

Guided mode resonator coupled with nanocrystal intraband absorption

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1. Material

1.1. Material synthesis

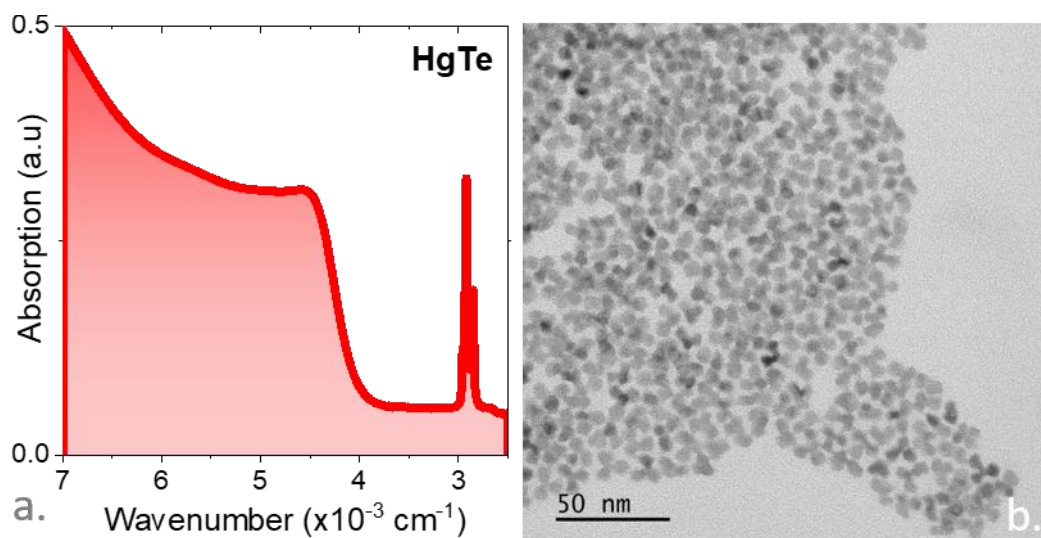


Figure S 1 Structural and spectroscopic properties of HgTe NCs. a. Absorption spectrum of HgTe NCs. b. TEM image of HgTe NCs.

1.2. Properties of the HgTe/HgSe mixture

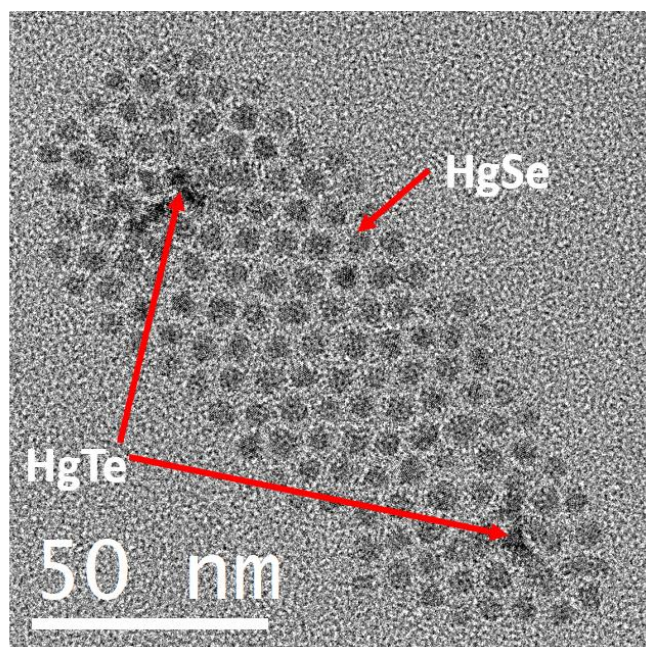


Figure S 2 TEM image of the HgSe/HgTe mixture.

