

Guided-Mode Resonator Coupled with Nanocrystal Intraband Absorption

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Cite This: *ACS Photonics* 2022, 9, 985–993



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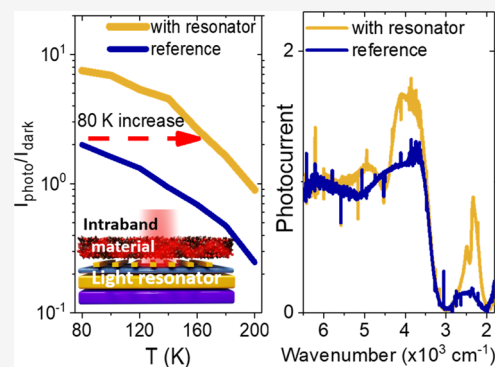
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ABSTRACT: Intraband absorption in doped nanocrystals offers an interesting alternative to narrow-band-gap materials to explore mid-infrared optoelectronic device designs. However, the performance of such a device clearly lags behind the ones relying on intrinsic materials. Livache et al. proposed a dye-sensitized approach to overcome the limitations observed from intraband materials (high dark current, slow response, low activation energy), where an intraband absorber is coupled with an undoped material, which takes care of the charge conduction. Here, we unveil the coupling between both materials using mid-infrared transient reflectivity (TR) measurement. We show that the hybrid material displays a unique feature in the TR signal that we attribute to a charge transfer for which the dynamics matches the hopping time. Then, we developed a strategy to enhance the photodetection performances of the hybrid material by coupling the intraband absorption to a light resonator for the first time. The latter is used to enhance the absorption by a factor of 4 and enables an increase in the operating temperature by 80 K compared to the reference device. The obtained device matches the performance of the best devices relying on intraband absorption.

KEYWORDS: intraband absorption, mid-infrared, doped nanocrystals, mercury chalcogenides, optical resonator



Intersub-band transitions have certainly been the highest realization of quantum-well-based technologies, leading to devices such as quantum cascade lasers¹ and quantum-well infrared photodetectors.² Intraband transitions are their zero-dimensional (0D) equivalent occurring in quantum dots and nanocrystals (NCs). This transition is not limited by the bulk band gap and they are inherently narrow energy transitions, well-suited to address the infrared range.

While the concept of intraband photoconduction has been demonstrated for NC array of mercury,^{3–6} lead,⁷ and silver^{8,9} chalcogenides, the level of performance achieved lags, by orders of magnitude, behind one of the quasi-intrinsic interband materials, at the same wavelength. In particular, a low operating temperature, 80 K typically, remains necessary while high operating temperature (HOT) operation is achieved for interband materials.¹⁰

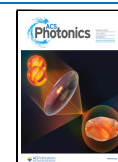
For pristine intraband NC arrays, similar to intersub-band heterostructures, doping is mandatory to reach the targeted absorption. However, it comes at a high cost. Doping is responsible for a large dark current, making the photoconductive signal only a small fraction of the dark current, up to the point where, generally, bolometric slow response¹¹ prevails above the photoconductive signal. Recently, Livache et al.¹² demonstrated that the large dark current and slow time

response can be tackled by replacing the pristine intraband NC array by a mixture of doped and undoped NCs. Specifically, doped HgSe NCs exhibiting intraband absorption are mixed with undoped HgTe NCs. The amount of HgTe in the mixture is chosen high enough to prevent percolation (*i.e.*, formation of a continuous transport path up to the electrode) of the electrons within the HgSe NC array. In this configuration, the mixture behaves as a mid-IR dye-sensitized solar cell, where HgSe absorbs the mid-IR light, while the HgTe particles drive the transport properties. While the concept is already established, the coupling between the two materials, particularly its dynamics remains unexplored. Here, using infrared transient reflectivity with a resolution of 50 fs, we provide evidence of charge transfer between the two materials.

Furthermore, although the mixture approach appears beneficial for dark current and time response, it also reduces

