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Letter

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Abstract: Colloidal quantum dots (CQDs) are promising materials for IR light detection due to their tunable bandgap and solution processing; but to date, the time response of CQD IR photodiodes has been inferior to that provided by Si and InGaAs. We reasoned that the high permittivity of II-VI CQDs leads to slow charge extraction due to screening and capacitance; whereas III-Vs – if their surface chemistry could be mastered – offer a strong covalent character for low permittivity and fast operation. In initial studies, we found that existing covalent character led to imbalanced charge transport in InAs, the result of unpassivated surfaces and uncontrolled heavy doping. We report surface management using amphoteric ligand coordination and find that it addresses simultaneously the In and As surface dangling bonds. The new InAs CQD solids combine high mobility ($0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) with a 4x reduction in permittivity compared to PbS CQDs. The resulting photodiodes achieve a response time faster than 300 ps – a more than 100x improvement compared to the best previously-reported CQD photodiodes – combined with an external quantum efficiency (EQE) of 30% at 940 nm.

Infrared photodetection underpins applications in medicine and bioimaging, information technology, machine vision, and security^{1,2}. Emerging technologies such as autonomous driving and augmented reality rely on Light Detection and Ranging (LiDAR) based on time of flight (ToF)³. This requires sensitive and ultrafast photodetection of infrared light with sub-ns resolution⁴. Today, this is achieved in the near-infrared (NIR) using indirect bandgap silicon detectors—limited by silicon’s low absorption coefficient—and, at longer wavelengths, using epitaxially-grown semiconductors such as III-Vs and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ^{5,6}.

Colloidal quantum dots (CQDs) are of interest by their low-temperature solution processing, which allows them to be integrated in post-processing with a silicon electronics front-end⁷⁻¹⁰. Their bandgap is size-tuned over a wide range of wavelengths. PbS, for example, has a widely-programmable absorption onset covering the visible and short-wavelength infrared (SWIR)^{11,12}; however, its high permittivity, stemming from its ionic character – $\epsilon_r = 180$ for bulk PbS¹³ – slows charge extraction both for bulk¹⁴ and CQD photodiodes¹⁵ due to screening and capacitance effects.

Indium arsenide (InAs) CQDs can be tuned in a similar spectral range as PbS CQDs, and offer the prospective advantage of a covalent lattice and hence lower permittivity^{16,17}. This, however, comes with a challenge: the surface in InAs CQDs is charge-imbalanced, leading to poor passivation and heavy doping, as surface states pin the Fermi level near the conduction band minimum. Much effort has been paid to improving mobility by decreasing interdot distance via ligand exchanges and surface treatments in CQD solids^{18,19}, but III-V CQDs require a new approach in order to neutralize CQD charge surface states and reduce trap density.

Trap states in InAs semiconductors originate from surface In and As dangling bonds²⁰. Growing epitaxially-matched inorganic shells on CQDs passivates surface defects, but it hinders CQD coupling and carrier transport^{21,22}. Using molecular metal chalcogenide complexes (MCCs, e.g. $\text{Sn}_2\text{S}_6^{4-}$ and $\text{In}_2\text{Se}_4^{2-}$) enhances carrier mobility in III-V CQD solids, leading to an impressive mobility of $15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, but introduces undesired in-gap states^{19,23}. Etching As sites using strong acids facilitates In-site passivation but leads to low mobility ($10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)^{18,20,24}.

Here we present a new surface passivation strategy that addresses charge imbalance and passivation in InAs CQD solids for infrared photodetectors. We introduced InBr₃ passivants to replace native insulating oleic acid ligands, thereby providing surface passivation and charge transport simultaneously. We found that InBr₃ is amphoteric, dissociating into an X-type ligand (Br⁻) that passivates In dangling bonds; and into a Z-type (InX₂⁺) ligand²⁵ that passivates As dangling bonds. We incorporate N,N-dimethylformamide (DMF) as a coordinating agent to stabilize otherwise unstable Br⁻ and InX₂⁺ passivants. We assess the co-passivated InAs surfaces using a suite of spectroscopies and density functional theory (DFT) calculations. The resulting InBr₃-InAs CQD solids achieve a mobility value of 0.04 cm²V⁻¹s⁻¹, >10 times higher than in halide-exchanged InAs solids¹⁸; and a low dielectric constant of 6.3 – a near 4x advance compared to PbS CQD solid counterparts. The corresponding photodiode devices achieve a 30% external quantum efficiency (EQE), a responsivity of 0.22 A W⁻¹, and measured detectivity of 10¹¹ cmHz^{1/2}W⁻¹ at the excitonic peak (940 nm). Ultrafast transient photocurrent (TPC) experiments reveal a fall time of 300 ps, equivalent of >1 GHz bandwidth. This is the first demonstration of efficient III-V CQD photodiodes and the fastest solution-processed infrared photodiode reported, with over a 100-fold improvement compared to the best CQDs photodiodes^{15,26}.

