Temperature-Dependent Charge Carrier Transfer in Colloidal Quantum Dot/Graphene Infrared Photodetectors

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Colloidal PbS quantum dot (QD)/graphene hybrid photodetectors are emerging QD technologies for affordable infra-red light detectors. By interfacing the QDs with graphene, the photosignal of these detectors is amplified, leading to high responsivity values. While these detectors have been mainly operated at room temperature, low-temperature operation is required for extending their spectral sensitivity beyond a wavelength of 3 μm. Here, we unveil the temperature-dependent response of PbS QD/graphene photodetectors by performing steady-state and time-dependent measurements over a large temperature range of 80–300 K. We find that the temperature dependence of photo-induced charge carrier transfer from the QD layer to graphene is (i) not impeded by freeze-out of the (Schottky-like) potential barrier at low temperatures, (ii) tremendously sensitive to QD surface states (surface oxidation), and (iii) minimally affected by the ligand exposure time and QD layer thickness. Moreover, the specific detectivity of our detectors increases with cooling, with a maximum measured specific detectivity of at least $10^{10}$ Jones at a wavelength of 1280 nm and temperature of 80 K, which is an order of magnitude larger compared to the corresponding room temperature value. The temperature- and gate-voltage-dependent characterization presented here constitute an important step in expanding our knowledge of charge transfer at interfaces of low dimensional materials and towards the realization of next-generation optoelectronic devices.
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KEYWORDS lead sulfide, PbS, ethanedithiol, EDT, 2D materials, low-temperature, optoelectronic device

ABSTRACT: Colloidal PbS quantum dot (QD)/graphene hybrid photodetectors are emerging QD technologies for affordable infrared light detectors. By interfacing the QDs with graphene, the photosignal of these detectors is amplified, leading to high responsivity values. While these detectors have been mainly operated at room temperature, low-temperature operation is required for extending their spectral sensitivity beyond a wavelength of 3 μm. Here, we unveil the temperature-dependent response of PbS QD/graphene photodetectors by performing steady-state and time-dependent measurements over a large temperature range of 80–300 K. We find that the temperature dependence of photo-induced charge carrier transfer from the QD layer to graphene is (i) not impeded by freeze-out of the (Schottky-like) potential barrier at low temperatures, (ii) tremendously sensitive to QD surface states (surface oxidation), and (iii) minimally affected by the ligand exposure time and QD layer thickness. Moreover, the specific detectivity of our detectors increases with cooling, with a maximum measured specific detectivity of at least 10^{10} Jones at a wavelength of 1280 nm and temperature of 80 K, which is an order of magnitude larger compared to the corresponding room temperature value. The temperature- and gate-voltage-dependent characterization presented here constitute an important step in expanding our knowledge of charge transfer at interfaces of low dimensional materials and towards the realization of next-generation optoelectronic devices.

Infrared (IR) light detection plays a vital role in optical communication, night vision, remote sensing, and spectral analysis. State-of-the-art commercially available IR detectors typically employ epitaxially grown InGaAs or HgCdTe, which are expensive in production and elaborate in read-out electronics integration.\(^1,2\) Alternative emerging concepts exploit IR sensitive colloidal quantum dots (QDs), produced by facile, inexpensive and scalable solution synthesis methods, and are easily integrated into photoconductive QD-based devices.\(^3,5\) Nevertheless, these QD-based photoconductors suffer from large film resistivities, and require high bias voltages with large detector width-to-length ratios due to hindered charge transport characteristics. These challenges can be mitigated by utilizing a hybrid QD/graphene field-effect transistor (FET) structure.\(^6\) The current mechanistic understanding of these QD/graphene FETs invokes a band alignment between graphene and the QD thin film with a Schottky-like potential barrier. Under illumination, photons are absorbed in the QD-layer, generating electron-hole pairs, and—due to the built-in electric field—one carrier type is accumulated in the QD thin film, while the other is transferred to the graphene channel altering the conductivity of this low-resistance graphene layer.\(^6,8\) The trapping of one carrier type generates photoconductive gain, leading to increased responsivity values, according to the equation: \(G = \frac{\tau_{\text{trans}}}{\tau_{\text{tr}}}\), with \(\tau_{\text{tr}}\) being the lifetime of trapped charge carriers in the QD thin film, and \(\tau_{\text{trans}}\) the drift time of charge carriers in the graphene FET.\(^6\) This allows realizing small hybrid detectors with a footprint of just a few \(\mu\)m², a width-to-length ratio reduced to unity, and an operation drain voltage below one volt. In the case of QD/graphene FETs, various QD materials have been investigated differing in the spectral sensitivity such as ZnO\(^9,10\) for UV detection, perovskites\(^11,12\) and CdSe\(^13\) for visible light detection, and PbS\(^5,7,14\) in the near-IR (NIR, 0.7–1.4 μm) and entering the short-wavelength IR (SWIR, 1.4–3 μm) range. The spectral photosresponse will likely be further pushed into mid-wavelength IR (MWIR, 3–8 μm), employing narrow bandgap semiconductor QDs such as HgTe.