Received: December 2, 2021

Published: February 10, 2022



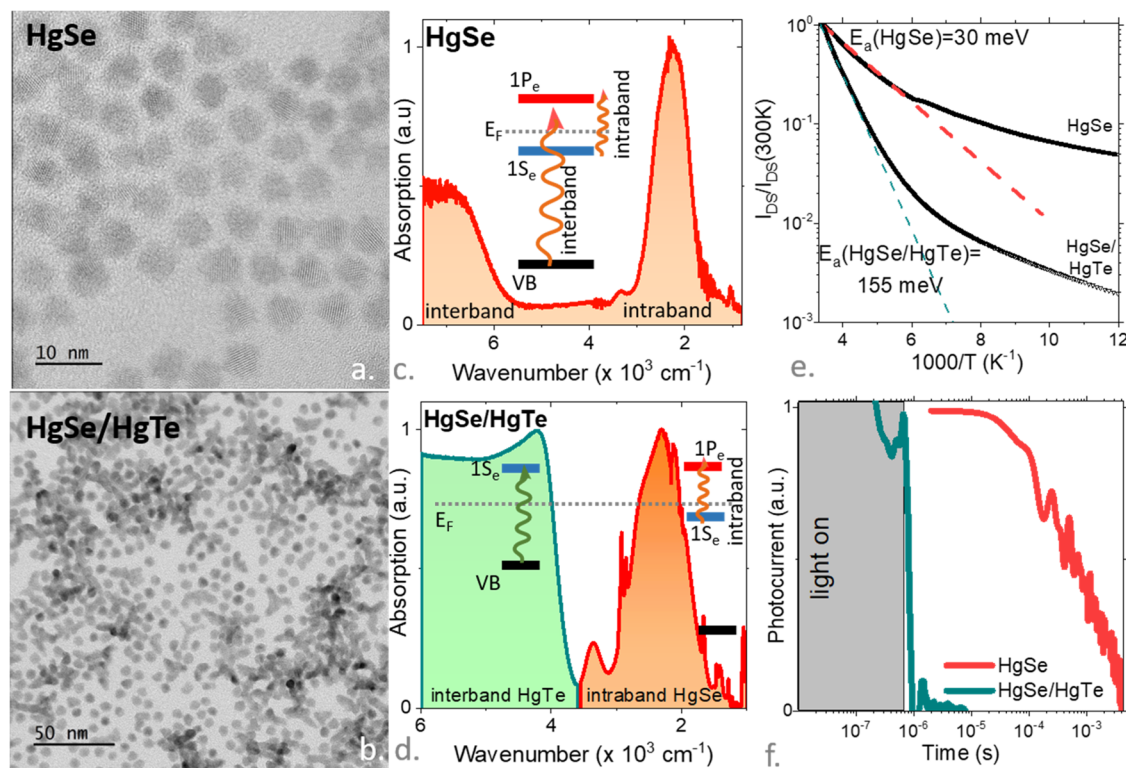


Figure 1. Intraband absorbing material properties. (a) TEM image of HgSe NCs, (b) TEM image of the HgSe/HgTe NC mixture, and (c) absorption spectrum of HgSe NCs. The inset indicates the involved transitions. (d) Absorption spectrum of the HgSe/HgTe NC mixture under an ink form. The inset indicates the involved transitions. (e) Normalized dark current value as a function of temperature for a film of HgSe NCs and for a film of the mixture of HgSe/HgTe NCs. The current is normalized by its value at 300 K. Dashed lines correspond to Arrhenius fits. (f) Time response to a pulse ($\lambda = 4.4 \mu\text{m}$) of light for a film of HgSe NCs and for a film of HgSe/HgTe NC mixture.

the film absorbance compared to the pristine material through the reduction of the intraband material volume fraction. Here, we show that by coupling the HgSe/HgTe metamaterial to a guided-mode resonator¹³ (GMR), we can enhance the intraband absorption and its associated photocurrent. This resonator enables us to maintain the photocurrent to dark current modulation while increasing the operating temperature by 80 K with respect to the metamaterial without an optical nanoresonator.

Intraband transitions in nanocrystals are an interesting alternative to interband transitions to achieve absorption of low-energy, infrared photons. Moreover, it may pave the way toward new device possibilities similarly to what has been demonstrated based on quantum cascade devices in III–V semiconductor heterostructures.^{1,14} The intraband absorption in the steady state requires doped nanoparticles.¹⁵ However, a moderate level of doping (one carrier per nanocrystal typically) is necessary to avoid plasmonic absorption in their inherent extremely short (<100 fs) photocarrier lifetime.¹⁶ Among the few potential material^{7–9} candidates, we choose to focus on HgSe^{3–5} since its electronic spectrum in the mid-IR has already been investigated, easing the further device integration.¹⁷

We synthesize HgSe nanocrystals using the procedure developed by Lhuillier et al.⁵ Briefly, mercury oleate reacts with trioctylphosphine selenium in oleylamine at a moderate temperature (100 °C). The obtained particles are quasi-round according to the transmission electron microscopy (TEM) image (Figure 1a) with a mean size of 5 nm. The absorption spectrum includes two components (Figure 1c). At high

energies (above 6000 cm^{-1}), there is a broadband interband absorption signal. At lower energies, there is no absorption until the intraband contribution of around 2200 cm^{-1} . Here, we choose the particle size to match the HgSe intraband absorption and the $3\text{--}5 \mu\text{m}$ transparency window commonly described as midwave infrared (MWIR). As already stated in the introduction, although photoconductive, an array of HgSe NCs presents a weak transport activation energy (30 meV, see Figure 1e), leading to a lack of detection performance improvement upon cooling. Furthermore, the slow response (several ms, see Figure 1f) is not compatible with imaging applications. However, as it has been demonstrated by Livache et al.,¹² both challenges can be solved by replacing the pristine HgSe array by a mixture of HgTe (Figure S1) and HgSe NCs. From TEM (Figures 1b and S2–4), the two types of particles can easily be distinguished since HgSe presents a quasi-spherical shape, while HgTe is a tripod.¹⁸ The absorption spectrum of the mixture preserves the intraband absorption of HgSe, while the contribution of HgTe now appears in the range of energy corresponding to the absorption gap (*i.e.*, 4000 cm^{-1}) between the interband and the intraband for HgSe, as shown in Figure 1d. The HgTe particle size is chosen such that the $1S_e$ state from HgTe is almost resonant with the HgSe $1P_e$ state, as shown by the energy diagram revealed by X-ray photoemission in Figure S7. This is critical to ensure an efficient charge transfer between the NCs. Empirically, the ratio of the two materials is determined in order that the relative magnitude of the intraband absorption of HgSe and the interband signal from HgTe is close to 1. In this case, the amount of HgTe is sufficient to prevent the transport

