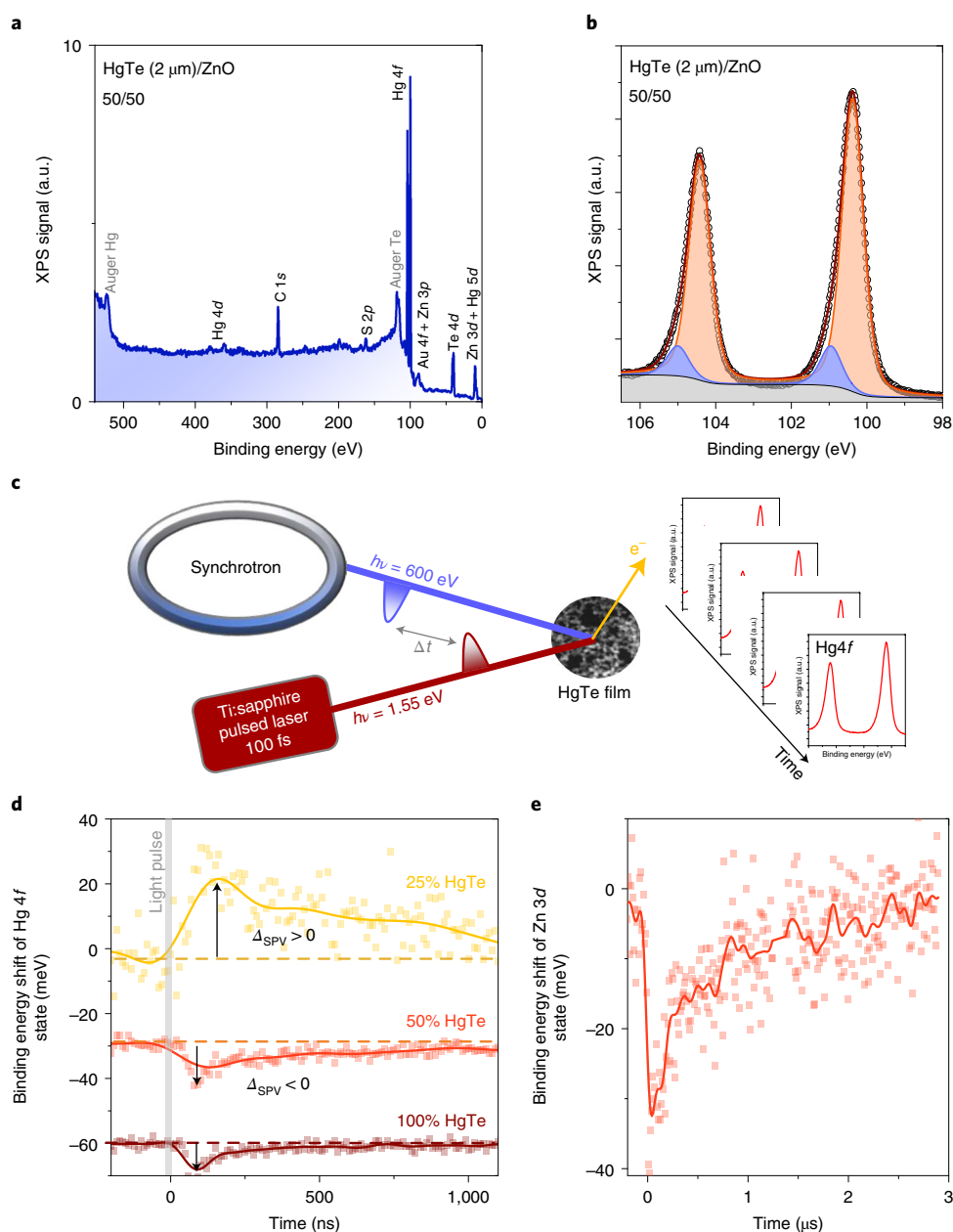


Fig. 5 | Static and time-resolved photoemission for HgTe:ZnO NC-based thin film. **a**, Overview spectrum of the HgTe:ZnO NC-based thin film. **b**, Photoemission spectrum relative to the Hg 4f states from HgTe:ZnO NC-based thin film. **c**, Schematic of the pump-probe photoemission set-up used to perform time-resolved photoemission. An 800-nm laser is used as the pump, while the soft X-rays from the synchrotron are used as the probe. Acquisition is made by focusing 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. In **d** and **e**, squares are experimental points and lines are averaged signal.