Fig. 1 | Stabilization of InAs CQDs. Scheme of InBr₃ ligand exchange and InAs quantum dot surface configuration according to DFT calculations: a larger stabilization energy was observed by adding DMF coordination in the system for both In-rich and As-rich surfaces.

We first synthesized InAs CQDs (semisphere, Supplementary Fig. 1) using a modified approach via the continuous injection^{27,28}. As-synthesized InAs CQDs are capped by insulating oleic acid ligands, which need to be removed for electrical coupling. The oleic acid capped InAs (OA-InAs) in octane show low photoluminescence quantum yield (PLQY < 1 %)²⁷, which we attribute to the presence of surface defects as negatively charged As dangling bonds²⁹ that are not passivated using oleic acid.

To increase understanding of the nature and role of the dangling bonds (DBs) and guide in the design of a surface exchange strategy to passivate InAs surfaces, we studied the zinc-blende InAs structure using DFT calculations and estimated the thermodynamic stability of their surfaces (see Supplementary text). The crystal facets exposed, including (111) and (100), are polar and terminated with positively charged In and negatively charged As.

The nature of zinc-blende InAs structure demands the simultaneous passivation of both In and As dangling bonds for efficient ambipolar optoelectronics – i.e. for high performance in devices whose operation relies on electrons and holes simultaneously, as distinct from unipolar devices such as field-effect transistors (FETs). The success of X-type on positively charged surfaces suggests³⁰ that halides could be promising candidates for In passivation. Z-type ligands binding as a neutral two-electron acceptor (a Lewis acid) have been demonstrated to passivate phosphide deep traps leading to enhanced photoluminescence efficiency³¹. This prompted us to design a dual passivation strategy that would seek to address In and As dangling bonds using X-type and Z-type ligands, respectively.

We hypothesized that metal halide salts such as InBr₃ could be candidates for this as when dissolved in certain polar solvents such as DMF, they would dissociate into the needed X-type (Br⁻) and Z-type (InBr₂⁺) ligands²⁵. To assess the potential of these ions as co-passivants, we performed DFT calculations on different InAs surfaces (see Suppl. Info for details). The calculation results indicate that Br⁻ passivates In-terminated surfaces whereas InBr₂⁺ addresses As-terminated surfaces (Supplementary Fig. 2, 3, and 4).

Based on these calculations, we designed a one-step, two-phase solution exchange method to replace OA long ligands with InBr₃ salts assisted by ammonium acetate (AA), which enables the removal of the original long organic ligands (OA)³². Before the ligand exchange, InAs CQDs are dispersed in octane and InBr₃ (0.1 mol L⁻¹, 0.18g in 5 mL) and AA (0.04 mol L⁻¹, 0.023g in 5 mL) are pre-dissolved in DMF. During the exchange, InAs CQDs transfer from nonpolar octane layer to polar DMF solution, which indicates that long OA ligands are replaced by InBr_x ligands.

Fig. 2 | Investigation of passivation using InBr₃-DMF complexes. **a**, Attenuated total reflection (ATR) FTIR of InAs CQD films before and after InBr₃ ligand exchange on glass. **b**, In L₃-edge XANES spectra of InAs CQD films and InBr₃ films (spin-coated from DMF solution) on Si wafer. **c**, Thermogravimetric analysis (TGA) of InAs CQDs and InBr₃ salt with/without AA samples. **d**, In 3d X-ray photoelectron spectroscopy (XPS) signal. **e**, As 3d XPS signal. **f**, Elemental ratio of InAs CQD films before and after InBr₃ ligand exchange.