Another direction in the field of infrared focal-plane arrays heads towards the implementation of multicolor pixels, where each pixel can differentiate between multiple IR wavelengths enabling better object identification.\(^15\) Two-color IR detectors have been realized for HgCdTe thin films\(^15\) and HgTe QDs, in vertically stacked photodiode configuration.\(^16\) However, the path to a larger number of detected colors is faced with much more complex fabrication. In this regard, relatively simple processing of QD/graphene FETs by thin-film QD patterning through a local deposition of QDs by means of nanoprinting,\(^14,17,18\) or stamp transfer\(^19\) offers potential for multicolor detector arrays, where each pixel may consist of multiple color-sensitive sub-pixels. For example, a three-color detector array has been demonstrated with QD-based photoconductors by dividing each pixel into sub-pixels.\(^15\) These detectors operated at room temperature with rather inferior specific detectivity in the MWIR, relying on large detector width-to-length ratios and required moderate drain bias.\(^15\) While NIR and SWIR detectors perform well at room temperature, this operational temperature...
is intrinsically problematic for a spectral range beyond 3 μm and cooling of the detector is required. Therefore, future multicolor IR photodetectors with spectral sensitivity in the MWIR will require NIR and SWIR detectors to operate at the same reduced temperature as MWIR detectors. This calls for extensive investigations into the low-temperature characteristics of current NIR and SWIR detectors.

The charge carrier transfer across the QD/graphene interface potential barrier is crucial for the operation of the detector and is known to be temperature-dependent. Following illumination, the separated charge carriers recombine by temperature-driven charge carrier transfer over the potential barrier. In fact, for phototransistors operating at low temperatures, blocking of the charge carrier transfer and loss of the detector’s functionality has been observed in a recent study with CsPbI$_3$ QD/graphene FETs at a temperature of 200 K and constant gate voltage, as fewer charge carriers are transferred from the QDs to the graphene. Temperature-dependent investigations on PbS QD/graphene FETs have not been reported to date, yet they are imperative for the development of QD-based multicolor detector developments. Here, we present a study on temperature- and gate voltage-dependent photoreponsivity of PbS QD/graphene FETs. As opposed to previous experiments with CsPbI$_3$ QDs, the photoresponse at low temperatures exceeds the room temperature value and changes its sign. As such, our findings demonstrate the importance of QD/graphene FETs for potential implementation in multicolor photodetector arrays, when combined with MWIR detectors fabricated on the same substrate, and guide the detector optimization by revealing fundamental principles of the photoreponse phenomena.

