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Journal

Nano Letters, 23(22)

ISSN

1530-6984

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Publication Date

2023-11-22

DOI

10.1021/acs.nanolett.3c02456

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Gate Controlled Excitonic Emission in Quantum Dot Thin Films

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ABSTRACT: Formation of charged trions is detrimental to the luminescence quantum efficiency of colloidal quantum dot (QD) thin films and light emitting devices as they predominantly undergo non-radiative recombination. In this regard, control of neutral exciton and charged trion formation is of interest for both fundamental characterization of the quasiparticles, and device performance and reliability optimization. Using CdSe/CdS QDs as a prototypical material system, here, we demonstrate a metal-oxide-semiconductor capacitor based on QD thin films for studying the effect of background charge on the luminescence efficiency and lifetime. The concentration ratio of the charged and neutral quasiparticles in the QDs is dynamically and reversibly controlled by applying a gate voltage while simultaneous steady-state and time-resolved photoluminescence measurements are performed. Notably, the photoluminescence intensity is modulated by up to two orders of magnitude with the applied gate voltage with a corresponding change in the effective lifetime. In addition, chip-scale modulation of brightness is demonstrated, where the photoluminescence is effectively turned on/off by the gate, highlighting potential applications in voltage-controlled electrochromics.

1. Introduction

Quantum dots (QD) have garnered a lot of attention in the past decade as lighting and display technologies, quantum bits for quantum computation, as well as sensing marker in biological systems.¹⁻⁶ Their diverse applications stem from a number of lucrative properties: size-tunable bandgap, narrow emission linewidth, high luminescence quantum yield, host for single electron spin just to name a few.⁷ The ease of fabrication with solution-based process accounts for its popularity in optoelectronic applications like solid-state lighting, QD light emitting diodes (LEDs) as well as high optical gain lasers spanning multiple colors.⁸⁻¹² The progress of QD electroluminescent devices has been hindered in part by performance degradation over time. Researchers have attributed the root cause of this deterioration to either accumulation of charge or electric field induced quenching. The effect of controlled charging was first explored by Galland *et al.* with spectro electrochemistry on single QD to elucidate the origin of photoluminescence (PL) blinking as a consequence of charging.¹³ This led to a series of investigations on the impact of charging in an assembly of QDs, where the reduction in PL was attributed to non-radiative Auger process arising from imbalance in charge injection.¹⁴⁻¹⁶ In addition, the effect of high electric field was also inspected in a number of works where the authors demonstrated PL quenching induced by minimizing the spatial overlap of electron and hole wavefunction in the core of the QD through application of high electric field, also known as quantum-confined Stark effect (QCSE). Subsequently this lowers the radiative recombination in the QD film, resulting in a proportional decrease in PL.^{4,17,18}

For next generation light emitting devices employing QD film as the emissive layer, the effect of diminished luminescence quantum yield due to charge accumulation and high field induced degradation cannot be distinguished.^{17,18} Researchers have proposed many alternative schemes to suppress Auger recombination by designing core/graded-shell QD using an

intermediate alloyed layer and utilizing very thick shell to segregate the photo-generated excitons from the interface trap states of the dots.^{14,19,20} The degree of high electric field effect can be subsided through efficient design of charge transport layers, but a large fraction of QDs in an ensemble can still preserve a net residual charge due to imbalance in the injection mechanism. For low-cost efficient LEDs, it is imperative to explore the carrier recombination dynamics of both electron and hole charging. Previous works studying charge injection focused mainly on the scenario of negatively charged excitons due to difficulty of hole injection into the QD assembly.^{13,14,21}

In this work, we develop a platform to systematically study the separate effects of electron/hole injection in a QD ensemble, thereby probing their recombination dynamics with steady-state and time resolved measurements. Inspired by the orders of magnitude modulation of luminescence intensity in monolayer transition metal dichalcogenides, we adopt a similar electrostatic approach to control background charge in nanoparticles through ionic liquid gating.^{22–26} The same principle is extended to large area modulation of nanoparticle luminescence intensity, thereby highlighting its potential use as voltage-tunable emitters in electrochromic application such as optical downconversion.