compared to the PL. The latter is attributed to the ligand exchange procedure used to make the film conductive. Furthermore, no signal is observed around 1,100 nm, the wavelength at which the PL of PbS NCs is expected to occur (also 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 blackbody radiation resulting from the Joule effect as current flows through the device. Under operation, the surface of the LED is found to be at $\sim 33^\circ\text{C}$ (Supplementary Note 8). The EL spectrum (Fig. 3b) 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 black-body radiation.

Discussion

We have successfully fabricated and operated an LED above $2\mu\text{m}$ and then aimed to reveal the working mechanisms and in particular the role of ZnO NCs within the emissive layer. In the device 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 the 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 properties²⁶. HgTe, with a PL peak above 2 μm , presents ambipolar conduction, as shown in the transfer curves (Fig. 4c) obtained from an electrolyte gated field-effect transistor. A scheme of this transistor is provided in Fig. 4a. For all films made of a ZnO:HgTe mixture in different volume ratios, we observed that this ambipolar nature is preserved (Supplementary Note 11). In this sense, the transport is fully driven by the HgTe NC array. This behaviour contrasts with the one previously observed by Qu et al.²⁶, using the same LED structure but based on wider-bandgap HgTe NCs (EL peak at 1,300 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; Fig. 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 (Supplementary Note 10), a shift of the neutrality point toward higher positive gate biases is observed (Fig. 4d). Simultaneously, the ratio of the electron mobility over the hole mobility drops. These two behaviours suggest that electrons are transferred from HgTe NCs to ZnO NCs, tuning the carrier density in the conductive HgTe array.

To further confirm this charge transfer, we followed the transient reflectivity signal for the mixture (Fig. 4e). In this HgTe:ZnO mixture, it appears that the carrier relaxation at long timescale is barely affected by the addition of ZnO (Fig. 4e, left inset). On the other hand, the rising time (linked to intra-conduction band relaxation) appears to depend on the presence of the ZnO. In particular, the relative magnitude of the fast component is reduced by the introduction of ZnO (Fig. 4e, right inset, (green arrow)). As shown in Fig. 1e,f, regime I, this fast component is related to hot states, $\sim 0.9\text{ eV}$ above the conduction band, which partly delocalize in the surrounding environment. Thus, the hot electrons generated in HgTe can easily be 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 becomes reduced. X-ray photoemission (XPS) investigations confirmed this charge transfer. The XPS overview spectrum in Fig. 5a shows the contribution from both HgTe and ZnO, as well as their thiol (S atoms) surface chemistry. The Hg 4f core levels include two contributions that are attributed to Hg bound to Te in the NC core (binding energy ($\text{Hg } 4f_{7/2}$) = 100.39 eV) and to Hg bound to S via surface thiols (binding energy ($\text{Hg } 4f_{7/2}$) = 100.97 eV) (Fig. 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 towards lower binding energies is observed when HgTe is added. This observation further supports an electron transfer from HgTe to ZnO.

Finally, time-resolved photoemission (TrXPS) measurements were performed to follow the light-induced shift of the core-level binding energy after laser excitation. This method is a pump-probe approach, in 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 presented in Fig. 5c. Although transient reflectivity gives insight into 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 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 in ZnO content (Fig. 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 (that is, 25% 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-bandgap nature of ZnO, which cannot be excited by the 800-nm laser source (Supplementary Note 12). However, in the presence of HgTe, the Zn 3d appears to be light-sensitive and presents a strong light-induced shift (Fig. 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 ensures both 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 Notes 5 and 6).