Figure 1a depicts a schematic of a PbS QD/graphene FET. Colloidal PbS QDs were nanoprinted on top of graphene FET (5 μm channel width, 50 μm channel length) fabricated on Si/SiO$_2$ substrates. The native oleic acid ligands of the QDs have been exchanged with 1,2-ethanediethiol via post-nanoprinting solid-state ligand-exchange. In a top-view optical bright-field image (Figure 1b) of a hybrid PbS QD/graphene FET, Si/SiO$_2$ substrate is seen as violet region, the Au electrodes appear yellow, and the PbS QD thin film after ligand exchange is green. The graphene stripe is covered by the QD thin film and not visible in the optical image. For operation, a small source-drain bias is applied between the electrodes. Light is absorbed in the QD thin film resulting in the formation of an electron-hole pair and the subsequent accumulation of one charge carrier type in the film and the opposite type being transferred to the graphene transistor. The carrier separation at the interface results in a change of the electric field and a measurable change in the conductivity of the graphene layer. An additional bottom-gate voltage is applied to optimize the responsivity magnitude. Figure 1c shows a typical wavelength-resolved photoresponse which follows the absorption spectrum of PbS QD colloidal dispersion (Figure S1), confirming the integrity of QD transformation after the printing and drying process. A detector array, consisting of three pixels, was fabricated (optical image in Figure S2a): one pixel is discussed in the main text and denoted “Device A1”, while the results for Devices A2 and A3 can be found in the Supplementary Information. All three pixels were fabricated utilizing the same QD ink. As mentioned above, higher photoreponsivity is expected with higher photocurrent gain. Longer trapping times can, for example, originate from charge carrier accumulation at the interface barrier or by trapping the carriers by QD trap states. The latter can be achieved by QD oxidation, resulting in QD surface trap states, therefore, the QD ink was exposed for an extended time to ambient conditions prior to nanoprinting. The QD layer thickness was kept constant within each pixel, but varied from pixel to pixel in the range of 170–230 nm, allowing the investigation of the QD layer thickness dependence on the temperature- and gate-voltage-dependent responsivity measurements.

The photoresponse of the devices was measured with a lock-in amplifier and a 5 Hz modulated signal (further details in the Methods Section). Figure 2a shows the photoresponse of
Device A1. At room temperature, two local maxima can be observed on the left and right sides of the charge neutrality point of graphene (CNP), while the phase of the signal jumps by 180° from the hole to the electron charge carrier regime of graphene (Figure 2b). The CNP varies only slightly when the device is cooled to 80 K, resulting in a nearly vertical line of no photoreponse as well as a phase jump in the responsivity and phase false-color maps (Figure 2a, b; highlighted by a black dashed line), respectively. Surprisingly, in Figure 2a the photoresponse vanishes at a diagonal line that is accompanied by a phase jump of 180° as observed in the corresponding values in Figure 2a and Figure 2b (highlighted by a dotted white line). The additional phase jump shows a change in polarity of the major charge carriers that are transferred to graphene and their exact sign was investigated by probing the transfer of charge carriers under illumination with time traces (Figure S3) at the local maxima (P1_A1 to P4_A1). The rising part of the current trace under illumination cannot be fitted with a single exponential function, but consists of at least one fast and one slow component. While the slow component is in the range of tens of seconds at room temperature, it is even slower at lower temperatures (Figure S3i, j). In this respect, the slow time constant is likely related to trap states within the QD thin film and charging/discharging of those, which at low temperatures is significantly slower than the measurement time at light modulation of 5 Hz. The faster component, which is ascribed to the band alignment and charge carrier transfer to graphene, is comparable or faster than 100 milliseconds (Figure S3). The results of both measurements, responsivity and time traces, allow identifying the two different regimes of charge carrier transfer shown in Figure 2c depicting the sign of the majority photo-generated charge carriers transferred to the graphene channel. Under illumination, holes are transferred to the graphene channel at high temperatures (300 K) while electrons are accumulated in the QD thin film (yellow area in Figure 2c). At low temperatures (80 K), an inverse behavior is observed, namely, under illumination electrons are transferred to the graphene and holes are accumulated within the QD thin film (pink area in Figure 2c). The appearance of the responsivity and phase measurements when comparing Device A1 to Devices A2–A3 (Figure S4) is highly similar, with only variation in the magnitude of photoreponse (with lower responsivity for thinner QD films), which proves the reproducibility of the obtained behavior in general.