2. Results and Discussion

The effect of charge injection into a thin film of QD is carried out by applying high electric field across CdSe/CdS core-shell QD film using an ionic liquid gate (Figure 1a). The use of organic electrolyte based ionic liquid, which are molten salts at room temperature, as gate dielectric has gained considerable interest due to its ability to induce large carrier concentration in the active channel of a transistor.^{27,28} By applying a potential to the ionic liquid with respect to the semiconductor (QDs), it is possible to create redistribution of ions such that an electric double layer (EDL) is formed at the solid-electrolyte interface. Given the very short Debye length in ionic

liquid and salt-based electrolytes, the applied voltage drops entirely across few nanometers of EDL, resulting in a large gate capacitance ($\sim 3.4 \mu\text{F cm}^{-2}$) which cannot be realized with solid-state gate.^{29,30} As a result, large concentration of excess charge can be accumulated on the QD ensemble facilitated by the source metal pad. In addition, the ionic liquid is conformal, so issues with pinholes in solid gate electrode will not arise in ionic liquid gating. The emission area from the QDs were defined by a dry patterning method using thin poly vinyl chloride as a mask, since the QD film is incompatible with wet lithography (see supporting information and Figure 1b). The cross-section transmission electron microscopy (TEM) image of the device verifies that the dry patterning step can provide few layer QD ensemble down to two layers without any residue as portrayed in Figure 1c. The chemical constituents of the various layers were confirmed with energy dispersive X-ray (EDX) mapping (Figure S1 and Table S1). A very thin layer of poly(methyl methacrylate) ($\sim 5\text{nm}$) serves as an interlayer between the ionic liquid-QD interface to prevent any unwanted reaction within the electrochemical potential window of the electrolyte.

We seek to measure the effect of different charging states in a core-shell CdSe/CdS quantum dots on the rates of radiative and non-radiative recombination, as shown schematically in Figure 1d. In the uncharged scenario, optical pumping with above bandgap excitation leads to formation of excitons within the core of the QD due to strong Coulombic interaction between the quasi particles. The result is dominant radiative recombination of excitons due to strong spatial overlap of the electron and hole wavefunction. Although some non-radiative process could be present due to interface traps acting as hot carrier trapping sites as well as exciton dissociation in close proximity to a metal conductor, the overall recombination is dictated by radiative processes.³¹ Using the analogy of a metal-oxide-semiconductor capacitor, for a negative gate bias below threshold voltage (V_{th}), where V_{th} corresponds to the gate potential where the QDs are neutral, the resulting electric field leads to accumulation of holes in the QD assembly.²² The excess hole

promotes the formation of positive trions in the QD whose recombination is dominated by non-radiative decay. Similarly, a gate bias above threshold voltage allows us to probe the recombination dynamics of negative trions formed by optical excitation in conjunction with electron injection.

First, we examined the relative rates by measuring the integrated PL counts of a charged ensemble of CdSe/CdS QDs as presented in Figure 2a. The background charge concentration in the QD ensemble can be estimated to a first order approximation to be $N = C_{\text{ox}}(V_g - V_{\text{th}})/e$, where C_{ox} is the total gate capacitance of the ionic liquid and polymer interlayer, V_g is the applied gate bias and e is the electronic charge. Due to the finite response time of the low mobility ions in the ionic liquid, the gate voltage was gradually ramped to the desired bias prior to the optical excitation of the QDs. As evidenced from this plot, for the same amount of background electron or hole concentration, there is an imbalance in the injected charge into the QD film due to unequal energy barrier of the respective carriers from the metal contacts, as will be explained later. There is more than one order change in PL counts transitioning between the bright (neutral exciton) and the dark (negative trions) state at positive gate voltages. The effect is less dramatic for the case of positive trions at negative gate voltages. This process is fully reversible; the QDs retain their initial brightness even after multiple periods of charging-discharging cycle spanning 10s of minutes (Figure S2). It is to be noted that despite creating a large electric field across the QD film, the implemented device structure accommodates enhanced charge injection from the underlying metal pad and modulates the degree of charging only on the QDs overlapping the source electrode as verified by PL imaging (Figure 2c). The absence of peak wavelength shift denotes that the PL intensity modulation is not caused by QCSE (Figure 2b and S3). The negligible gate leakage current within the relevant voltage range further corroborates the existence of excess charge residing within the thin film of QDs (Figure S4).