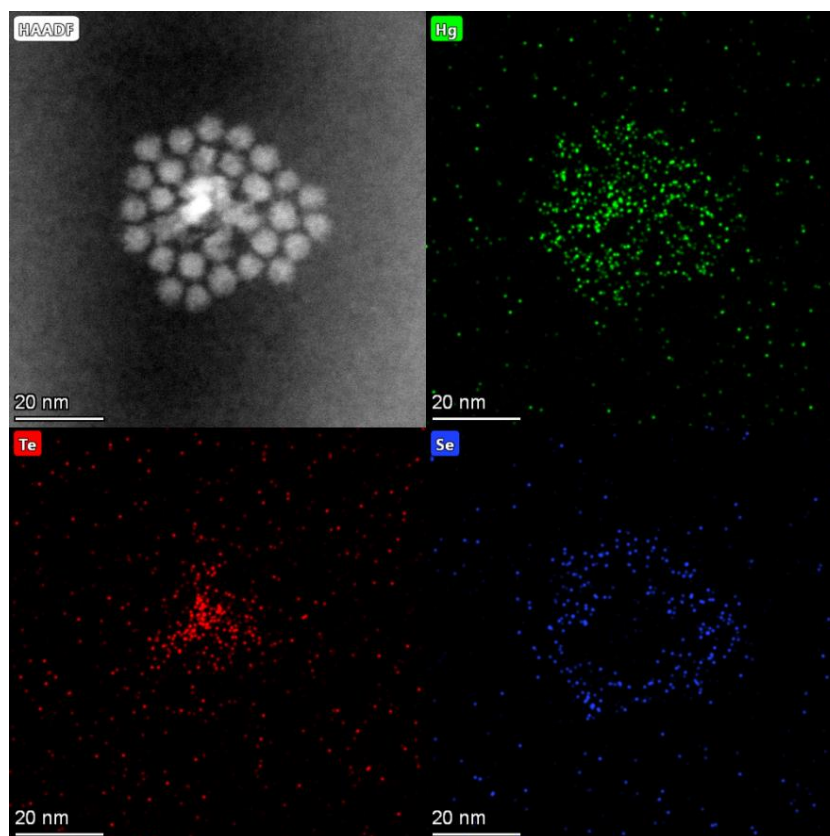


Figure S 3 (top left) HAADF image of HgSe/HgTe mixture. Hg (top right), Te (bottom left) and Se (bottom right) EDX map of the same area.

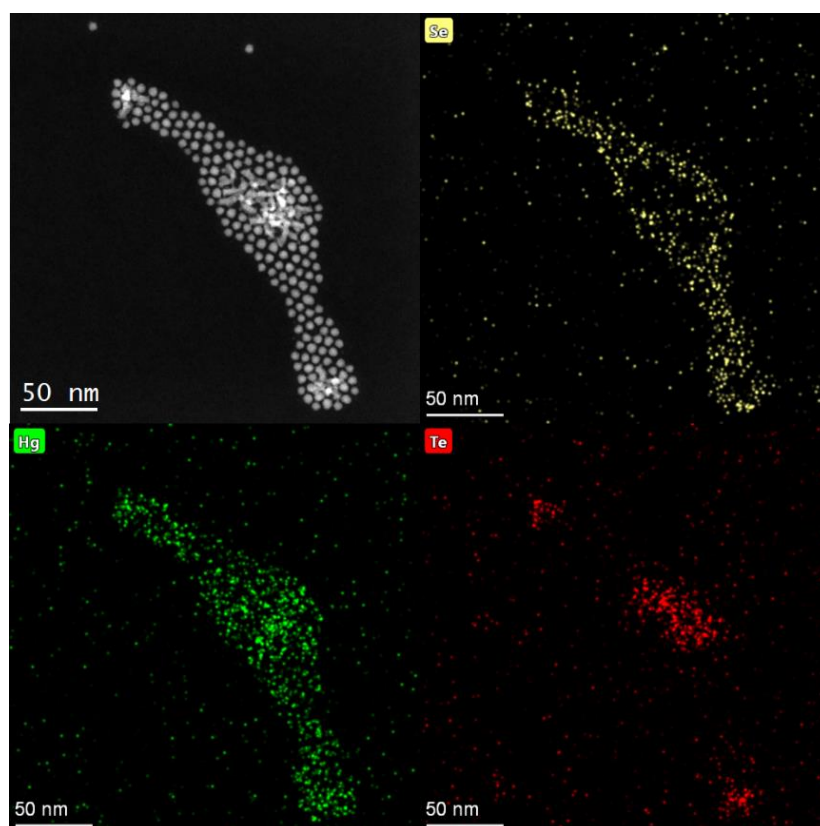


Figure S 4 (top left) HAADF image of HgSe/HgTe mixture. Hg (top right), Te (bottom left) and Se (bottom right) EDX map of the same area.

Estimation of HgTe/HgSe nanocrystals ratio: EDX measurement is conducted in a Zeiss Supra 40 SEM with an operating bias of 10 keV. With a 1 μm scale resolution, this strategy directly averaged the Te/Se ratio over a large number of NCs. From EDX analysis, we can deduce that $n_{Te} = 3.2 \cdot n_{Se}$ with n_{Te} the Te atomic fraction. The ratio between HgTe NCs and HgSe NCs can be expressed as:

$$\frac{N_{HgTe}}{N_{HgSe}} = \frac{n_{HgTe}}{n_{HgSe}} \times \frac{a_{QD-Se}}{a_{QD-Te}}$$