Figure 2. Temperature- and gate-voltage-dependent measurement of Device A1. False-color maps are shown for (a) responsivity and (b) phase. The sign of transferred charge carrier under illumination (c) is deduced from a combination of the responsivity measurement and the transfer characteristics of the FET. (d) Energy levels of graphene and QD thin film are depicted without the materials being in contact with each other. The conduction band is in blue, valence band is in red, and the Fermi level is shown as an extended black dotted line for comparison with the Fermi level position of the QD thin film at different temperatures. In (e) the band alignment at 300 K and 80 K is drawn with photo-induced charge carriers and their transfer to graphene.
The transfer of holes to graphene at room temperature is in agreement with literature employing the same QD material-ligand-graphene combination, and a band alignment between graphene and the QD layer has been proposed as a reason for photo-induced charge transfer and photodetector operation mechanism. However, low-temperature measurements on PbS QD/graphene FETs have not been reported to date. Hence, to explain the observed behavior, we extend the room temperature band alignment model to low temperatures. For simplicity, we describe the QD thin-film energy levels and alignment as continuous bands. The Fermi level of the QD layer at 300 K is closer to the vacuum level with respect to the graphene (Figure 2d), and upon contacting the two materials, electrons from the QD layer are transferred to the graphene to equilibrate the Fermi levels, resulting in a Schottky-like potential barrier as shown in Figure 2e. Upon illumination of the detector with energies larger than the bandgap of the QD, electron-hole pairs are generated within the QD thin film. The internal electric field, created by the potential barrier, will spatially separate charge carriers having electrons accumulated in the QD thin film and holes extracted to graphene resulting in the measured photo-generated current variations in the graphene channel. The Fermi level and the conduction band (CB) and valence band (VB) energies of QDs with respect to the vacuum energy depend on interface dipoles between the QD surface and ligands as well as on the intrinsic ligand dipole. They can be altered by QD size, stoichiometry, ligands, remote doping, and trap states. In Device A the ligands are exchanged with 1,2-ethanethiol and, additionally, the QD surface possesses PbSO\textsubscript{3} and PbSO\textsubscript{4} moieties from surface oxidation resulting in trap states with a deep energy distribution and highest state density located at the range of 0.1-0.3 eV. While at room temperature some of these trap states are thermally accessible and thus partially occupied, at lower temperatures the trap states will freeze out and the majority of these trap states may be depopulated. While for QDs no temperature-dependent CB and VB measurements have been reported, the temperature dependence of trap states in TiO\textsubscript{2} nanoparticles was measured with electron paramagnetic resonance measurements, observing that holes were permanently trapped at surface oxides below 150 K and under illumination. The surface charges likely lead to changes in the surface dipole and, therefore, should influence the CB and VB energies positions dramatically. For the PbS QD/graphene FETs, a shift of the energy levels for the QDs, as shown in the low-temperature scenario in Figure 2d, can explain the observed temperature behavior for Devices A. Aligning the Fermi levels with graphene would result in electron transfer from graphene to the QD layer. The resulting potential barrier would lead to photogenerated holes being accumulated in the QD thin film and electrons transferred to graphene (Figure 2e). Additionally, applied gate voltages shift the Fermi level of graphene (-4.6 eV) by about 100 meV in either direction depending on the sign and magnitude of the applied gate voltage. Therefore, both temperature and gate voltage, can alter the band alignment between graphene and the QD thin film, and even lead to changes in the type of transferred photo-induced charge carriers.