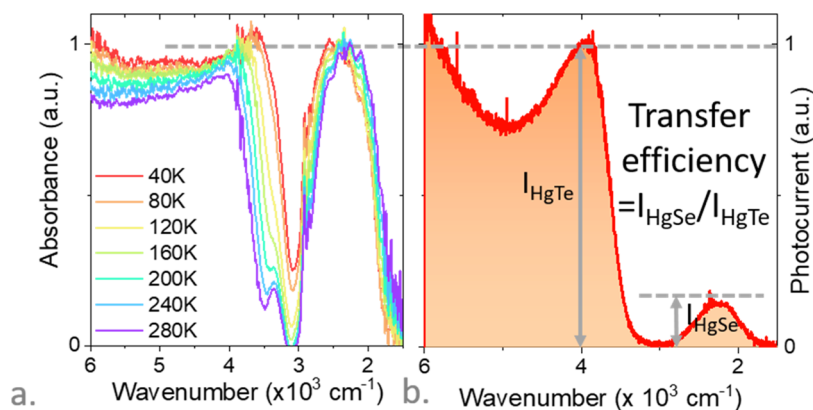


Figure 2. Charge transfer in the HgSe/HgTe mixture. Absorption at various temperatures (a) and photocurrent at 80 K (b) spectra of the HgSe/HgTe NC mixture.

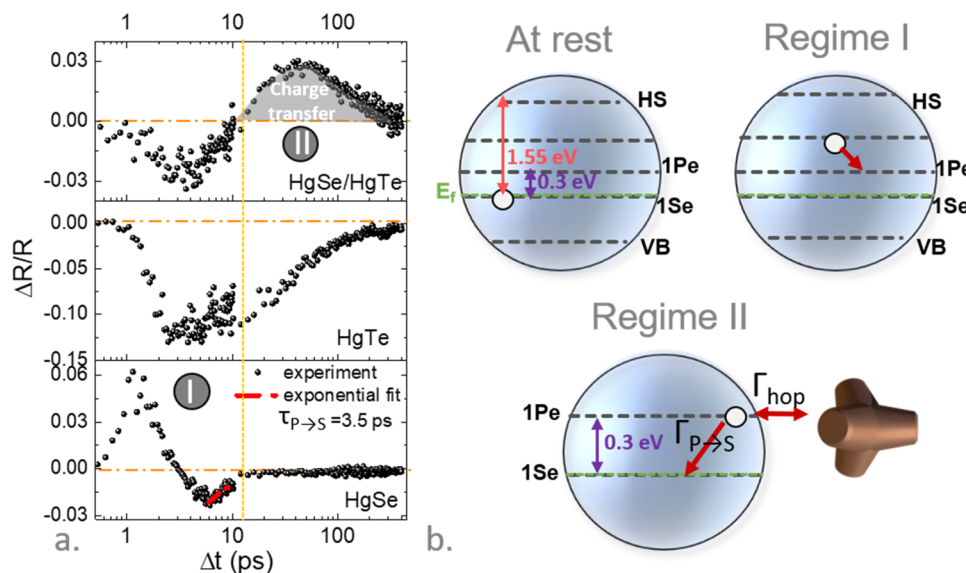


Figure 3. Carrier relaxation in an array of HgX nanocrystals. (a) Transient reflectivity signal as a function of time for the film made of HgSe (bottom), HgTe (middle), and HgSe/HgTe mixture (top). The yellow vertical dashed line splits regimes I and II. (b) Schematic of the HgSe NC electronic structure for different time ranges as defined in the bottom panel of (a).

percolation within the HgSe NC array and the detection properties are improved. From Figure 1e, we observe a drastic increase in the transport activation energy, reaching 155 meV, revealing that the dark current is strongly reduced under cryogenic conditions. Additionally, the time response is strongly reduced and is as short as 1 μ s, as shown in Figure 1f.

Although the absorption of the mixture is set to achieve a similar optical density for both materials, the photocurrent spectrum reveals fairly different photocurrent contributions, as shown in Figure 2. Due to measurements being conducted at 300 K for absorption and 80 K for photoconduction, the difference might result from a temperature effect. As shown in Figure S6, we then conduct a systematic investigation of the pristine materials (HgSe and HgTe) and mixture absorption as a function of temperature. As the temperature is reduced, HgTe and HgSe interband gaps are reduced (*i.e.*, red shift, $+240 \mu\text{eV}\cdot\text{K}^{-1}$ for HgTe), while the intraband gap of HgSe is increased (*i.e.*, blue shift, $-115 \mu\text{eV}\cdot\text{K}^{-1}$).^{19,20} In the mixture, the same shifts were observed. On the other hand, the relative magnitude of the two absorption peaks is only marginally affected, as shown in Figure S6. Thus, the change in the

relative peak magnitude in the photocurrent rather relates to a transport process.

As a photon, whose energy matches the intraband transition, is absorbed, an electron from the conduction band ground state ($1S_e$) is promoted to the excited state ($1P_e$) in a HgSe NC. This electron needs then to be transferred to the HgTe conduction band to contribute to transport and to the device's photocurrent. This charge transfer process shows that absorption and photocurrent spectra cannot be matched. As the intraband contribution from HgSe to the photocurrent is only 1/6 of the one from the interband of HgTe, one can attribute the value of $\approx 17\%$ to the whole charge transfer and transport process.

This raises the need for a deeper analysis of the coupling between both populations, and particularly, the dynamics of this transfer needs to be unveiled. To do so, we use IR transient reflectivity measurement in a pump–probe configuration. The setup is operated in a nondegenerate mode where the pump operates at 800 nm (1.55 eV–35 fs pulse duration), while the probe is set at 4 μm (0.32 eV–50 fs pulse duration) matching the intraband gap of HgSe.