Where $\frac{n_{HgTe}}{n_{HgSe}}$ is the atomic ratio determined from EDX, a_{QD-Te} (resp. a_{QD-Se}) is the number of Te (resp. Se) atoms in one nanoparticle. From TEM images, we found that HgSe is a 6.4 nm sphere and HgTe an 8-10 nm tripod (modeled as 3 spheres with 6 nm diameter). Therefore, we have $V_{HgTe} = 3 \cdot V_{Pod-HgTe}$, with V_{HgTe} the volume of a HgTe tripod NC and $V_{Pod-HgTe}$ the volume of one arm of the HgTe tripod. Then, knowing the volume V_{HgSe} of a HgSe NC, and the unit cell volume $V_{Unit\ cell-HgTe}$ (resp. $V_{Unit\ cell-HgSe}$), we can write:

$$\frac{a_{QD-Se}}{a_{QD-Te}} = \frac{\frac{V_{HgSe}}{V_{Unit\ cell-HgSe}}}{\frac{V_{HgTe}}{V_{Unit\ cell-HgTe}}} \approx \frac{1}{2.1}$$

Finally, the nanoparticles ratio is:

$$\frac{N_{HgTe}}{N_{HgSe}} \approx 1.5.$$

Table S 1 Atomic fraction for each component by EDX analysis

Component	Atomic fraction (%)
Hg	48.9
Te	38.8
Se	12.3

HgTe/HgSe ink: 500 μL of the mixture NC solution in toluene is mixed with 500 μL of exchange solution as previously reported¹ and 1 mL of DMF to induce phase transfer toward polar phase. 5 mL of hexane is added to the solution and mixed with vortex and sonication. After a few seconds, two phases are clearly visible and the hexane phase is removed. The solution is cleaned with hexane two more times. Then, the solution is precipitated by adding toluene and centrifuged at 6000 rpm for 3 min. Supernatant is discarded and the NCs are redispersed in 70 μL of DMF.