To summarize, we have designed an LED presenting emission in the extended short-wave infrared (2–2.3 μm range) using HgTe NCs as the emissive material. The diode stack is based on glass/ITO/ZnO/HgTe/ZnO/PbS/Au layers. Compared to their counterparts at shorter wavelengths (1.6 μm and less), the LED structure requires adjustments and, in particular, a compromise between the resistance and the transparency of the bottom electrode. The 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 differ strongly. 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 damage.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41566-021-00902-y>.

Received: 27 March 2021; Accepted: 30 September 2021;

Published online: 13 December 2021

References

1. Nizamoglu, S., Ozel, T., Sari, E. & Demir, H. V. White light generation using CdSe/ZnS core-shell nanocrystals hybridized with InGaN/GaN light emitting diodes. *Nanotechnology* **18**, 065709 (2007).
2. Wood, V. & Bulović, V. Colloidal quantum dot light-emitting devices. *Nano Rev.* **1**, 5202 (2010).
3. Liu, B. et al. Record high external quantum efficiency of 19.2% achieved in light-emitting diodes of colloidal quantum wells enabled by hot-injection shell growth. *Adv. Mater.* **32**, 1905824 (2020).
4. Tessler, N., Medvedev, V., Kazes, M., Kan, S. & Banin, U. Efficient near-infrared polymer nanocrystal light-emitting diodes. *Science* **295**, 1506–1508 (2002).
5. Pradhan, S. et al. High-efficiency colloidal quantum dot infrared light-emitting diodes via engineering at the supra-nanocrystalline level. *Nat. Nanotechnol.* **14**, 72–79 (2019).
6. Vasilopoulou, M. et al. Efficient colloidal quantum dot light-emitting diodes operating in the second near-infrared biological window. *Nat. Photon.* **14**, 50–56 (2020).
7. Wei, Y.-C. et al. Overcoming the energy gap law in near-infrared OLEDs by exciton–vibration decoupling. *Nat. Photon.* **14**, 570–577 (2020).
8. Faist, J. et al. Quantum cascade laser. *Science* **264**, 553–556 (1994).