A higher gain in photodetectors comes at the cost of operational speed. The light modulation of 5 Hz excludes contributions from trap states with trapping or de-trapping times sufficiently longer than 0.2 s and, therefore, the initially designed long trapping constants require slower light modulation frequencies, which may not be practical for detector operation. For further optimization of low-temperature device operation, a second detector array with five pixels was fabricated in the same way as Device A. One pixel denoted Device B is discussed in the main text and Devices B\textsubscript{2–5} in the Supplementary Information. This time, the QD ink was freshly prepared and stored under air and moisture-free conditions until the nano-printing, ensuring negligible surface oxidation. The results of the temperature-dependent photoreponse for Devices B\textsubscript{1–5} (Figures 3a, S5) are similar in appearance among themselves with a vertical line of no photoreponse (accompanied with the phase change) coinciding with the CNP (Figure 3b, dashed black line), and an area with a change of the transferred charge carrier type (Figure 3b, dotted white line). The charge transfer under illumination was locally probed with time traces, at the points P\textsubscript{1\textsubscript{B1}}, P\textsubscript{3\textsubscript{B1}}, and P\textsubscript{4\textsubscript{B1}} photo-induced holes and at point P\textsubscript{2\textsubscript{B1}} photo-induced electrons were transferred to the graphene (Figure 3c, S3).

The behavior of Device B at 300 K is generally similar to Device A discussed above. The Fermi level alignment results in a formation of upward Schottky-like potential barrier, photogenerated electrons are being accumulated in the QD thin film, and photogenerated holes are being transferred to graphene (Figure 3d, e). At 250 K, in contrast, Fermi levels of the QDs and graphene may equalize and, therefore, the gate voltage induced Fermi level shift of graphene may become decisive for the formation of an electron or hole blocking potential barrier (Figure 3d, e). Further cooling of Device B would change the averaged surface dipole strength back to a similar level as at room temperature. The origin of such non-monotonic behavior is likely related to the complex interplay between several temperature-dependent factors such as QD-surface/ligand interatomic distance, ligand vibrations and rotations, and PbS bandgap narrowing (Figure S6), which altogether may impact on the surface dipoles in a sophisticated way. This is in stark contrast to Devices A (based on partially oxidized QDs), where trap states may entirely dominate the responsivity dependence on temperature. The responsivity and phase measurements of Devices B\textsubscript{1–5} are highly similar in their appearance and only vary in responsivity magnitude as the film thickness (92–171 nm) decreases, but differ strongly from those of Devices A. To exclude any dependence of the ligand exchange duration on the device performance, Devices B were briefly exposed to 1,2-ethanethiol and characterized, followed by a longer ligand exposure time and second characterization with only minor changes in the responsivity behavior (Figure S5). The high dependence of responsivity measurements on the temperature and the gate voltage could potentially be used as a sensing method for QD surface treatments, and vice versa, surface treatments could be used for hybrid photodetector optimization with a response at a desired temperature and gate voltage. It is probable that some hybrid detectors with their tested surface treatments are non-responsive at room temperature, but may function at lower temperatures and optimized gate voltages. Therefore, temperature-dependent measurements might be essential for the discovery and optimization of functional QD-ligand-graphene hybrid detectors.
Figure 3. Temperature- and gate-voltage-dependent measurement of Device B1. False-color maps are shown for (a) responsivity and (b) phase. The sign of transferred charge carrier under illumination (c) is deduced from a combination of the responsivity measurement and the transfer characteristics of the FET. (d) Energy levels of graphene and QD thin film are depicted without the materials being in contact with each other. The conduction band is in blue, valence band is in red and the Fermi level is shown as an extended black dotted line for comparison with the Fermi level position of the QD thin film at different temperatures. In (e) the band alignment at 300 K and 250 K is drawn with photo-induced charge carriers and their transfer to graphene.