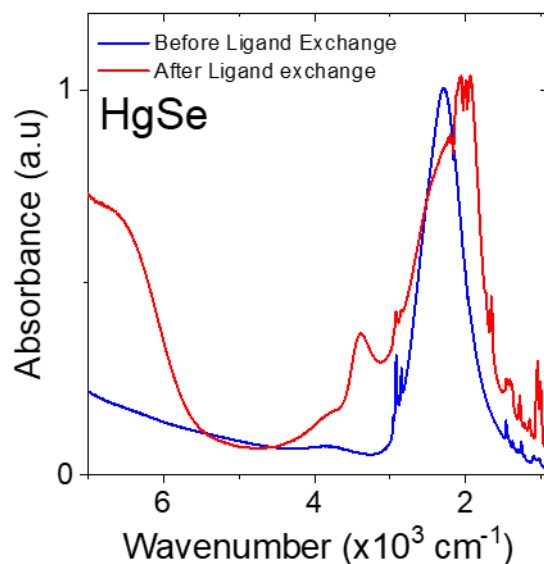


Figure S 5 Absorption spectrum of HgSe NCs before and after ligand exchange

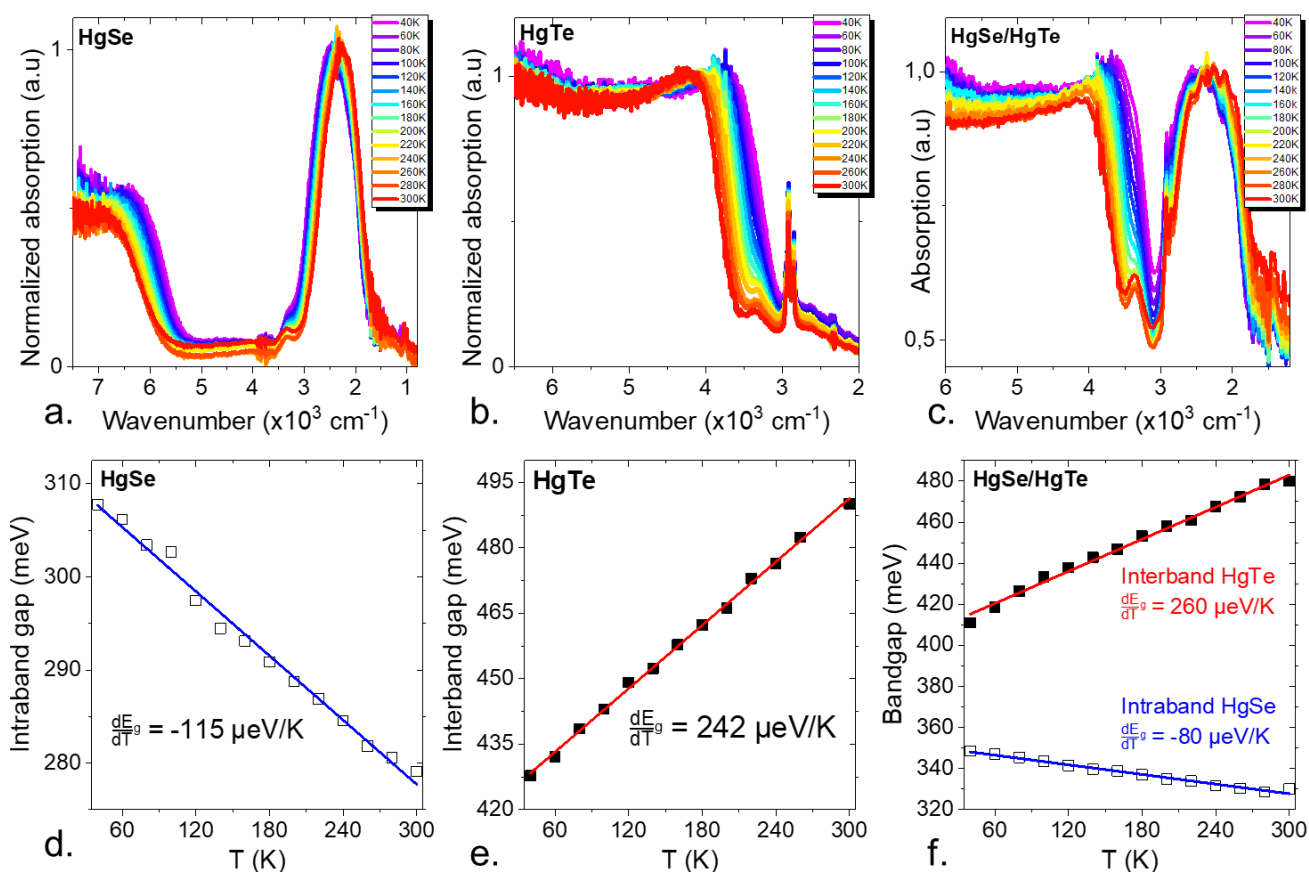


Figure S 6 Temperature dependence of the spectra of HgSe, HgTe and their mixture. Normalized absorption spectrum of HgSe NCs (a), HgTe NCs (b) and HgSe/HgTe mixture (c). Measurements are conducted in a transmission configuration while the material is deposited on a double side polished undoped Si wafer. Bandgap shift as a function of temperature of HgSe NCs (d), HgTe NCs (e) and HgSe/HgTe mixture (f).

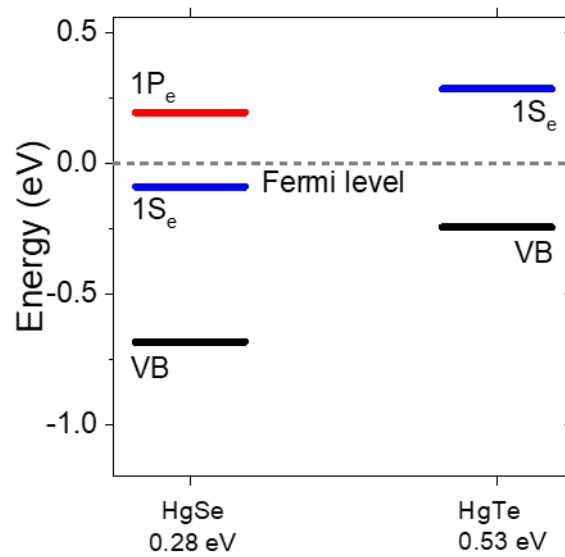


Figure S 7 Band alignment of HgSe and HgTe revealed from X-ray photoemission. Figure is adapted with permission from ref 2. Copyright 2019 Springer Nature <https://creativecommons.org/licenses/by/4.0/>.

2. Electromagnetic simulation

Calculations have been achieved with Matlab library based on Rigorous Coupled-Wave Analysis (RCWA).³ The Maxwell equations are solved in each layer and interface conditions are applied to find the final solution of the whole structure. We considered incoming plane wave under normal incidence, either with transverse magnetic (TM) or transverse electric (TE) polarization, *i.e.*, with magnetic field or electric field parallel with the slits of the gratings, respectively. Grating is supposed to be invariant along *y* direction, and repeated infinitely along *x* direction with a period of 10 μm . Inputs needed for this simulation are the device structure and the optical index of the different materials.

Table S 2 Layer thicknesses for each layer of the device

Layer	Interdigitated on Au/Al ₂ O ₃ for GMR
External Environment	Air
Film	Mix HgSe:HgTe d=270 nm
Structure	Mix HgSe:HgTe/Au t _g =50 nm
Dielectric	Al ₂ O ₃ L _{Al2O3} =40 nm
Gold mirror	Au 200 nm

Regarding the optical indices, for Al₂O₃ we use $n=1.6$ and $k=0$, and $n=1$ for the air. Concerning the gold⁴, we use previously reported refractive indices. For the real part of the nanocrystals index, we use $n=2.3$ ⁵. For the imaginary part, we use the shape of the absorption feature. The absorption coefficient of HgTe is measured to be $3 \times 10^3 \text{ cm}^{-1}$ giving $k=0.04$ at the band edge.