9. Adelin, B. et al. Electrically pumped all photonic crystal 2nd order DFB lasers arrays emitting at 2.3 μm . *APL Photon.* **2**, 036105 (2017).
10. Kim, M. et al. Interband cascade laser emitting at $\lambda = 3.75 \mu\text{m}$ in continuous wave above room temperature. *Appl. Phys. Lett.* **92**, 191110 (2008).
11. Vurgaftman, I., Meyer, J. R. & Ram-Mohan, L. R. High-power/low-threshold type-II interband cascade mid-IR laser-design and modeling. *IEEE Photon. Technol. Lett.* **9**, 170–172 (1997).
12. Kasper, E. & Oehme, M. Germanium tin light emitters on silicon. *Jpn. J. Appl. Phys.* **54**, 04DG11 (2015).
13. Stange, D. et al. Short-wave infrared LEDs from GeSn/SiGeSn multiple quantum wells. *Optica* **4**, 185–188 (2017).
14. Triki, M., Nguyen, B. T. & Vicet, A. Compact sensor for methane detection in the mid infrared region based on quartz enhanced photoacoustic spectroscopy. *Infrared Phys. Technol.* **69**, 74–80 (2015).
15. Rastogi, P. et al. Complex optical index of HgTe nanocrystal infrared thin films and its use for short wave infrared photodiode design. *Adv. Opt. Mater.* **9**, 2002066 (2021).
16. Gréboval, C. et al. Mercury chalcogenide quantum dots: material perspective for device integration. *Chem. Rev.* **121**, 3627–3700 (2021).
17. Keuleyan, S., Lhuillier, E. & Guyot-Sionnest, P. Synthesis of colloidal HgTe quantum dots for narrow mid-IR emission and detection. *J. Am. Chem. Soc.* **133**, 16422–16424 (2011).
18. Zhang, H. & Guyot-Sionnest, P. Shape-controlled HgTe colloidal quantum dots and reduced spin-orbit splitting in the tetrahedral shape. *J. Phys. Chem. Lett.* **11**, 6860–6866 (2020).
19. Prado, Y. et al. Seeded growth of HgTe nanocrystals for shape control and their use in narrow infrared electroluminescence. *Chem. Mater.* **33**, 2054–2061 (2021).
20. Keuleyan, S., Kohler, J. & Guyot-Sionnest, P. Photoluminescence of mid-infrared HgTe colloidal quantum dots. *J. Phys. Chem. C* **118**, 2749–2753 (2014).
21. Melnychuk, C. & Guyot-Sionnest, P. Slow Auger relaxation in HgTe colloidal quantum dots. *J. Phys. Chem. Lett.* **9**, 2208–2211 (2018).
22. Lim, J. et al. Ultrafast intraband Auger process in self-doped colloidal quantum dots. *Matter* **4**, 1072–1086 (2021).
23. Boschetto, D. et al. Small atomic displacements recorded in bismuth by the optical reflectivity of femtosecond laser-pulse excitations. *Phys. Rev. Lett.* **100**, 027404 (2008).
24. Geiregat, P. et al. Continuous-wave infrared optical gain and amplified spontaneous emission at ultralow threshold by colloidal HgTe quantum dots. *Nat. Mater.* **17**, 35–42 (2018).
25. Al-Otaify, A. et al. Multiple exciton generation and ultrafast exciton dynamics in HgTe colloidal quantum dots. *Phys. Chem. Chem. Phys.* **15**, 16864–16873 (2013).
26. Qu, J. et al. Electroluminescence from HgTe nanocrystals and its use for active imaging. *Nano Lett.* **20**, 6185–6190 (2020).
27. Chuang, C.-H. M., Brown, P. R., Bulović, V. & Bawendi, M. G. Improved performance and stability in quantum dot solar cells through band alignment engineering. *Nat. Mater.* **13**, 796–801 (2014).
28. Greboval, C. et al. Infrared narrow band gap nanocrystals: recent progresses relative to imaging and active detection. Preprint at <https://arxiv.org/abs/2001.11554> (2020).
29. Svane, A. et al. Quasiparticle band structures of β -HgS, HgSe and HgTe. *Phys. Rev. B* **84**, 205205 (2011).
30. Delin, A. & Klüner, T. Excitation spectra and ground-state properties from density-functional theory for the inverted band-structure systems β -HgS, HgSe and HgTe. *Phys. Rev. B* **66**, 035117 (2002).
31. Allan, G. & Delerue, C. Tight-binding calculations of the optical properties of HgTe nanocrystals. *Phys. Rev. B* **86**, 165437 (2012).
32. Lhuillier, E., Keuleyan, S. & Guyot-Sionnest, P. Optical properties of HgTe colloidal quantum dots. *Nanotechnology* **23**, 175705 (2012).
33. Moghaddam, N. et al. The strong confinement regime in HgTe two-dimensional nanoplatelets. *J. Phys. Chem. C* **124**, 23460–23468 (2020).
34. Rogach, A. et al. Colloidally prepared HgTe nanocrystals with strong room-temperature infrared luminescence. *Adv. Mater.* **11**, 552–555 (1999).
35. Rogach, A. L., Koktysh, D. S., Harrison, M. & Kotov, N. A. Layer-by-layer assembled films of HgTe nanocrystals with strong infrared emission. *Chem. Mater.* **12**, 1526–1528 (2000).
36. Sergeev, A. A. et al. Tailoring spontaneous infrared emission of HgTe quantum dots with laser-printed plasmonic arrays. *Light Sci. Appl.* **9**, 16 (2020).
37. Zhao, Y., Wang, V., Lien, D.-H. & Javey, A. A generic electroluminescent device for emission from infrared to ultraviolet wavelengths. *Nat. Electron.* **3**, 612–621 (2020).
38. O'Connor, É. et al. Near-infrared electroluminescent devices based on colloidal HgTe quantum dot arrays. *Appl. Phys. Lett.* **86**, 201114 (2005).
39. Koktysh, D. S. et al. Near-infrared electroluminescence from HgTe nanocrystals. *ChemPhysChem* **5**, 1435–1438 (2004).
40. Maniyara, R. A. et al. Highly transparent and conductive ITO substrates for near infrared applications. *APL Mater.* **9**, 021121 (2021).
41. Pradhan, S., Dalmases, M. & Konstantatos, G. Solid-state thin-film broadband short-wave infrared light emitters. *Adv. Mater.* **32**, 2003830 (2020).
42. Amelot, D. et al. Revealing the band structure of FAPI quantum dot film and its interfaces with electron and hole transport layer using time resolved photoemission. *J. Phys. Chem. C* **124**, 3873–3880 (2020).
43. Gréboval, C. et al. Time-resolved photoemission to unveil electronic coupling between absorbing and transport layers in a quantum dot-based solar cell. *J. Phys. Chem. C* **124**, 23400–23409 (2020).
44. Livache, C. et al. Charge dynamics and optoelectronic properties in HgTe colloidal quantum wells. *Nano Lett.* **17**, 4067–4074 (2017).
45. Gréboval, C. et al. Impact of dimensionality and confinement on the electronic properties of mercury chalcogenide nanocrystals. *Nanoscale* **11**, 3905–3915 (2019).