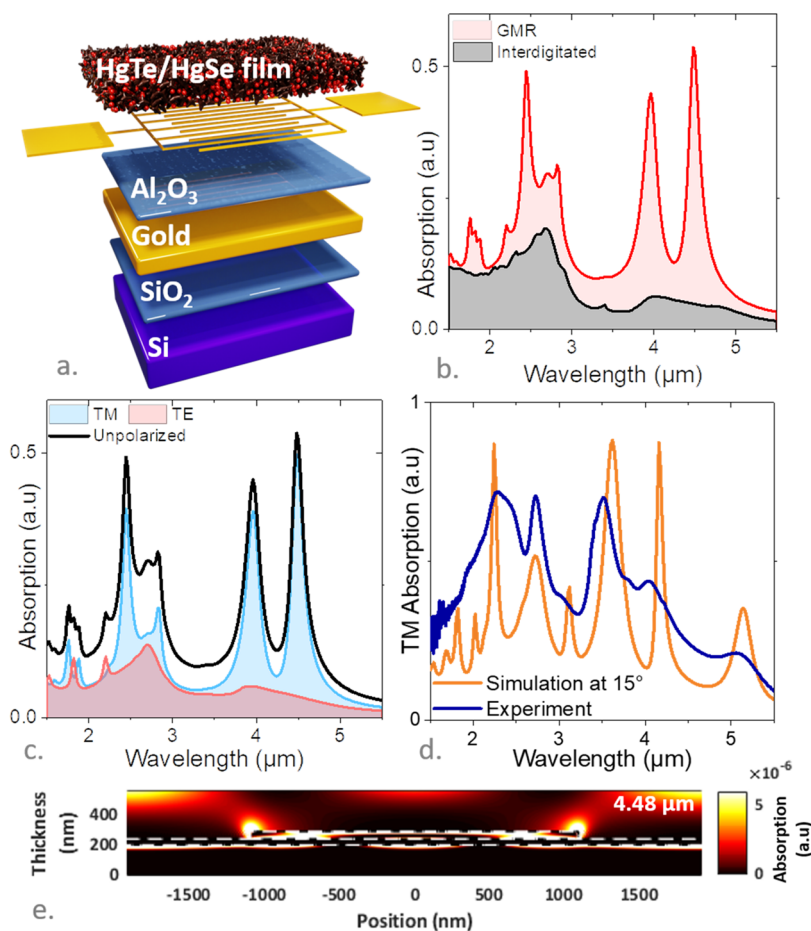


Figure 4. Intraband guided-mode resonator. (a) Schematic of the GMR device coupled with an intraband absorbing film made of the HgSe/HgTe NC mixture. (b) Simulated absorption spectra for reference interdigitated electrodes (i.e., without resonance) and for GMR electrodes. (c) Simulated absorption spectrum for GMR electrodes for unpolarized light and its TE and TM components. (d) Comparison of the measured absorption (mean collect angle is 15° , with a 10° aperture) and simulated absorption with a 15° (plane wave) along TM polarization. (e) Absorption cross-sectional mapping at $4.48 \mu\text{m}$. The colored part corresponds to absorption.

While this configuration does not exactly allow for accurate determination of exciton lifetimes and intrinsic processes in each of the host NCs, we propose a comparative analysis on transient signals measured for only HgTe, only HgSe, and a HgSe/HgTe mixture. All samples are processed in the same way as for photoconduction experiments (i.e., with the same ligand exchange). Figure 3a shows the transient reflectivity signals for the three samples. The electronic structure of HgSe is shown in Figure 3b. At rest, the Fermi level lies in the conduction band between the $1S_e$ and $1P_e$ states. Thus, valence band states are filled with electrons, while the $1P_e$ state and upper states (called hot states (HS) in Figure 3b) remain empty. With an initial long ligand (DDT), the $1S_e$ state is mostly filled (two electrons per NC); however, after ligand exchange, the population of the NC appears to be slightly reduced (0.2 to 2 electron per HgSe NC range (see Figure S5)).^{11,17}

Under excitation, the pump is absorbed and a hot electron is generated. Note that due to the high energy of the pump with respect to the interband band gap, the initial electrons can either be located in the $1S_e$ state or in the valence band. In the latter case, the carriers being less hot, they will thermalize on a shorter time scale since the cooling rate seems to be unaffected by the pump excitation in such NCs.²¹ We observe photon-induced absorption (PIA with positive $\Delta R/R$ observed in

regime I, lasting from 0 to 3 ps). A possible mechanism is that the hot charges generate a Stark effect that slightly affects the energy of the intraband transition, but other effects may be responsible for this early signal such as hot intraband transitions or a shift resulting from exciton–exciton interactions. As the electrons cool (regime I), they will reach the $1P_e$ state, at which point the transient reflectivity signal will become negative due to a reduced number of arriving states for the $1S_e$ to $1P_e$ transition. Then, the electron cools from $1P_e$ to $1S_e$ (end of regime I); this relaxation time $\tau_{P \rightarrow S}$ has been found to be 3.5 ps. This duration is in line with the intraband relaxation dynamics in CdSe or HgTe^{21–23} nanocrystals for which the relaxation decay is found to be in a 1–10 ps range.²⁴ Note that in the case of pristine HgTe, only a negative signal is observed (middle panel of Figure 3a).