The absorption map is deduced from the electric field at each point:

$$Absorption = \frac{\pi}{\lambda} \int_S \text{Im}(\varepsilon(M)) (|E_y|^2) dS, \quad \text{in TE polarization}$$

$$Absorption = \frac{\pi}{\lambda} \int_S \text{Im}(\varepsilon(M)) (|E_x|^2 + |E_z|^2) dS, \quad \text{in TM polarization}$$

In **Figure S 8 Absorption maps at the resonant wavelengthes of the GMR device**.we show the absorption map for the different resonance observed in the Figure 4 of the main text. **Table S 3** quantizes the absorption at the wavelength corresponding to these resonances and also quantize the part of the absorption occurring within the semiconductor. Finally, **Figure S** shows the dispersion map for the TE and TM polarization.

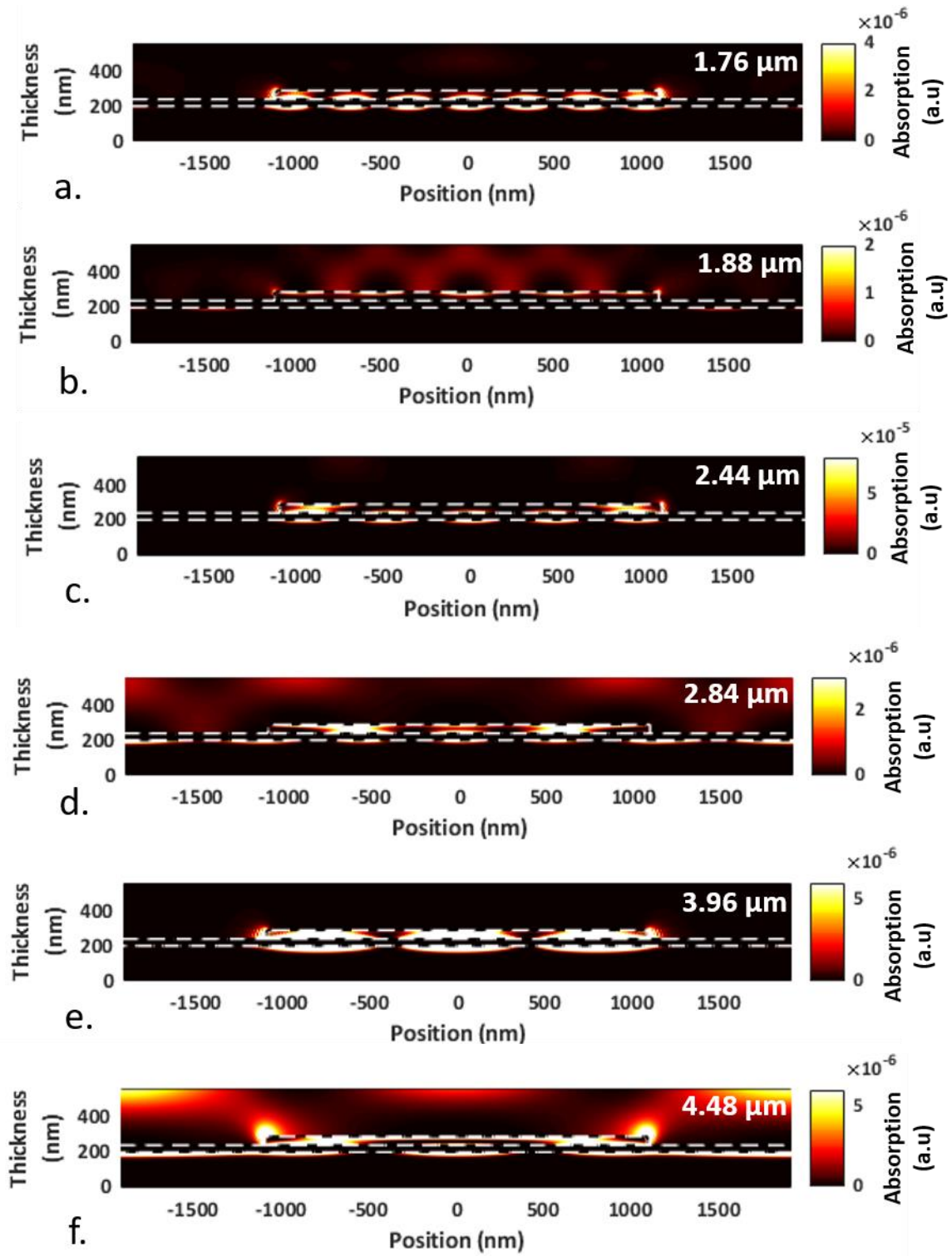


Figure S 8 Absorption maps at the resonant wavelengths of the GMR device.

Table S 3 Absorption of the device and the nanocrystal array at the resonance wavelengths in the GMR device.