To track the removal of long ligands in the exchanged film, we carried out Fourier transform infrared spectroscopy (FTIR) measurements (Fig. 2a). OA-InAs CQDs show typical CH resonances at ~2900 cm⁻¹ and C=O vibrations owing to OA on CQD surface at ~1540 cm⁻¹. After the ligand exchange, the OA signals disappear. The C=O signal at ~1640 cm⁻¹ is attributed to DMF complexes, which differs from the peak position of free DMF at 1675 cm⁻¹.

To assess the role of DMF complex, we performed synchrotron (In L₃-edge) X-ray absorption near edge structures (XANES) (Fig. 2b). XANES features of In are not very sensitive to anion substitutions but to the coordination number³³. InBr₃-InAs films show a similar peak position as pure InBr₃ films deposited from DMF solution, but a shift compared to that of OA-InAs films. The peak position difference suggests that In in InBr₃-InAs and InBr₃ have sixfold coordination (In connects to 6 atoms) whereas OA-InAs only has only fourfold coordination³³.

119 Considering the presence of DMF, its potential interactions with the passivants and the sixfold
120 coordination of In, we calculated the stabilization energy of Br⁻/DMF and In-Br/DMF co-passivants. In
121 the case of zinc-blende InAs structure, there are 1.5 DBs (electrons from As or holes from In) at (100)
122 surfaces and 0.75 DBs at (111) surfaces²⁰. These sites are hard to passivate as the ligands can only provide
123 an integer number of carriers. These results suggest a larger stabilization energy by adding DMF
124 coordination for both In-rich and As-rich surfaces (Fig. 1, Supplementary Fig. 2-4). The lower surface
125 energies through Br/In-Br + DMF co-passivation suggest that the dangling bonds on InAs CQD surface
126 are passivated by DMF complexes.

127 We carried out thermogravimetric analysis (TGA) (Fig. 2c) to study the stability of InAs CQDs and
128 gain insights into the composition of the final CQD solids. We analyzed the decomposition of ligands and
129 solvent at different temperatures for the exchanged CQDs comparing TGA traces of pure InBr₃, AA-
130 InBr₃, OA-InAs, and InBr₃-InAs: the weight loss of 1% in the range from 50°C to 158°C is attributed to
131 the free DMF solvent (boiling point 153°C) in InBr₃-InAs solids; the weight loss of ≈2.5% in the range
132 from 162°C to 240°C is attributed to the DMF from the decomposition of DMF-InBr_x complex; the
133 weight loss of ≈3.5% in the range from 240°C to 340°C may be the AA/InBr₃ complex decomposition
134 (similar to the decomposition of AA-InBr₃); the final weight loss of ≈36.5% from 340°C to 420°C is
135 attributed to the decomposition of InBr₃ and residual OA. The decomposition of DMF-InBr_x complex
136 agrees with the InBr₃-DMF co-passivation mechanism³⁴.

137 We performed InBr₃-DMF ligand exchange on OA-capped InAs (OA-InAs) CQDs. After ligand
138 exchange, the In-to-As ratio is close to 1:1 (Fig. 2f) vs. 3:1 before exchange. This high In-to-As ratio of
139 OA-InAs is attributed to the free In-oleate in the solution that was not removed during CQD purification,
140 evidenced by the decreased In signal peak width after ligand exchange (Fig. 2d) and the high C-to-As
141 ratio before exchange. After InBr₃-DMF ligand exchange, the C:In ratio decreased to ≈2:1. Fig. 2e shows
142 the As signal after ligand exchange without any As signal oxidized. The appearance of N and Br signal
143 suggests the existence of DMF and Br- in InBr₃-InAs films, supporting the results above.

144 Based on the successful ligand exchange, we characterized the absorption of CQDs before and after
145 the ligand exchange in solution (Fig. 3a). OA-capped CQDs show an excitonic peak at 916 nm with a
146 peak-to-valley ratio of ≈2.6. After ligand exchange, the excitonic peak redshifts to 928 nm and the peak-
147 to-valley ratio decreases to ≈2.2. This indicates that quantum confinement is preserved after exchange.

Fig. 3 | Improved transport properties and low dielectric constant of InBr₃-InAs CQD films. **a**, Absorption of InAs CQD solution before and after ligand exchange. **b**, Azimuthal integration of (GISAXS) patterns of InAs CQD films with GISAXS 2D pattern (inset) of InBr₃-InAs CQD film. **c**, Transfer curves of InBr₃-InAs CQD film in linear and saturation regimes with the field-effect transistor (FET) device structure (inset). **d**, The real and **e**, Imaginary refractive index of InAs compared to PbS QDs. **f**, Dielectric constant of InBr₃-InAs and PbI₂-PbS CQD films.