The best performance was achieved for Device B1 at the temperature 80 K and the gate voltage of 2 V where the wavelength, frequency and irradiance dependence were additionally investigated. The spectral dependence of the photoresponse shows a quantum confinement-related excitonic peak at 1320 nm (Figure 4a) with a slight bathochromic shift in comparison to the room temperature responsivity spectrum (Figure S6). The frequency dependence of responsivity, normalized to the drain current, is shown together with the drain-current-normalized noise-current in Figure 4b. Dividing the responsivity with the fitted noise and normalizing it with the detector area results in the specific detectivity, which is plotted as the inset. The specific detectivity increases up to 27 Hz and decreases at higher frequencies. At 27 Hz a tradeoff between reduced 1/f noise and decreased responsivity is found, which is in the range of the fast rise times (below the measurement resolution for the recorded time traces of 61 ms) as observed for the detector (Figure S3h). Up to this point, the devices were characterized at high irradiance to obtain a clear signal, which results in lower responsivity and specific detectivity values. Higher responsivity can be achieved with increased drain bias, which also leads to higher noise-current—both parameters are linearly dependent on the drain bias within an ohmic operational range—leaving the specific detectivity unaffected. However, reducing the irradiance leads to higher responsivities and thus higher specific detectivities, as shown in Figure 4c. When the irradiance is reduced until the signal-to-noise ratio approaches unity, responsivity values as high as 7180 A W⁻¹ at a drain current of 2.5 μA were measured. Together with the corresponding drain-current-normalized noise-current (5.4×10⁻⁷ Hz⁰·⁵) a specific detectivity of 8.4×10⁹ Jones is calculated using the following equation:

\[
D^* = \frac{R \times \sqrt{A}}{i_n} = \frac{\sqrt{BW \times A}}{NEP}
\]

where \(R\) is the responsivity (A W⁻¹), \(A\) is the device area (cm²), \(i_n\) is the noise current (A Hz⁰·⁵), \(BW\) is the measurement bandwidth, and \(NEP\) is the noise equivalent power. For accurate characterization the specific detectivity was calculated additionally from the \(NEP\) (5×10⁻¹⁴ W) and the equivalent noise bandwidth (\(ENBW\)) of the lock-in, which defines the measurement bandwidth, resulting in a similar specific detectivity of 9.7×10⁹ Jones. The \(ENBW\) is dependent on the filter settings and the measurement time constant, for our measurements 0.094 Hz. At a modulation frequency of 27 Hz, the specific de-
tectivity will exceed $10^{10}$ Jones. In comparison with room temperature measurements of the same detector, the specific detectivity is nearly 10 times higher at 80 K.\textsuperscript{14} Even though the specific detectivity of state-of-the-art epitaxial grown InGaAs photodetectors is still superior to our hybrid devices, the latter bear advantages for potentially low-cost fabrication, CMOS compatibility, scalability, and—at the same time—the spectral sensitivity can readily be tuned by QD materials and sizes. Further improvements of the specific detectivity may be achieved by increasing the light absorption cross-section of the QD thin film and further noise reduction.\textsuperscript{14} A looped transconductance measurement at 80 K reveals gate-voltage-dependent hysteresis of the device (Figure 4d), which can be quenched under constant illumination with energies above the QD bandgap but persists at lower photon energies. Gate voltage induced hysteresis at room temperature for graphene FETs is assigned to trapping and de-trapping of charges in the gate oxide in proximity to the graphene channel.\textsuperscript{45} Here, charge carriers most likely are being transferred and accumulated in the QD thin film at low temperatures, resulting in the hysteresis, which can be quenched by photo-induced charge carrier accumulation in the QD thin film. This supports that the interface between graphene and the QD thin film is gate-dependent and does not freeze out at low temperatures.

![Figure 4](image)

**Figure 4.** Low-temperature measurement of Device B1. (a) Shows the spectral dependence of the responsivity. (b) Shows the frequency dependence of current-normalized responsivity (black dots), and current-normalized noise-current without illumination (red squares). The specific detectivity is shown in the inset. (c) Irradiance dependence of the responsivity; the sensitivity limit of the reference detector was reached at $10^{-6}$ Wcm\textsuperscript{-2} and lower light intensities were calibrated to the monochromator entrance slit width. (d) Gate-dependent hysteresis of the detector without illumination (black line), and during illumination (red).