In the case of the mixture (top panel of Figure 3a), the transient reflectivity signal is first negative. We then observe a positive contribution at a long (>10 ps regime II in Figure 3) time scale, a duration longer than intraband relaxation in both pristine materials. The observation of this signal, which is not observed in any of the two pristine materials, is interpreted as the signature of the charge transfer between HgSe and HgTe. Indeed, in the mixture, there is a new relaxation pathway for carriers, where the carriers can relax either within the initial particle or through charge transfer. The fact that we observe a

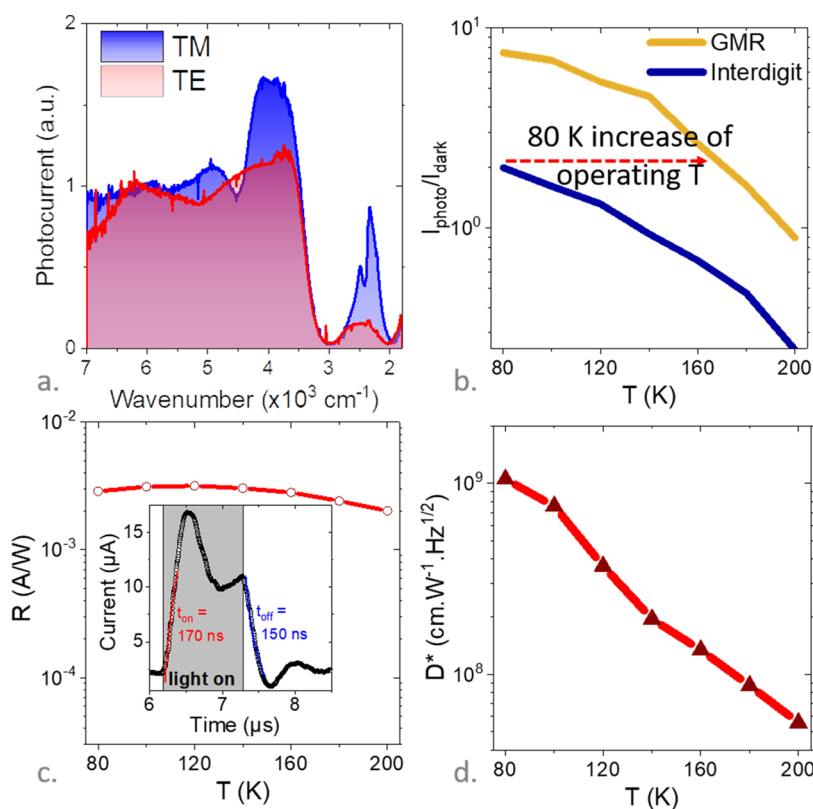


Figure 5. Performance of the intraband device coupled with GMR. (a) Photocurrent, under 0.1 V and at 80 K, spectrum for the GMR device along the two polarizations. (b) Ratio of the intraband photocurrent (i.e., QCL illumination at $4.4 \mu\text{m}$) over the dark current as a function of temperature for reference interdigitated electrodes (i.e., without resonance) and for GMR electrodes. (c) Responsivity, at 1.5 V, under blackbody illumination for the GMR device as a function of temperature. The inset is the photocurrent time trace as a response to a $1 \mu\text{s}$ long pulse of light at $4.4 \mu\text{m}$, spectrally matched with intraband absorption. (d) Specific detectivity (at 1 kHz, under 1.5 V) for the GMR device as a function of temperature under blackbody illumination.

positive signal suggests that electron transfer occurs from HgTe to HgSe. A carrier excited in HgTe leads to an increase in the population of HgSe, which increases the intraband absorption. This relaxation from HgTe to HgSe is consistent with the band alignment revealed by photoemission (Figure S7) and also with the non-unity efficiency of the charge transfer from HgSe to HgTe revealed by the photocurrent spectrum (Figure 2b).

This charge transfer hypothesis is further reinforced by the fact that the charge transfer characteristic time scale is found to be in a 30–50 ps range, a time scale that actually matches the hopping time. In a diffusive model, the latter is given by $\tau_{\text{hop}} = \frac{eR^2}{\mu k_b T}$, where e is the proton charge, R is the particle radius, μ is the carrier mobility, k_b is the Boltzmann constant, and T is the temperature. Because the transfer occurs between two types of particles, we generalized this expression to $\tau_{\text{HgSe} \rightarrow \text{HgTe}} = \frac{eR_{\text{HgSe}}R_{\text{HgTe}}}{\mu k_b T} \approx 50 \text{ ps}$, assuming $R_{\text{HgSe}} = 2.5 \text{ nm}$, $R_{\text{HgTe}} = 5 \text{ nm}$, and $\mu \approx 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.^{25,26} This value well matches the typical dynamics of the new positive contribution observed in the mixture. The determined dynamics also explains the relative magnitude of the intraband contribution in the photocurrent spectrum. For a carrier in the $1P_e$ state of HgSe, two relaxation paths are possible: a charge transfer within 30 ps or an internal relaxation in 3.5 ps. Thus, the efficiency of the charge transfer is only $\frac{\tau_{\text{p-s}}}{\tau_{\text{HgSe} \rightarrow \text{HgTe}}} = 12\%$, which should be considered as an order of magnitude, given the

temporal broadening of each feature. This is, on the other hand, consistent with the 17% ratio that has been determined from the photocurrent magnitude, as shown in Figure 2b.