To assess the interparticle distance and the necking produced after ligand exchange, we carried out grazing-incidence small-angle X-ray scattering (GISAXS) measurements (Fig. 3b). After InBr₃ ligand exchange, the interdot distance decreased from 4.6 nm to 3.6 nm, as extracted from the azimuthally integrated coherence peak. This is consistent with OA replacement by inorganic ligands.

To characterize charge transport in the exchange solid, we measured mobility using FET devices³⁵. FET output characteristics reveal the n-type transport enhancement mode for InBr₃-InAs CQD films (Supplementary Fig. 5). The carrier mobility is $0.032 \pm 0.003 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the linear regime (μ_{lin}) and $0.040 \pm 0.005 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the saturation regime (μ_{sat}) is, (Fig. 3c), over 10 times higher than the two-step ligand exchange¹⁸. The current on/off ratio is only about 10, indicating that the thickness of the CQD layer exceeded the depth of the accumulation channel formed in the CQD solid upon applied gate bias and that the electron concentration is high in InBr₃-InAs CQD solids.

We extracted the carrier concentration through mobility and conductivity, obtaining a value of $1.11 \times 10^{17} \text{ cm}^{-3}$ and $1.39 \times 10^{17} \text{ cm}^{-3}$ from μ_{lin} and μ_{sat} , respectively. This suggests that the InBr₃-InAs CQD solids are n-type doped. We confirmed the n-type transport polarity of InBr₃-InAs CQD films using ultraviolet photoelectron spectroscopy (UPS), which revealed a conduction band minimum (CBM) at -4.62 eV, a valance band maximum (VBM) at -5.92 eV, and a Fermi level (E_F) at -4.79 eV (Supplementary Fig. 8a). This agrees with the carrier concentration obtained from FET results.

To assess the optical properties of exchanged InAs films, we measured the complex refractive index and compared it with PbS CQD films for reference. We found that the real part of the refractive index is higher in PbS CQD films (Fig. 3d, 3e), which could be attributed to its higher permittivity. To characterize the dielectric constant at electrical frequencies, we measured the capacitance in a diode device configuration (Supplementary Fig. 6 and Fig. 3f). We obtained $\epsilon_r = 34.8$ for PbS CQDs and a much lower value ($\epsilon_r = 6.3$) for InAs solids.

Fig. 4 | Fast photodetector using low- ϵ InAs CQDs. **a**, Schematic of photodiode device structure. **b**, I - V characteristics of InBr₃-InAs CQD photodiodes dark and illuminated condition. **c**, External quantum efficiency (EQE) biased from 0 to 1 V and internal quantum efficiency (IQE, divide EQE (@ 0 V) by EQE (@ 1 V)). **d**, Detectivity of InBr₃-InAs CQD photodiodes. **e**, Device area dependent response time of InBr₃-InAs CQD photodiodes. **f**, Comparison of the response time of devices with InAs CQD and PbS CQD films with different device areas.

183 Considering the energy levels of InAs QD solids, we designed a device architecture consisting of
184 ITO / ZnO / InAs / Au. Unfortunately, this arrangement resulted in poor diode behavior and high dark
185 currents (Supplementary Fig. 7a). Reasoning that this structure may have produced back injection of
186 electrons from InAs into Au, we added a layer of 10 nm of MoO₃ as an electron blocking layer between
187 InAs and Au (Fig. 4a, Supplementary Fig. 8b). We observed a decrease in dark current by 3 orders
188 magnitude to $\approx 70 \text{ nA cm}^{-2}$ at 1.0 V reverse bias (Fig. 4b) accompanied by a significant increase in EQE
189 from 9% to 30% at 0 V bias (Fig. 4c), a responsivity of 0.22 A W^{-1} (Supplementary Fig. 9) and measured
190 detectivity of $10^{11} \text{ cmHz}^{1/2}\text{W}^{-1}$ at the excitonic peak (940 nm, Fig. 4d). This is the highest EQE reported
191 for an InAs QD photodetector.

192 We then characterized the time response of the InAs QD photodiodes after ultrafast photoexcitation
193 using 100 fs laser pulses. We designed an electrical footprint that enables us to measure EQE/ *JV* curves
194 and incorporate small pixels with diameters from 1400 μm to 100 μm (Supplementary Fig. 10).