Next, we explore the evolution of lifetime of the quasiparticles in the various charged states using time resolved photoluminescence measurements. For the three regions of interest (neutral excitons, positive and negative trions), the PL decay of the QD nanoparticles is measured under pulsed excitation (Figure 3a). Here we note that, even without applying any bias to the QD film, we still see a multi-exponential decay due to the existence of a non-radiative recombination pathway by exciton quenching to the neighboring conductor surface. Therefore, we employ a biexponential model to fit the fast and slow component of the lifetime decay using the equation below³²,

$$I(t) = A_{\text{fast}}e^{-t/\tau_{\text{fast}}} + A_{\text{slow}}e^{-t/\tau_{\text{slow}}} + B \quad (1)$$

where $A_{\text{fast(slow)}}$ is the amplitude weighting factor of the fast (slow) component of the decay, $\tau_{\text{fast(slow)}}$ is the fast (slow) effective lifetime and B is the background count. During a decay cycle, a QD can either be in a charged state with formation of trions, or it can be uncharged while forming excitons. In an ensemble, the net occupation probabilities of the QDs in the charged and uncharged state must be unity. This is imposed by,

$$A_{\text{fast}} + A_{\text{slow}} = 1 \quad (2)$$

The fast decay component is dictated by several non-radiative channels including Auger recombination of trions, interface trap charge induced decay and exciton dissociation to metal surface, whereas the slow component is predominantly radiative recombination lifetime of excitons in the uncharged state. As shown in Figure 3a, the initial fast decay varies in the different charged state whereas the slow decay is effectively similar for a given optical pump fluence. Therefore, using Eqs. (1) and (2), we perform a global fitting, keeping the slow lifetime fixed for a given pump fluence, while optimizing the amplitude weighting factor and the fast lifetime. This enables us to extract the individual fast lifetimes corresponding to the different charged states and

the common slow lifetime (see Table S2 in supporting information). Despite having a shorter Auger lifetime of positive trions at a negative bias, they exhibit a similar decay profile as the uncharged state which is explained by only a small fraction of the ensemble QDs being charged in this state.³³ As a result, the fast component of the lifetime is not too dissimilar, leading to a marginal decrease in PL intensity as portrayed earlier (Figure 2a).

The difficulty of hole injection was previously observed in single nanocrystal and ensemble studies, where the observation was rationalized from energy barrier perspective.^{14,32} Indeed, this holds true for our device structure where the metal work function of platinum poses a larger energy barrier to hole injection into the core of the QD as opposed to electrons.³⁴ On the contrary, the QD film undergoes significant charging from electron injection, which translates into more than an order of magnitude change in integrated PL counts, as supported by the stark difference in the fast and slow components of the lifetime decay at +2.5V (Figure 3b). Once the negative trions undergo fast non-radiative recombination on the timescale of 100s of picoseconds, the remainder uncharged QDs then radiatively recombine with their slow lifetime being exhibited in the decay profile. Note that at +2.5V the fast decay component overlaps with the instrument response function (IRF), suggesting the measurement was limited by the IRF and the actual fast decay lifetime could be even shorter. For the range of optical pump fluence studied, the different components of the lifetime remain constant, indicating the absence of biexcitons (Figure S5).^{22,35}

The versatility of ionic liquid gating complemented with uniform close packing of nanocrystals from solution-processed films inspired us to demonstrate millimeter-scale luminescent film whose brightness can be reversible tuned by controlled charge injection (Figure 4). As the gate bias is gradually ramped to charge the QD ensemble with electrons, the PL intensity of the nanocrystal film drops by two orders of magnitude, which is apparent from the complete dimming of PL in the luminescent film area. Reversible modulation of brightness is achieved by

discharging the film with equal magnitude of gate potential having opposite polarity (see supplementary video). This highlights the promise of voltage tunable phosphor with emission in the near infra-red regime and beyond.