While we have revealed that the fast coupling between the two materials is responsible for the enhanced detection performance, an open question is still unaddressed at this stage: the reduction of the intraband absorption resulting from the reduction of the HgSe volume fraction. Increasing the film thickness²⁷ might be a possible strategy. However, this approach is generally balanced by the short transport diffusion length,^{28,29} indicating that thicker films, in spite of larger absorption, do not necessarily generate more photocurrent. Here, we rather choose to couple the intraband absorbing layer with an optical nanoresonator. This strategy allows multipassing of light through the film, leading to absorption enhancement while maintaining the film thickness compatible with the transport diffusion length. Several types of resonators have already been coupled with NCs to enhance the absorption including Fabry-Pérot^{10,30,31} cavities or plasmonic gratings. Here, we choose to focus on guided-mode resonators (GMRs).^{13,32,33} The latter relies on the diffraction of a propagative mode, while most plasmonic approaches are based on near-field diffraction. As a result, the electromagnetic field is not necessarily in the immediate vicinity of the metal grating, reducing thermal losses. A schematic of the targeted device is shown in Figure 4a, and additional information relative to the fabrication is given in Figures S10 and 11. A gold mirror is deposited on a Si/SiO₂ substrate and is used to generate a

back-side reflection. We then deposit, by atomic layer deposition, a thin (40 nm) layer of alumina, which isolates the bottom gold mirror from the top deposited gold grating. The latter has a dual role: (i) to generate the GMR and (ii) to be used as an interdigitated electrode for transport. The period p of the grating is chosen so that $p = \lambda/n$, where λ is the resonance wavelength and n is the refractive index of the film. We use electromagnetic simulations based on rigorous coupled-wave analysis³⁴ (RCWA) to simulate the structure and optimize other geometrical parameters (height of the electrode and thicknesses of alumina and NC film). Simulations of the GMR absorption are given in Figures 4b–e and S8,9. The benefit of the GMR electrodes compared with reference interdigitated electrodes is shown in Figure 4b. In particular, we observe a clear absorption resonance at 4.4 μm (i.e., 2200 cm^{-1}), which is the main targeted one. As the GMR signal is the result of one-dimensional (1D) grating, we expect the signal to be strongly polarized and the resonance occurs only along TM polarization (Figure 4c). Using infrared microscopy, we measure the device absorption. Optics induce a 15° angle for light collection responsible for a shift of the peak resulting from the device dispersion (see the dispersion map in Figure S9). A comparison of the experimental and simulated absorption is shown in Figure 4d and displays a good correlation for the energy of the resonance. Experimental peaks are broader but this is mostly the effect of optics, which actually collects light with a 10° angle around a 15° tilt. In addition to the targeted resonance designed to match the intraband absorption of HgSe, we observe several additional resonances at 1.76, 1.88, 2.44, 2.84, 3.96, and 4.48 μm . A spatial mapping of the absorption loss for each resonance is given in Figures S8 and 4e. For some of them, the losses are clearly located within the metal and will not contribute to the photocurrent. In Table S3, we provide an estimation of the absorption occurring within the NC film for each peak. Out of these six resonances, the two main contributions expected are the one at 4.4 μm (matching the intraband contribution of HgSe) and the one at 2.44 μm (matching the interband signal of HgTe).

This prediction can be confirmed by measuring the photocurrent spectra of the device along the two polarizations, as shown in Figure 5a. While the TE polarization only presents the same feature as the one observed for the reference electrode, in TM, we observe two highly enhanced signals matching the interband of HgTe and the intraband of HgSe. The latter is notably enhanced by a factor 4 compared to the TE polarization. To better quantify the benefit of the GMR electrode, we then illuminate the sample with a quantum cascade laser that is spectrally matched with the intraband absorption. This way, we can exclude the contribution from high-energy-absorbing transitions. We then plot the ratio of the photocurrent over the dark current as a function of temperature and observe a clear enhancement corresponding to a factor 4. Alternatively, the GMR enables an increase in the operating temperature by 80 K (Figure 5b) with respect to the device without light trapping (i.e., interdigitated electrodes).

Under blackbody illumination (filtered with a Ge window to remove the signal below 2 μm), we have determined the device responsivity to be 3 $\text{mA}\cdot\text{W}^{-1}$, with only a weak temperature dependence (Figure 5c). Using a pulsed QCL matching the intraband, we determine the rise and fall time to be 170 and 150 ns, respectively, as shown in the inset of Figure 5c. The noise in the device appears to be 1/f limited,^{35,36} as shown in

Figure S12. The specific detectivity was found to be 10⁹ Jones at 80 K for a 5 μm cutoff wavelength (under 1.5 V and for a signal at 1 kHz, as shown in Figure Sd) and drops by one decade if the temperature is increased up to 160 K. A comparison of this performance with a state-of-the-art nanocrystal-based intraband material is provided in Table S4 and shows that the device is clearly among the best-performing ones.

To summarize, we have used a mixture of HgSe and HgTe as a dye-sensitized infrared sensor where infrared sensing occurs through intraband absorption. Such a hybrid material preserves the intraband absorption of HgSe while reducing the dark current, increasing the activation energy, and fastening the time response. We have also unveiled the carrier dynamics in this material using infrared transient spectroscopy. We show that the relaxation of the 1P_e state to the 1S_e state in HgSe occurs within ≈ 3.5 ps. The mixture displays a new feature that is not present in pristine materials, which we attribute to charge transfer. The latter process occurs with a dynamics of 30–60 ps that can be related to the hopping time from HgSe to HgTe. Lastly, to improve the device performance, we have coupled this hybrid material to a guided-mode resonator, whose resonance spectrally matches the intraband absorption. The photocurrent signal resulting from the intraband contribution is enhanced by a factor of 4. This enables an increase in the operating temperature by 80 K compared to the reference device without a resonator. The achieved detectivity, for 5 μm cutoff detection, reaches 10⁹ Jones at 80 K and presents a time response below 200 ns for matching state-of-the-art devices based on intraband absorption.