195 To assess the impact of device capacitance, we studied the response time for different pixel areas.
196 The fall time decreases from 50 ns for 1.5 mm^2 to 300 ps for 0.01 mm^2 pixels (Fig. 4e). The magnification
197 of transient photocurrent spectra for the lowest pixel area is shown in the inset. PbS QDs devices show a
198 similar trend but ≈ 2 orders of magnitude longer fall time compared to InAs diodes (Fig. 4f). This can be
199 ascribed to the higher capacitance in PbS compared to InAs QDs. These results also suggest that we have
200 not reached the mobility-limited transport regime even at the smallest pixel area, as fall time keeps
201 decreasing with decreasing device area and does not reach a plateau (Fig. 4f).

202 We then measured the -3 dB cut-off frequency using a vertical-cavity surface-emitting laser
203 (VCSEL) light source modulated at different frequencies (Supplementary Fig. 11). The response stays
204 constant until 25 MHz and crosses -3 dB at about 150 MHz (Fig. 4f). TPC results for the same diameter
205 pixel (0.2 mm^2) reveal a fall time of $\approx 2 \text{ ns}$, which would correspond to a 3 dB cut-off frequency of ≈ 175
206 MHz. We note that due to the low power of the VCSEL and focusing limitations, we could not obtain cut-
207 off frequency for smaller pixels. Based on the TPC decay of the fastest pixels, we can expect a $\approx 1 \text{ GHz}$
208 bandwidth for 0.01 mm^2 devices.

209 In sum, we have introduced an amphoteric passivation strategy to co-passivate both In and As on InAs
210 CQD surfaces providing passivation and charge transport for low permittivity CQD solids. We revealed
211 the important role of DMF as a coordinating agent that stabilizes both X- and Z-type passivants.
212 Consequently, we were able to achieve for the first time efficient InAs CQDs photodiodes showcasing an
213 EQE of ~30% at 0 V and a specific detectivity of $10^{11} \text{ cmHz}^{1/2}\text{W}^{-1}$ at the near-infrared. The low
214 permittivity and passivation of the InAs CQD solid result in a fall time of 300 ps, the fastest CQD
215 photodiode. Our findings open the door to the realization of high-performance optoelectronic devices
216 based on III-V CQDs.

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285 Methods

286 **Materials.** All the chemicals are purchased from commercial suppliers and used as received. Suppliers
287 disclaimer: "Certain commercial equipment, instruments, or materials are identified in this paper to
288 specify the experimental procedure adequately. Such identification is not intended to imply
289 recommendation or endorsement by the National Institute of Standards and Technology, nor is it
290 intended to imply that the materials or equipment identified are necessarily the best available for the
291 purpose."

292
293 **InAs CQDs Synthesis,** InAs QDs were synthesized using a modified approach via the continuous injection
294 by reacting In(oleate)₃, tris(trimethylgermyl)arsine ((TMGe)₃As) under an N₂ atmosphere at 300°C using a
295 modified approach^{27,28}.

296 **Device fabrication.** The InBr₃/AA solution-phase ligand-exchange process was carried out in a test tube in
297 an N₂-filled glovebox. InBr₃ (0.1 molL⁻¹, 0.18g) and ammonium acetate (0.04 molL⁻¹, 0.023g) are pre-
298 dissolved in 5 mL of dimethylformamide (DMF). A 5 ml amount of CQD octane solution (10 mg mL⁻¹) was
299 added to 5 ml of the precursor solution. These were vortexed for 1–2 min until the CQDs completely
300 transferred to the DMF phase, followed by washing three times with octane. After ligand exchange, CQDs
301 were precipitated via the addition of toluene (~10 mL) and separated by centrifugation. After 10 min of
302 vacuum drying, the CQDs were then redispersed in DMF (200 mg mL⁻¹) to form the film on ZnO
303 nanoparticle coated ITO substrate by spin-coating at (1000 to 2000) rpm. Finally, 100 nm of Au was
304 thermally deposited as a back electrode.

X-Ray Photoelectron Spectroscopy (XPS). XPS spectra were measured in N₂ by using a Thermo Scientific K-Alpha System with an Al K α source. The films were spin-coated on Si substrates. Scans were taken in 0.05 eV steps with a 50 eV pas energy. The atomic ratios were obtained by integrating under the area of each peak and scaled by atomic sensitivity factors. We normalized all of the element areas with respect to As to obtain accurate atomic ratios.