3. Conclusions

In summary, we have demonstrated a platform for controlled injection of charge in an assembly of QDs that allows us to investigate the deterioration of luminescent devices with charge accumulation. The polarity of gate bias enables us to selectively probe the different charging states in the QD film in terms of transient quasiparticle lifetime that is dictated by the various recombination channels in the system. The resulting modulation of PL is found to be dependent on the fast non-radiative recombination lifetime of the charged nanoparticles as well as the degree of charging in the ensemble. With feasibility of large-scale operation, the device structure can be applied as bias-dependent phosphor across wide range of emission wavelengths.

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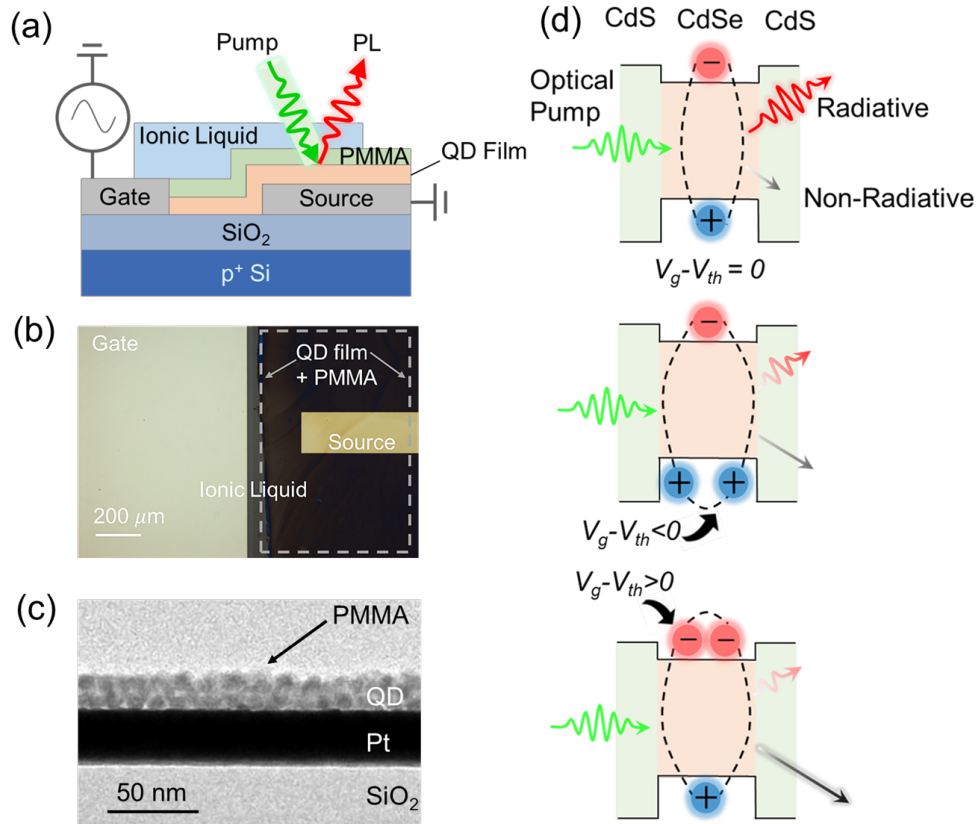


Figure 1. Charge injection in a quantum dot film. (a) Schematic cross-section of the device used to systematically study the recombination dynamics in thin film QD at various charging states. (b) Optical micrograph showing a uniform film of QD and PMMA over the source metal pad, using a dry patterning step. The spin-coated QD film area is highlighted by dashed lines. The ionic liquid, overlapping the entire field of view shown in the optical image, effectively applies the electric field across the QDs sitting on the source metal which is accommodated by injection of charge of relevant polarity. (c) TEM cross-section image along the source metal pad showing a very thin film of QDs on platinum. (d) Illustration of a core-shell CdSe/CdS QD with quasi type-II band alignment in (top to bottom) neutral, positive and negatively charged states. In the neutral state, optical pumping creates excitons which mainly undergo radiative recombination. In the presence of an extra hole (electron), positive (negative) trions are formed which have enhanced non-radiative recombination channels as depicted by the length of the straight grey arrows.