Peak position	% TM absorption	% absorption within NCs
1.76 μm	29%	42%
1.88 μm	22%	79%
2.44 μm	79%	44.5%
2.84 μm	41%	64%
3.96 μm	78%	12.5%
4.48 μm	99%	60.80%

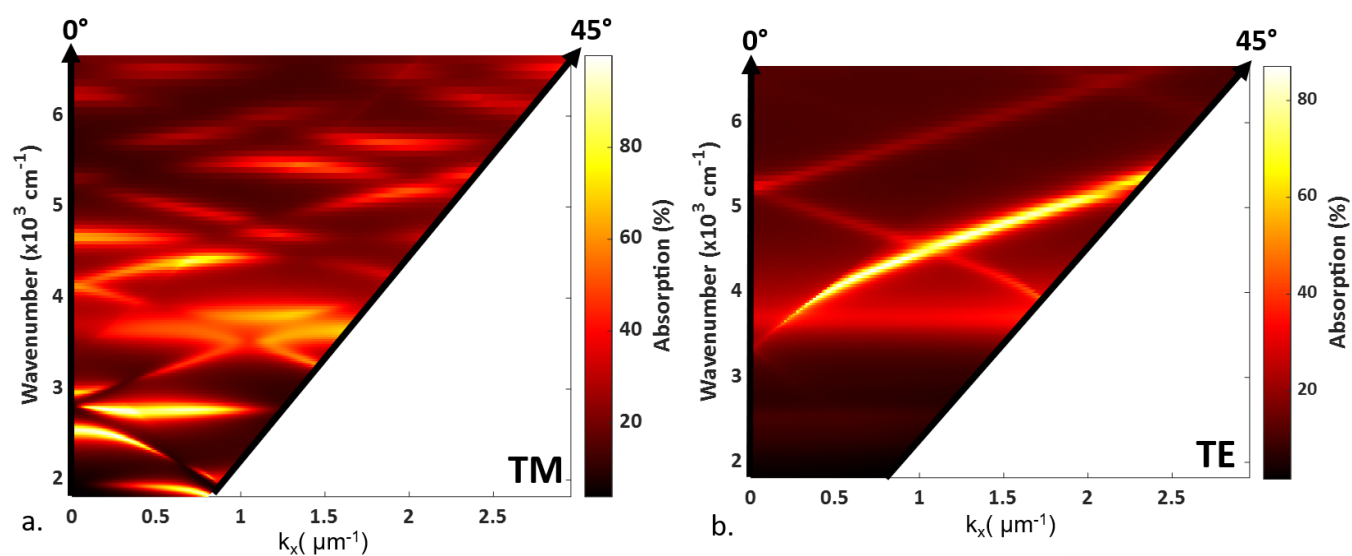


Figure S 9 Dispersion of the GMR grating. Dispersion map for the TM mode (a.) and TE mode (b.).

3. Device fabrication

Step 1: Deposition of the gold mirror. The surface of Si/SiO₂ wafer (400 nm oxide layer) is cleaned by sonication in acetone. The wafer is rinsed with acetone, then isopropanol and dried with a N₂ gun. A final cleaning is made using an O₂ plasma. An adhesion promoter (TI PRIME) is spin-coated onto the substrate and baked at 120 °C for 2 min. AZ5214E is spin-coated and baked at 110 °C for 90 s. The substrate is exposed under UV through a pattern mask for 1.5 s. The film is then baked at 125 °C for 2 min in order to invert the resist. Then a 40 s flood exposure is performed. The resist is developed using a bath of AZ726 for 32 s, rinsed in pure water and finally dried with N₂. We then deposit 5 nm of chromium and 80 nm of gold using thermal evaporation. The patterned sample is introduced in an EDWARDS evaporator for a deposition of 5 nm of aluminum. The lift-off is performed by dipping the film in acetone for 1 hour. The gold mirror is rinsed using isopropanol and dried with a N₂ flow.

Step 2: Insulating gold mirror. Then the sample is loaded into an Atomic Layer Deposition (ALD) deposition system AT400 from ANRIC technologies for a 400 min deposition of Al₂O₃. The obtained alumina layer is 40 nm thick.

Step 3 Deposition of the interdigitated electrodes and macroscopic pads for reporting electric contacts. After having rinsed the sample with acetone and isopropanol, the adhesion promoter and the resist are deposited as described in step 1. The sample is then exposed through a second chromium mask for 1.5 s. The same resist inversion process as described in step 1 (annealing + flood exposure) is performed before developing the sample in AZ726 developer for 25 s and rinsing it in pure water. The patterned sample is then introduced into a VINCI evaporator for deposition of 5 nm of chromium and 150 nm of gold. At the end, the sample is dipped in acetone overnight to remove remaining resist. The electrodes are 1 mm long, 10 µm large and spaced by 20 µm. In the main article, they are called “conventional electrodes”, in contrast to nanoelectrodes used to induce GMR.