Fourier transform infrared (FTIR) spectroscopy measurements. FTIR measurements were performed on a Bruker Vertex 80, (8000 to 600) cm⁻¹; resolution 4 cm⁻¹, in top-configuration (attenuated total reflection, ATR).

Absorption Measurements. The optical absorption measurements were performed with a Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. The solutions were placed in a quartz cuvette with a 1 mm path length.

Transmission electron microscopy measurements (TEM). TEM images were acquired on a Hitachi HF 3300 electron microscope operating at 300 keV. TEM samples were prepared by drop-casting a purified solution of CQDs from n-octane onto a 300 mesh copper grid with a carbon film (SPI supplies).

X-ray scattering measurements. Grazing incidence small-angle X-ray scattering (GISAXS) samples were prepared by spin-coating a layer of InAs film following the same procedure as the device fabrication on a Si substrate. The measurements were carried out at the CMS beamline of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) office of the Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory. GISAXS images were collected with an imaging detector at a distance of 0.178 m using X-ray wavelength of 1.033 Å. Nika software package was used to sector average the 2D GISAXS images. Data plotting was done in Igor Pro (Wavemetrics, Inc., Lake Oswego, OR, USA).

Thermal gravimetric analysis measurement (TGA). TGA measurements were conducted using a PerkinElmer Pyris 1 TGA. About (6 to 8) mg of quantum dot solids were taken on a platinum pan. An equilibration or isothermal step at 50 °C for 15 min and later heated to 800 °C with a heating rate of 10°C/min were carried out under nitrogen. The residual weight of InAs QDs after 780°C increased from 37% to 56% after ligand exchange, which confirms the reduced amount of organic ligands as OA was replaced. We also analyzed the decomposition of ligands and solvent at different temperatures for the exchanged CQDs comparing TGA traces of pure InBr₃, AA-InBr₃, OA-InAs, and InBr₃-InAs: The weight loss of 1% in the range from 50 °C to 158 °C is attributed to the free DMF solvent (boiling point 153 °C) in InBr₃-InAs solids; the weight loss of ≈2.5 % in the range from 162 °C to 240 °C is attributed to the DMF from the decomposition of DMF-InBr_x complex; the weight loss of ≈3.5% in the range from 240 °C to 340 °C may be the AA/InBr₃ complex decomposition (similar to the decomposition of AA-InBr₃); the final weight loss of ≈36.5% from 340 °C to 420 °C is attributed to the decomposition of InBr₃ and residual OA.

FET fabrication. Bottom-gate top-contact FET configuration is used as follows: 70 nm of titanium (Ti) gate was thermally evaporated onto a glass substrate, followed by 15 nm of ZrO₂ as a dielectric layer using atomic layer deposition (ALD). After 300°C baking for 1 hour, the pre-exchanged InAs CQDs dissolved in DMF was spin-coated onto the substrate. Then 70 nm of Au source/drain electrodes were thermally deposited using an Angstrom Engineering Amod deposition system. Agilent semiconductor analyzer was used to characterize the FET devices. We calculated carrier mobility from the slope of the drain-source current (I_{DS}) vs. gate voltage (V_{GS}) according to the equation $I_{DS} = \frac{\mu_{lin} C_i W}{L} (V_{GS} - V_{TH}) V_{DS}$ (1) and $I_{DS} = \frac{\mu_{sat} C_i W}{2L} (V_{GS} - V_{TH})^2$ (2), where μ_{lin} and μ_{sat} are the carrier mobility in the linear regime and saturation regime, respectively; I_{DS} is the drain-source current; L and W are the channel length (50 μm) and channel width (2.5 mm) respectively; C_i is the capacitance per area (450 nF cm⁻²), and V_{GS} and V_{TH} are the gate voltage and threshold voltage, respectively. We also obtained the carrier density following the formula

$$\sigma = L/(R A) \text{ (3) and } n = \sigma/(q \mu) \text{ (4)}$$

where σ is the conductivity; L is channel length; R is the resistance of the device; A is the cross area of the film between source and drain electrodes; n is the carrier concentration (electron concentration in this test); q is the elementary charge; μ is the mobility.