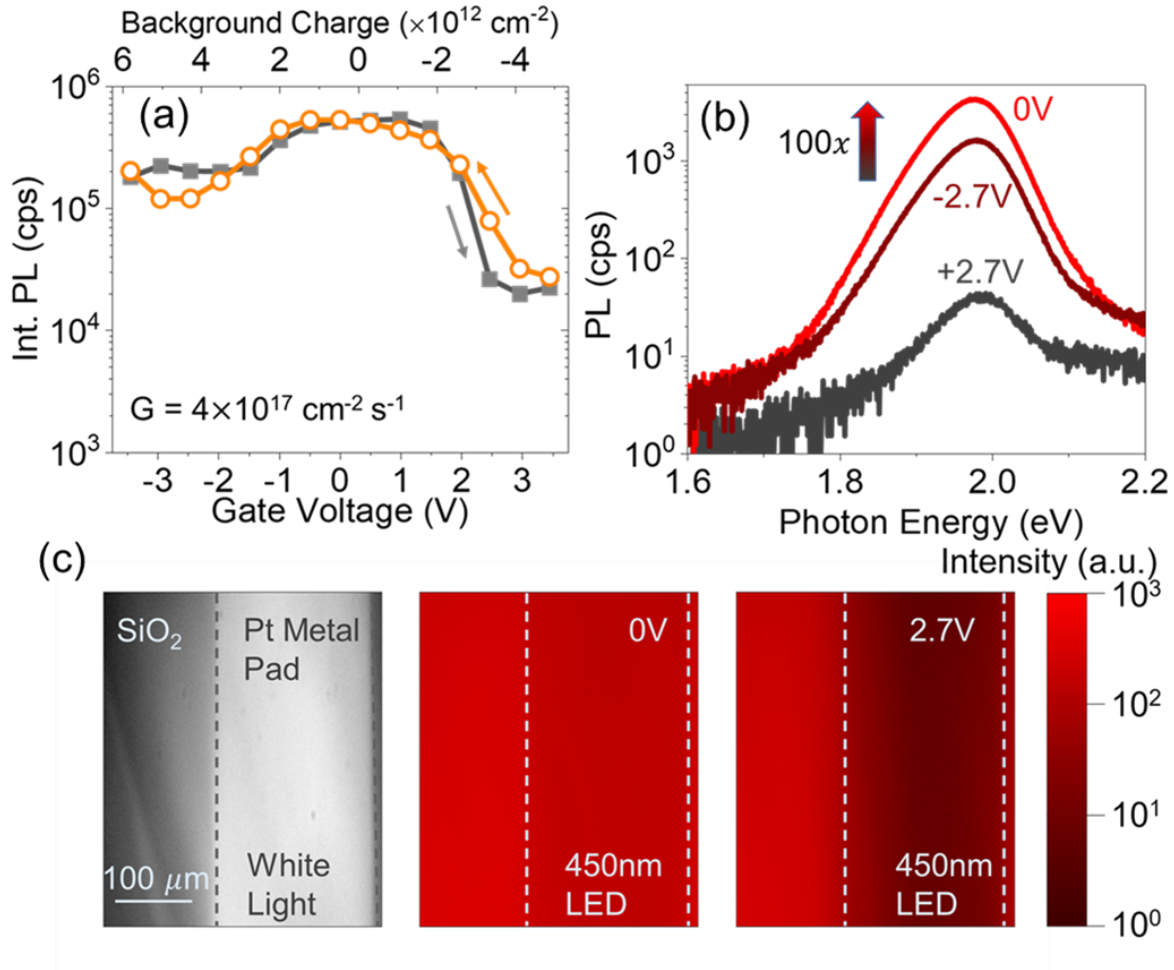


Figure 2. Modulation of photoluminescence intensity (a) Integrated PL counts as a function of applied gate bias for CdSe/CdS QDs with an optical generation rate of $4 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$. A reversible change in PL can be observed while transitioning between the different charging states of the QD when the gate bias is swept in either direction. Orange (grey) arrow denotes the direction of the gate voltage sweep. The sign of the background charge denotes electron (hole). (b) PL spectra of the QDs under different charging conditions as in (a). The corresponding gate biases are shown in the plot. (c) PL image of the QD ensemble under white light and above bandgap excitation from a 450nm LED. When electrostatically gated, only the QDs over the metal pad undergo charging and demonstrate a modulation of PL intensity under optical pumping. The metal pad edges are shown by dashed lines in each plot along with the applied gate bias.