METHODS

Chemicals. Mercury chloride (HgCl₂, Sigma-Aldrich, 99%), mercury acetate (Hg(OAc)₂, Alfa Aesar, >98%) (Note: as mercury compounds are highly toxic, they need to be handled with special care), tellurium powder (Te, Sigma-Aldrich, 99.99%), selenium powder (Se, Alfa Aesar, >99%), trioctylphosphine (TOP, Alfa, 90%), oleic acid (OA, Sigma, 90%), oleylamine (OLA, Acros, 80–90%), dodecanethiol (DDT, Sigma-Aldrich, 98%), lithium perchlorate (LiClO₄, Sigma-Aldrich, 98%), poly(ethylene glycol) (PEG, M_w = 6 kg·mol), absolute anhydrous ethanol (VWR), methanol (VWR, >98%), acetone (VWR), isopropanol (IPA, VWR), hexane (VWR, 99%), 2-mercaptoethanol (MPOH, Merck, >99%), *N,N* dimethylformamide (DMF, VWR), toluene (VWR, 99.8%), and methylisobutylketone (MIBK, VWR, >98.5%) are used in the experiment. All chemicals are used without further purification.

1 M TOP/Te Precursor. A total of 2.54 g of Te powder is mixed in 20 mL of TOP in a three-neck flask. The flask is kept under vacuum at room temperature for 5 min and then the temperature is increased to 100 °C. Furthermore, degassing of the flask is conducted for next 20 min. The atmosphere is switched to nitrogen and the temperature is increased to 275 °C. The solution is stirred until a clear orange coloration is obtained. The flask is cooled to room temperature and the color changes to yellow. Finally, this solution is transferred to a nitrogen-filled glovebox for storage.

1 M TOP/Se Precursor. A total of 1.54 g of Se powder is sonicated in 20 mL of TOP until a colorless solution is obtained.

HgSe 2.2k. In a 50 mL three-neck flask, 500 mg of Hg(OAc)₂, 10 mL of oleic acid, and 25 mL of oleylamine are

degassed under vacuum at 85 °C. Meanwhile, 1.6 mL of TOP/Se (1 M) is extracted from the glovebox. After the atmosphere is switched to N₂ and the temperature is stabilized at 100 °C, the TOP/Se solution is quickly injected. After 3 min, 1 mL of DDT (6.6 mmol) is injected, and a water bath is used to quickly decrease the temperature. The content of the flask is split over two tubes and EtOH is added. After centrifugation, the formed pellets are redispersed in one tube with toluene. The solution is precipitated for a second time using ethanol. Again, the formed pellet is redispersed in toluene. At this step, the CQDs are centrifuged in pure toluene to get rid of the lamellar phase. The solid phase is discarded. The stable phase is transferred in a weighted tube and finally precipitated using methanol. The solid is dried under vacuum for 30 min (in a glovebox vacuum chamber). Finally, CQDs are redispersed with 50 mg·mL⁻¹ toluene.

HgTe 4k. In a 100 mL three-neck flask, 543 mg of HgCl₂ and 50 mL of oleylamine are degassed under vacuum at 110 °C. Meanwhile, 2 mL of TOP/Te (1 M) is extracted from the glovebox and mixed with 8 mL of oleylamine. After the atmosphere is switched to N₂ and the temperature is stabilized at 80 °C, the TOP/Te solution is quickly injected. After 3 min, 10 mL of a mixture of DDT in toluene (10% of DDT) is injected, and a water bath is used to quickly decrease the temperature. The content of the flask is split over four tubes and MeOH is added. After centrifugation, the formed pellets are redispersed in one tube with toluene. The solution is precipitated for a second time using ethanol. Again, the formed pellet is redispersed in toluene. At this step, the CQDs are centrifuged in pure toluene to get rid of the lamellar phase. The solid phase is discarded. The stable phase is transferred in a weighted tube and finally precipitated using methanol. The solid is dried under vacuum for 30 min (in a glovebox vacuum chamber). Finally, CQDs are redispersed with 50 mg·mL⁻¹ toluene.

Preparation of the HgSe/HgTe Mixture. Two solutions of HgSe and HgTe are mixed to obtain an absorbance ratio of 1:1. A drop of the mixture is dried on the diamond cell of a Fisher ISS0 Fourier transform infrared spectrometer. In ATR configuration, between 8000 and 400 cm⁻¹, we acquire a spectrum of the mixture. Transmission electron microscopy of the mixture confirms the presence of the two materials. Owing to their very different shapes, they can be easily distinguishable from each other by regular imaging, where HgSe appears as a quasi-sphere and HgTe appears as branched particles, as shown in Figure S2. This is then further confirmed using EDX (energy dispersive spectroscopy) mapping, as shown in Figures S3 and S4.

Transmission Electron Microscopy. For TEM imaging, a drop of diluted NC solution is cast on a copper grid covered with an amorphous carbon film. The grid is degassed overnight under a secondary vacuum. A JEOL 2010F is used at 200 kV for the acquisition of images.

Scanning Transmission Electron Microscopy (STEM) Characterization. Electron microscopy characterization is performed using an FEI Talos transmission electron microscope operating at a 200 kV accelerating voltage. These characterization studies include bright-field high-resolution TEM (HRTEM), STEM (probe semiconvergence angle of 10.5 mrad), and EDX chemical analysis.