Ultraviolet photoelectron spectroscopy (UPS) measurement. A CQD film on indium tin oxide (ITO) glass on was measured in a PHI5500 Multi-Technique system with a base pressure of $\sim 10^{-9}$ Torr and the Fermi energy calibrated to 0 eV. A helium discharge source ($\text{HeI } \alpha$, $h\nu = 21.22$ eV) was used and the samples were kept at a take-off angle of 88° . During measurement, the sample was held at a -15 V bias relative to the spectrometer to efficiently collect low-kinetic energy electrons. Fermi level (E_F) was calculated from the equation: $E_F = 21.22 \text{ eV} - \text{SEC}$, where SEC is the Secondary Electron Cut-off. The difference between VBM level and Fermi level, η , was determined from VBM onset in the VBM region³⁶.

Photodiode fabrication. The ITO glass substrates were cleaned by sonication in acetone and isopropanol for 30 min each. After drying, the ZnO nanoparticle via sol-gel method using Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) as a precursor in ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and spin-coated onto ITO glass substrates at 2000 rpm for 30 s, followed by 340°C -annealing in air for 40 min. Then InBr_3 - InAs CQDs in DMF (200mg mL⁻¹) was spin-coated on the substrate. The photodetector was finalized by sequential deposition of 10 nm of MoO_3 and 120 nm of Au that serves as the top electrode. The photodetector area was described in Supplementary Fig. 10.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Author Contributions

B.S., A.M.N., C.Z., L.K.S., and M.J.C. contributed equally to this work. B.S. and F.P.G.A. conceived the idea of this study. B.S. developed the CQD passivation system. A.M.N. carried out the device time response measurements. C.Z. and O.V. performed the simulation studies. L.K.S. and L.L. synthesized the CQDs. M.J.C. did the EQE and dark current measurements. X.L. did the ligand exchange. B.S., L.K.S., X.L., S.W. B., S. L., J. A., and M. L. carried out material characterization and device fabrication. A.R.K. and L.J.R. carried out GIWAXS measurements. P. L. and Z. H. L. performed UPS measurements, F.P.G.A. and E.H.S.

384 supervised the project. B.S., A.M.N., C.Z., F.P.G.A., and E.H.S. wrote the manuscript. All authors discussed
385 the results and assisted in the preparation of the manuscript.

386 **Competing Interests**

387 The authors declare no competing financial interests.

388 **Additional information**

389 Supplementary information is available for this paper at XXX.

Figures

Figure 1

Stabilization of InAs CQDs. Scheme of InBr₃ ligand exchange and InAs quantum dot surface configuration according to DFT calculations: a larger stabilization energy was observed by adding DMF coordination in the system for both In-rich and As-rich surfaces.

Figure 2

Investigation of passivation using InBr₃-DMF complexes. a, Attenuated total reflection (ATR) FTIR of InAs CQD films before and after InBr₃ ligand exchange on glass. b, In L₃-edge XANES spectra of InAs CQD films and InBr₃ films (spin-coated from DMF solution) on Si wafer. c, Thermogravimetric analysis (TGA) of InAs CQDs and InBr₃ salt with/without AA samples. d, In 3d X-ray photoelectron spectroscopy (XPS) signal. e, As 3d XPS signal. f, Elemental ratio of InAs CQD films before and after InBr₃ ligand exchange.

Figure 3

Improved transport properties and low dielectric constant of InBr₃-InAs CQD films. a, Absorption of InAs CQD solution before and after ligand exchange. b, Azimuthal integration of (GISAXS) patterns of InAs CQD films with GISAXS 2D pattern (inset) of InBr₃-InAs CQD film. c, Transfer curves of InBr₃-InAs CQD film in linear and saturation regimes with the field-effect transistor (FET) device structure (inset). d, The real and e, Imaginary refractive index of InAs compared to PbS QDs. f, Dielectric constant of InBr₃-InAs and PbI₂-PbS CQD films.

Figure 4

Fast photodetector using low- χ InAs CQDs. a, Schematic of photodiode device structure. b, I-V characteristics of InBr₃-InAs CQD photodiodes dark and illuminated condition. c, External quantum efficiency (EQE) biased from 0 to 1 V and internal quantum efficiency (IQE, divide EQE (@ 0 V) by EQE (@ 1 V)). d, Detectivity of InBr₃-InAs CQD photodiodes. e, Device area dependent response time of InBr₃-InAs CQD photodiodes. f, Comparison of the response time of devices with InAs CQD and PbS CQD films with different device areas.

Supplementary Files

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