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2021

Methods

HgTe NCs 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 trioctylphosphine telluride (TOP:Te) (1 M) were extracted from the glovebox and mixed with 8 ml of oleylamine. The atmosphere was switched to N_2 and the temperature was set at 70 °C. When the temperature stabilized, the TOP:Te solution was quickly injected. After 3 min of reaction, 10 ml of dodecanethiol (DDT)/toluene (1:9 in volume) solution was injected and a water bath was used to quench the reaction. The NCs were precipitated with methanol and redispersed in CHCl_3 twice, then the nanocrystals dispersed in CHCl_3 were centrifuged to remove the unstable phase. The stable phase was precipitated again with methanol and stored in CHCl_3 at a concentration of 30 mg ml^{-1} . To shift the emission to 2.15 μm (resp. 2.3 μm), the reaction was conducted at 75 °C (resp. 80 °C).

Transmission electron microscopy. A drop of diluted NC solution was dropcast 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/scanning TEM observations were made on a Titan Themis 200 microscope (FEI/Thermo Fisher Scientific) equipped with a geometric aberration corrector on the probe. The microscope was also equipped with 'Super-X' systems for energy dispersive X-Ray spectroscopy (EDX) analysis with a detection angle of 0.9 steradian. The observations were made at 200 kV with a probe current of ~35 pA and a half-angle of convergence of 17 mrad. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired with a camera length of 110 mm (inner/outer collection angles of 69 and 200 mrad, respectively).

UV-vis spectroscopy. The spectra of the NC solution or thin films were recorded using a JASCO V-730 spectrometer.

Infrared absorption spectroscopy. Infrared absorption spectroscopy was conducted using a Fisher IS50 Fourier-transform infrared (FTIR) spectrometer. To measure the absorption of the obtained NCs, an attenuated total reflectance (ATR) configuration with a white-light source, a CaF_2 beamsplitter and deuterated triglycine sulfate (DTGS) detector was used. Typically, a drop of NC solution was deposited and dried on the diamond cell. Spectra were acquired from 12,000 cm^{-1} to 2,100 cm^{-1} with a resolution of 4 cm^{-1} while averaging over 32 spectra.

Infrared photoluminescence spectroscopy. Infrared PL spectroscopy was carried out with a Fisher IS50 FTIR spectrometer. The infrared-emitting NCs were dropcast 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 FTIR spectrometer, in which CaF_2 was chosen as the beamsplitter and the extended InGaAs sensor as the detector. Spectra were typically acquired from 8,000 cm^{-1} to 3,000 cm^{-1} with a resolution of 4 cm^{-1} while averaging over 32 spectra.