FTIR Spectra. FTIR spectra are acquired using a Fisher ISS0 Fourier transform infrared spectrometer. To measure CQD absorption, we use the spectrometer in ATR

configuration. A drop of a CQD solution is dried on the diamond cell. The source is infrared light and the detector is a DTGS ATR. Spectra are typically acquired between 8000 and 400 cm⁻¹ with a 4 cm⁻¹ resolution and averaged 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 a 1 kHz repetition rate and centered at 800 nm, with a 35 fs pulse duration and 1.5 mJ energy per pulse. The laser pulse is split into two parts, with an energy balance of 10/90%. The time delay between the two pulses is controlled using a motorized micrometric step motor. The highest energy arm is used to pump an optical parametric amplifier (OPA), which is used to generate a beam at 4 μm (≈0.3 eV) that spectrally matches the intraband signal from HgSe. For the experiment presented here, we used the 800 nm pulse as a pump and the OPA pulse as a probe. Typical focal spot sizes are around 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.

Photocurrent Spectra. The device is enclosed in a closed-cycle cryostat and cooled to the desired temperature. The head of the cryostat is brought in the sample compartment of a Fischer iSS0 FTIR spectrometer and illumination is provided by the focused Globar source through two ZnSe windows (one on the outer cryostat enclosure and one on the cold shield). The photocurrent is amplified using a Femto DLPCA-200 transimpedance amplifier, which also serves as a bias source. The output of the amplifier is sent back to the FTIR spectrometer through the ad hoc external detector adapter. All spectra are normalized to the background spectrum, acquired with a flat-response DTGS detector in the same spectral range to account for source and optical path spectra.

Activation Energy. Devices are mounted on the cold finger of a closed-cycle cryostat equipped with a cold shield. The samples are cooled to 80 K, and the current flow is measured with a Keithley 2634b source meter, which also biased the sample. Temperature is measured with a Lakeshore 325 temperature controller using a calibrated sensor on the sample holder. The resulting $I(T)$ curves are fitted to an Arrhenius model ($I_0 = Ae^{-E_a/kT}$) between 300 K and 80 K, allowing for the extraction of the activation energy E_a .

Responsivity Measurement. The source is a quantum cascade laser (QCL) at 4.4 μm or a blackbody at 980 °C placed 30 cm away from the sample. The QCL spot size is 0.17 mm². The flux can be chopped from 1 Hz to 100 kHz. The current from the device is amplified using a FEMTO DLPCA-100 at a 1.5 V bias and then fed into a Rohde&Schwarz RTE 1102 oscilloscope. When the blackbody is used, a germanium filter is utilized to suppress the high-energy part of the blackbody spectrum. The total power is calculated according to

the formula $P = A_D \cdot \pi \cdot \cos(\beta) \cdot \sin^2(\alpha) \cdot \int_{\lambda_{\min}}^{\lambda_{\max}} \frac{hc^2}{\lambda^5} \cdot \frac{1}{e^{hc/kT}} d\lambda$,

where α is the solid angle illuminated, β is the angle of the sample (0° corresponds to sample perpendicular to the light illumination), A_D is the device area, h is the Planck constant, c is the velocity of light, k is the Boltzmann constant, and T is the temperature. The light is chopped from 1 to 100 Hz. The photocurrent is measured using a Zurich Instruments MFLI lock-in amplifier under a 1.5 V applied bias. The sample is mounted on the cold finger of a close cycle cryostat.

Noise Measurement. The current from the device (at a 1.5 V bias, kept in the dark) is amplified using a Femto DLPCA-200, and then fed into an SRS SR780 spectrum analyzer. The sample is mounted on the cold finger of a close cycle cryostat.

Determination of Detectivity. The specific detectivity (in Jones) of the sample is determined using the formula $D^* = \frac{R\sqrt{A}}{S_1}$, where R (in $A \cdot W^{-1}$) is the responsivity, S_1 is the noise ($A/\sqrt{Hz}$), and A is the area of the device (cm^2).

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsphotonics.1c01847>.

- (i) Additional material characterization (microscopy and spectroscopy), (ii) additional electromagnetic simulations (absorption amp and dispersion amp), (iii) procedure for device fabrication, (iv) procedure for device characterization, and (v) comparison of performance with state-of-the-art intraband devices (PDF)

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Notes

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■ ACKNOWLEDGMENTS

The project was supported by the ERC starting grant blackQD (grant no 756225) and Ne2Dem (grant no 853049). The authors acknowledge the use of clean-room facilities from the “Centrale de Proximité Paris-Centre”. This work was also supported by the Region Ile-de-France in the framework of DIM Nano-K (grant dopQD) and by the French state funds managed by the ANR within the Investissements d'Avenir Programme under reference ANR-11-IDEX-0004-02 and more specifically within the framework of the Cluster of Excellence MATISSE and also by the grant IPER-Nano2, Copin (ANR-19-CE24-0022), Frontal (ANR-19-CE09-0017), Graskop (ANR-19-CE09-0026), NITQuantum (ANR-20-ASTR-0008-01), Bright (ANR-21-CE24-0012-02), and MixDferro (ANR-21-CE09-0029). AC thanks Agence innovation defense for PhD funding. DB acknowledges the financial support from the French department of defense (DGA) in the frame of the Oscillateur térahertz project (grant no 2018 60 0071 00 470 75 01)

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