In Summary, QD/graphene FETs have been fabricated and characterized over a wide range of temperatures and gate voltages. While a decrease in photoresponse is expected at lower temperatures due to freezing out the temperature-driven charge carrier transfer over the potential barrier, we have found the opposite: a complex temperature- and gate-voltage-behavior with the highest photoresponse at 80 K. Surface alterations, such as surface oxidation, proved to have a significant influence on the temperature- and gate-voltage-dependence. Hence, these measurements could be utilized for QD surface analytics. Interestingly, the charge carrier type transferred from the QD layer...
to the graphene under illumination can switch its sign, depending on the temperature and gate voltage, which may be explained with temperature-sensitive surface dipoles resulting in a temperature-driven shift of the conduction- and valence bands consequently altering the band alignment to graphene. Detectors fabricated from less oxidized QDs with less surface trap states have shown to be faster with the highest photoresponse and specific detectivity of 10^10 Jones at the wavelength and temperature of 1280 nm and 80 K, respectively. Our findings open a new measurement methodology for hybrid photodetectors leading to a better understanding of charge transfer between QDs and 2D materials not just for photodetectors, but also for other QD-based optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information. Additional optical images, QDs absorbance spectra, time traces at specific measurement conditions, and temperature- and gate-voltage-dependent responsivity measurements of seven additional devices (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
M.J.G., I.S., M.V.K. conceived and designed the experiments. M.J.G. fabricated the graphene FETs, built the low-temperature responsivity setup, carried out the photoresponsivity measurements, and synthesized the PbS QDs with assistance from D.N.D. C.U.H. nanoprinted the PbS QDs, with contributions to the experimental design and discussions with D.P. Furthermore, S.Y. contributed to experimental design, discussions, and result analysis of the photoresponsivity measurements. Noise measurements were conducted by D.B. Time traces were fitted by G.K. including extraction of time constants and discussed with M.C. The paper was written by M.J.G. with contributions by all authors and all authors have given approval to the final version.

Notes
The authors declare no competing financial interest.

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METHODS

Sample fabrication. Samples were prepared as reported elsewhere. Briefly, wet chemical transferred graphene on p-doped Si with 285 nm SiO2 was lithographically patterned and O2 plasma etched into a transistor channel. The Cr/Au electrodes were defined by lithography and electron beam assisted thermal evaporation. Colloidal PbS QDs with oleic acid ligands in n-tetradecane were nanoprinted on top of the graphene channel under ambient conditions (25°C, 35-40% relative humidity). The access solvent evaporates instantaneously and the insulating oleic acid ligands were exchanged with 1,2-ethanediethiol in acetonitrile. Devices A were treated 15 s with 10% 1,2-ethanediethiol solution. Devices B were first treated 2 s with 2% 1,2-ethanediethiol solution followed by characterization. In a follow-up Devices B were further treated 15 s with 10% 1,2-ethanediethiol and characterized. After each 1,2-ethanediethiol treatment, the samples were washed with acetonitrile, hexane, and dried by spinning the sample at 3000 rpm.

Colloidal PbS QDs. The synthesis was done as reported by Hines and Scholes with slight modifications. Briefly, Pb(II) acetate·3 H2O (1.5 g, 3.96 mmol), oleic acid (10 mL), and 1-octadecene (40 mL) were degassed at 120 °C, 1 h under vacuum in a three-neck flask. Subsequently, hexamethylidisilathiane (420 µL/2 mmol in 10 mL 1-octadecene) was injected at 143 °C, N2 atmosphere, and rigorous stirring. The reaction was quenched after 10 min by cooling to room temperature with an ice-water bath. The QDs were precipitated with ethanol, collected by centrifugation and redispersed in hexane. This procedure was repeated two more times and finally, QDs were dispersed in n-tetradecane. Before nanoprinting, the QDs dispersion was filtered through a 0.1 µm polytetrafluoroethylene syringe filter.

Nanoprinting. We followed a previously published protocol. Briefly, a gold-coated glass printing nozzle with an opening diameter of about 2 µm was filled with the PbS QDs dispersion (40 mg mL⁻¹) in n-tetradecane. The nozzle opening was positioned in close proximity (6-7 µm) above the graphene FET, which was grounded over 10 kΩ. Droplets were ejected by applying a square wave voltage pulse (290 V, 1 kHz) between gold-coated nozzle and substrate. The QDs films were printed layer by layer, the solvent evaporated instantaneously.