Infrared ultrafast spectroscopy. Time-resolved reflectivity measurements were performed in a standard pump-probe set-up, using a commercial laser system at a repetition rate of 1 kHz and centred at 800 nm, with pulse duration of $\Delta\tau = 35$ fs and 1.5 mJ per pulse. The laser pulse was split into two parts with an energy balance of 10%/90%. The time delay between the two pulses was controlled by a motorized micrometric stepmotor. The highest-energy arm was used to pump an optical parametric amplifier (OPA), which allowed wavelength tuning from ~1 μm to ~20 μm . 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 was 60 $\mu\text{J cm}^{-2}$. The typical focal spot size was ~500 μm for the pump and 250 μm 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 because 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. For photoemission spectroscopy, we used the Tempo beamline of synchrotron Soleil. Films of NCs were spin-cast onto a Au-coated Si substrate (the gold layer was 80 nm thick). The ligands of the NCs 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. The samples were then introduced to the analysis chamber. The signal was acquired by a MBS A-1 photoelectron analyser equipped with a delay line detector developed by Elettra⁴⁶. Acquisition was carried out at constant pass energy (50 eV) within the detector. A photon energy of 150 eV was used for the acquisition of the valence band and workfunction and a photon energy of 600 eV for analysis of the core levels. A Au substrate was used to calibrate the Fermi energy. The absolute value of the incoming photon energy was determined by measuring the first and second orders of the Au 4f core-level peaks. Then, for a given analyser pass energy, we measured the Fermi edge and set its binding energy to zero. The same

shift was applied to all spectra acquired with the same pass energy. To determine the workfunction, we applied a bias of 18 V, the exact value of which had been determined by looking at the shift of a Fermi edge.

Time-resolved X-ray photoemission measurements. The sample was excited by an 800-nm Ti:sapphire laser (RegA, Coherent). The pulse duration was ~60 fs and the repetition rate was 284 kHz. Ten percent of the maximum laser power was used to excite the sample. The output equivalent continuous-wave (c.w.) 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 $\mu\text{m} \times 2$ mm (laser beam). The FWHMs were 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 (that is, the detection of the photoelectron analyser was synchronized with the laser pulse excitation), and the temporal resolution was determined by the time response of the high-resolution photoelectron analyser. The latter was estimated to be 30 ns, limited by the spread of the electrons between the hemispheres. 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 enabled us to follow energy shifts as small as 5 meV. Because 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 Ωsq^{-1}) 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 being dried completely with a 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 the ITO substrates at a rate of 4,000 r.p.m. 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 (width of 1 mm). Photoresist was then developed using AZ 726 developer for 20 s before being rinsed with deionized water and dried. After another 5 min of plasma cleaning, the substrates were etched in a 25% HCl (in water) bath for 10 min at 40 °C before being dipped immediately in deionized water. Finally, the liftoff of photoresist was conducted in an acetone bath.

n-type ZnO layer deposition. On top of a patterned ITO substrate, ZnO nanoparticles dispersed in toluene (40 mg ml^{-1}) were spin-coated at a speed of 2,000 r.p.m. 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.

Emitting ZnO/HgTe layer deposition. First, HgTe and ZnO solutions in CHCl_3 at the same concentration of 30 mg ml^{-1} were prepared. 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 comprises 50% of the mixture solution. The mixture solutions were spin-coated on top of the ZnO bottom layer at a speed of 4,000 r.p.m. 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 to stay for 10 s before drying 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 ~120 nm.

p-type PbS layer. Ethanedithiol (EDT)-capped PbS NCs 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 2,500 r.p.m. on 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 ~60 nm.