Step 4 Deposition of nanoelectrodes. After having rinsed the sample with acetone and isopropanol, a layer of A6 PMMA 950 is spin-coated onto the substrate and baked for 15 min at 150 °C. The samples are transferred in a Zeiss Supra 40 SEM with Raith ELPHYS Quantum device for electron beam lithography. The operating bias is set to 20 kV and the aperture to 20 µm. The current is measured at 100 pA. The dose is set at 180 µC.cm⁻². The PMMA is developed by dipping the film in a solution of MIBK:isopropanol (1:3) for 50 s and rinsed in pure isopropanol for 20 s. A 3-min plasma cleaning is made. We then deposit a 5 nm layer of chromium and a 50 nm layer of gold using thermal evaporation. The lift-off is performed by dipping the film in acetone overnight. Sonication at low power is necessary to remove the remaining resist. 20 pairs of digits are deposited as electrodes. The electrodes are 500 µm long. For a resonance at 4.4 µm the digits are 2.2 µm wide and spaced by 3.85 µm.

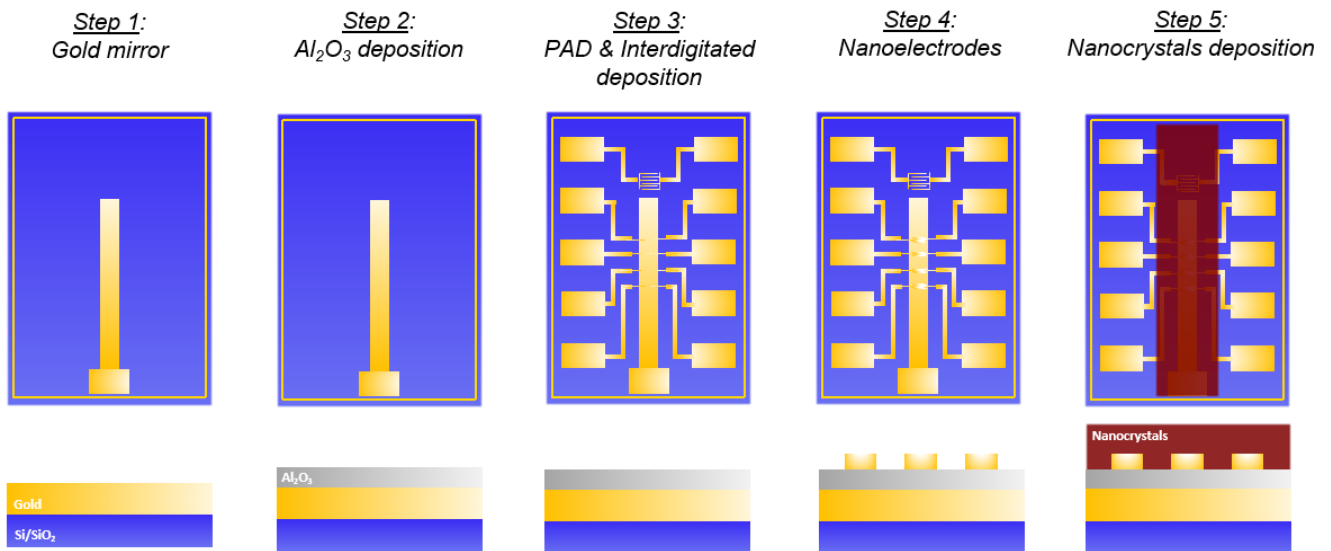


Figure S 10 Main fabrication steps of the electrodes used to induce a GMR. Top part is a top view, while bottom part is a side view. Step 1 relates to the gold mirror deposition. Step 2 relates to the deposition of Al_2O_3 dielectric to avoid shorts through the back mirror. Step 3 relates to the conventional interdigitated electrodes and macroscopic pad deposition. Step 4 relates to the fabrication of the interdigitated electrodes inducing GMR through e-beam lithography. Step 5 relates to the NC film deposition.