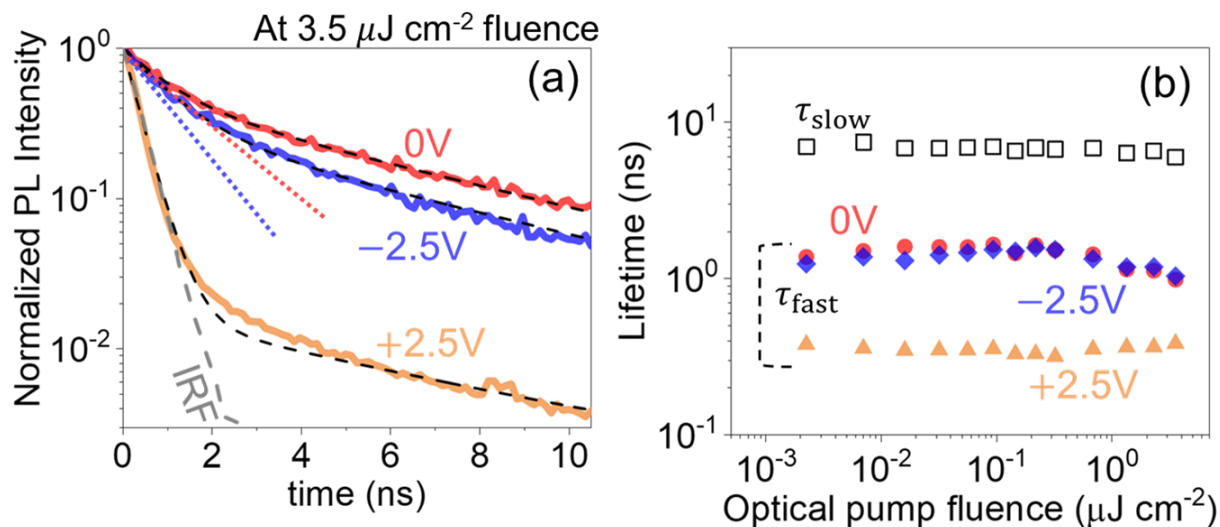


Figure 3. Time resolved photoluminescence spectroscopy. (a) Lifetime decay trace for CdSe/CdS thin film QDs at different gate biases. All the decay curves show an initial fast decay component corresponding to non-radiative processes, followed by a slow decay pertinent to the radiative recombination of uncharged QDs. A biexponential model (black dashed lines) provides a reasonable fit to the fast lifetimes, keeping the slow decay component constant for all the charge states at any given fluence. The instrument response function (IRF) of the detector is shown in the same plot as dashed line. Note that at +2.5V the fast decay component overlaps with the IRF, suggesting the measurement is limited by the IRF and the actual fast decay lifetime could be even shorter. The dotted lines are guide to the eye for the initial sharp decay. **(b)** Fast decay (solid marker) and slow decay lifetime (open marker) extracted from the biexponential fitting at various optical pump fluences (Table S2).