Top contact. After deposition of the PbS NC layers, the sample was set in a thermal evaporator. An 80-nm layer of Au was deposited in vacuum below 5×10^{-6} mbar through a shadow mask. The pixel size, which is defined as the overlap of the ITO and Au contact, was 1 mm^2 .

Infrared electroluminescence spectroscopy. The EL was measured from the in operando device in the following way. The emitting device was placed at the focal point of a golden off-axis parabola with a 5-cm focal lens and overture of 10 cm. This allowed us to cover a large solid angle, given that the emission is isotropic. The outgoing reflected beam was nearly parallel to the propagation direction. We used two additional off-axis parabolas with 18-cm and 9-cm focal lengths, respectively, to ensure a reduction of the beam size by a factor of two, which led to a photon density that was twice as large and therefore improved the signal-to-noise ratio. We placed a mechanical modulator (chopper) in the focal spot between

these two off-axis parabolas to modulated the continuous emitted beam at an arbitrary selected frequency of 456 Hz. The collimated beam was sent into a FTIR spectrometer (Fischer IS50 with step scan). The detector was connected to a lock-in amplifier (SR830 Stanford Research Systems), which selectively detected 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 spectra were acquired using the step-scan mode of the FTIR spectrometer. We acquired the spectrum as a function of the current/voltage applied to the device to measure the spectra corresponding to several emitting conditions (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 $N_p = \frac{P}{h\nu} = \frac{\lambda P}{hc}$, where λ is the wavelength of the EL peak, h Planck's constant and c the speed of light. The number of electrons injected per second can be obtained by $N_e = \frac{I}{e}$, where I is the current flow in the device. The EQE can thus be calculated as $\frac{N_p}{N_e} = \frac{\lambda e P}{h c I}$ and the irradiance of the device as $R = \frac{L_0}{s_2} = \frac{P}{\pi s_2}$, where s_2 is the area of the pixel.

Data availability

The data that support the findings of this study are available upon reasonable request. Source data are provided with this paper.

References

46. Bergéard, N. et al. Time-resolved photoelectron spectroscopy using synchrotron radiation time structure. *J. Synchrotron Rad.* **18**, 245–250 (2011).

Acknowledgements

We thank P. Hollander and D. Henry for experimental support. The project is supported by ERC starting grant blackQD (grant no. 756225, E.L.) and Ne2Dem (grant no. 853049, S.I.). We acknowledge the use of clean-room facilities at the Centrale de Proximité

Paris-Centre. This work has been supported by the Region Ile-de-France in the framework of DIM Nano-K (grant dopQD, E.L.) and in the framework of the SESAME Electrophenon (grant no. 14014520, D.B.). We acknowledge financial support from the French Department of Defence (DGA) in the frame of the Oscillateur térahertz project (grant no. 2018 60 0071 00 470 75 01, D.B.), and of PALM in the framework of the TPS grant (grant no. ANR-10-LABX-0039-PALM, D.B.). This work was supported by French state funds managed by the ANR within the Investissements d'Avenir programme under reference ANR-11-IDEX-0004-02 (E.L.) and, more specifically, within the framework of the Cluster of Excellence MATISSE and also by the grant IPER-Nano2 (ANR-18CE30-0023-01, E.L.), Copin (ANR-19-CE24-0022, E.L.), Frontal (ANR-19-CE09-0017, M.G.S.), Graskop (ANR-19-CE09-0026, E.L.), TOCYDYS (ANR-19-CE30-0015-03, D.B.) and NITQuantum (ANR-20-ASTR-0008-01, E.L.), Bright (ANR-21-CE24-0012-02, E.L.) and MixDFerro (ANR-21-CE09-0029, E.L.). J.Q. thanks the Chinese Scholarship Council for PhD funding and A.C. thanks Agence Innovation Defense.

Author contributions

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. and E.B. measured the EL spectra. Synchrotron measurements were performed 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 interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41566-021-00902-y>.

Correspondence and requests for materials should be addressed to Emmanuel Lhuillier.

Peer review information *Nature Photonics* thanks Ni Zhao and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.