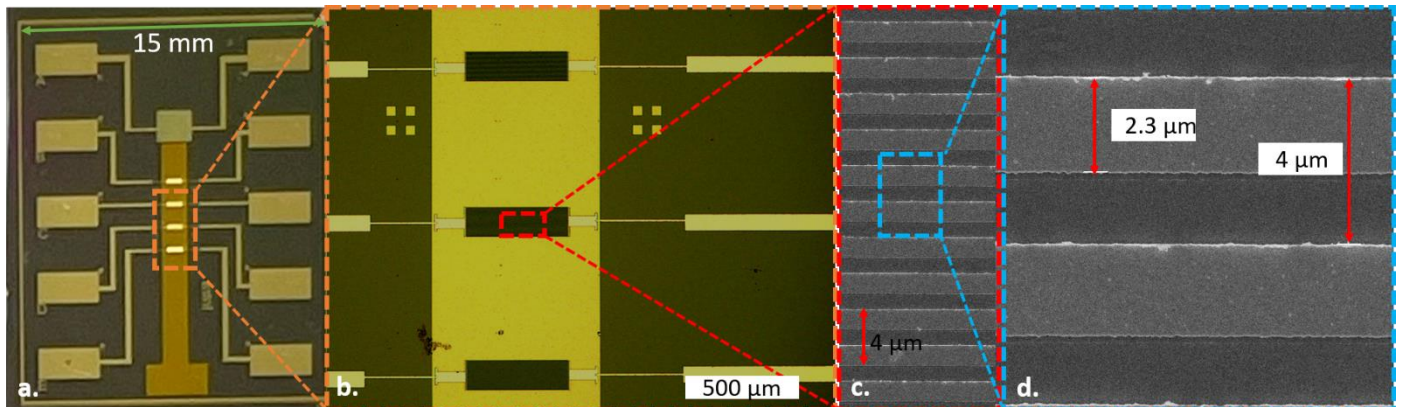


Figure S 11 Images of the GMR device. a. Optical image of the chip with 4 GMR device and an interdigitated electrode used as reference. b. Optical image on the optically active area of the chip. c. Electron microscopy image of the grating used also as electrode. d. Zoomed Electron microscopy image on two periods of the grating.

4. Device characterization

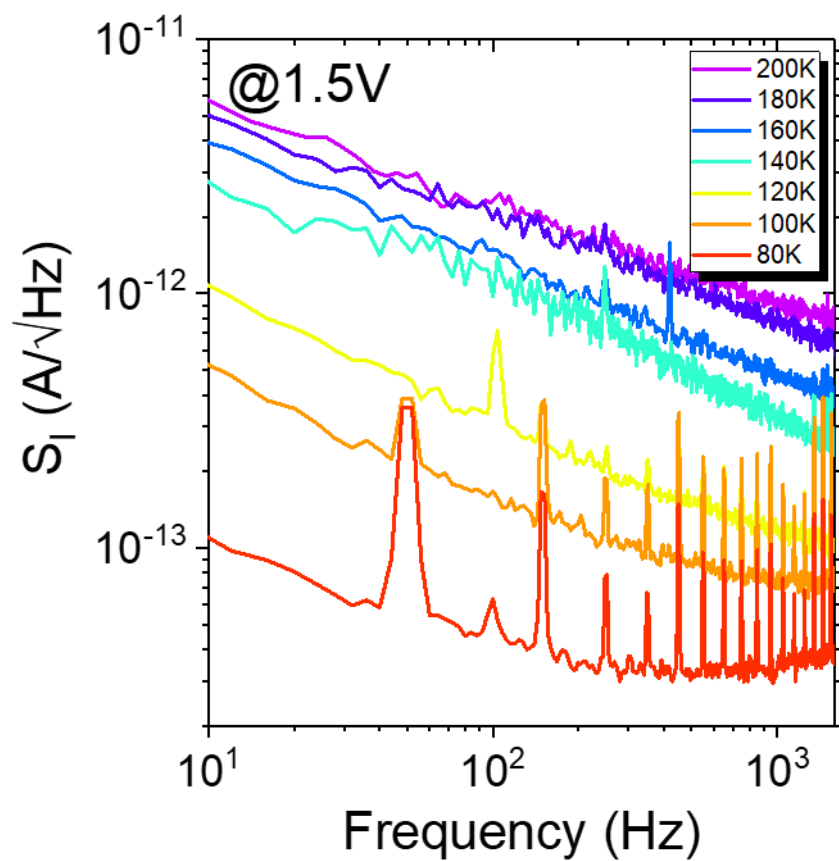


Figure S 12 Noise measurements. Noise spectral density in the GMR device under 1.5 V and under different temperature.

5. Comparison with state-of-the-art intraband device

Table S 4 provides a comparison of state-of-the-art photodetection relying on intraband absorbing nanocrystal-based devices.

Table S 4 Figure of merit for nanocrystal-based photodetector based on intraband absorption

Intraband absorbing material	Device structure	λ (μm)	R (A.W ⁻¹)	D* (Jones)	Operating T (K)	Times response	Reference
HgSe	Photoconductor	4.4 μm	5×10^{-4}	8.5×10^8	80 K	-	⁶
HgSe	Photoconductor	6 μm	0.8	$\approx 10^8$	300 K	-	⁷
HgSe	Diode	4 μm	5×10^{-3}	10^9	80 K	<200 ns	⁸
HgSe	Photoconductor	4.4 μm	3×10^{-3}	10^9	80 K	<200 ns	This work
	+ resonator		2×10^{-3}	6×10^7	200 K		
Ag₂Se	Photoconductor	4.8 μm	8×10^{-6}	-	25 K	seconds	⁹
Ag₂Se	Photoconductor	4.5 μm	3.5×10^{-4}	-	90 K	-	¹⁰
Ag₂Se	Barrier device	4.5 μm	13×10^{-3}	3×10^5	300 K	seconds	¹¹
Ag₂Se/PbS	Diode	4.5 μm	18×10^{-3}	8×10^6	300 K	-	¹²
PbS	Photoconductor	5-9 μm	$\approx 10^{-4}$	$\sim 10^4$	80 K	>200 ms	¹³

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