Photoresponsivity setup. Light from a Thorlabs SLS201 broadband light source was optically modulated with a MC2000B-EC Thorlabs chopper, and focused onto and monochromated with a Princeton Instruments SpectraPro HRS-300 spectrometer (grating 150 G/mm, blaze 0.8 µm), higher spectral orders are filtered out with long pass filters (550 nm, 780 nm, 1000 nm). The monochromated light was collimated with a lens and split with a 50/50 polkadot beamsplitter onto a UM-9B-L reference detector (NEP 7.5×10⁻³ WHz⁻¹/2, Ø = 9 mm, D* = 10⁹ Jones, at room temperature) connected to a SR860 lock-in, and onto an optically accessible JANIS ST-100 cryostat (temperature range 80-300 K, 10⁻⁷ hPa) with a quartz glass window. The sample was glued with silver paint and wire bonded onto a custom made AlN ceramic chip carrier. The samples were mounted inside the cryostat and electrically connected to a Keithley 2614B SMU applying 0.5 V drain bias through the device under test (QD coated graphene FET) and 100 Ω serial resistance. The voltage fluctuations over the 100 Ω resistor were measured with a SR865 lock-in. The gate voltage was applied with the second channel of the Keithley 2614B and the gate leakage did not exceed 10 nA.

Noise setup. A battery-powered SR570 current amplifier together with a NI USB-6281 data acquisition board with a 40 kHz lowpass filter were used for noise measurements. The sampling rate was 625 kHz. The acquired signal was band-limited with a tab finite 100 impulse response digital filter (FIR) to 78 kHz and subsequently downsampled by a factor of four. 0.5 V drain bias was applied through the current amplifier and ten time traces each 1 s long were recorded, the estimated power spectral densities of these traces were averaged using Bartlett’s method at each gate voltage and temperature. The 50 Hz line frequency was removed from the frequency spectra.
Figure S1. Absorbance spectra of the PbS QD dispersions used for the nanoprinting of Devices A and B, diluted in tetrachloroethylene.

Figure S2. Top view optical bright-field image of (a) Device A1-3, and (b) Device B1-5.
Figure S3. Time traces measured at selected temperatures and gate voltages for Device A1 (a-d), and Device B1 (e-h). Red vertical lines highlight the time under illumination, while no light was shining on the sample in the white areas. The irradiance was $1.4 \times 10^{-4}$ Wcm$^{-2}$ at 1200 nm for all measurements. Rising currents under illumination originate from the transfer of the same charge carrier type as the major charge carrier type within the graphene channel—which switches from holes at gate voltages below the CNP to electrons at gate voltages above the CNP. Declining currents under illumination originate from the transfer of the opposed charge carrier type as in the graphene channel. (i, j) are normalized time traces under illumination fitted with one fast and one slow exponential function for P1$_{A1}$ and P4$_{A1}$, respectively.
Figure S4. Device A: (a) temperature and gate voltage-dependent responsivity (top row) and corresponding phase (bottom row) measurements. (b) QD layer thickness of the devices after ligand exchange with 1,2-ethanediithiol. The QDs layer thicknesses were measured with a Bruker Dimension Fastscan in tapping mode.
Figure S5. **Device B**: temperature and gate voltage-dependent responsivity (top row) and corresponding phase (bottom row) measurements after (a) brief ligand exchange and (b) extended ligand exchange. (c) QD layer thicknesses of the devices after ligand exchange with 1,2-ethanediethiol. The QD layer thicknesses were measured with a Bruker Dimension Fastscan in tapping mode.

<table>
<thead>
<tr>
<th>device</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
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Figure S6. Spectral dependence of the responsivity at low (80 K) and high (300 K) temperatures for Device B1. The excitonic peak shifts bathochromic by about 45 meV.

References