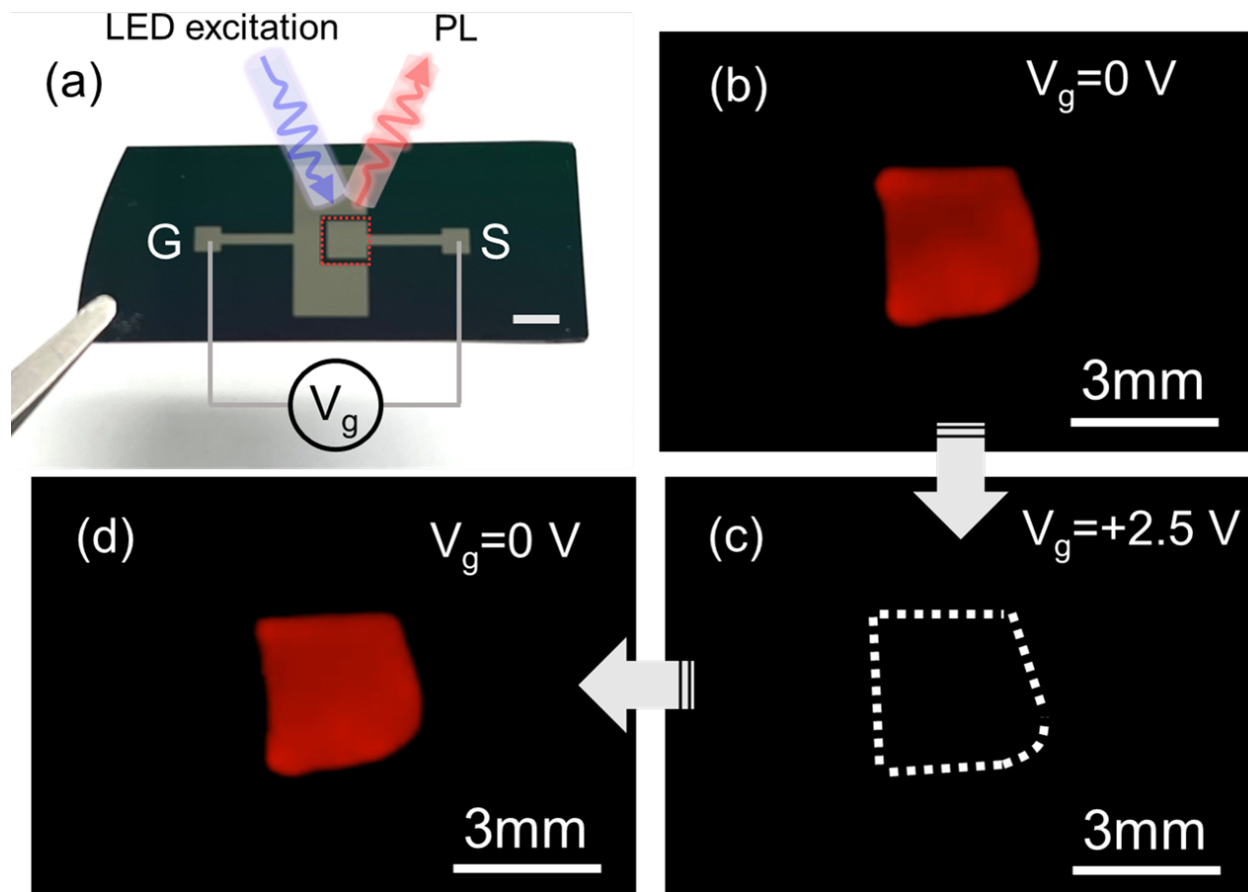


Figure 4. Reversible modulation of PL intensity in large area luminescent film. (a) Optical image of the millimeter scale device along with schematic diagram showing how the gate bias is applied and the film is optically pumped. The QD film over the large source pad is highlighted by dotted lines. Scale bar: 3mm. (b-d) Snapshots from recorded video, showing reversible modulation of brightness at initial (0 V), charged (+2.5 V) and discharged states (0 V again). The corresponding applied gate biases are also shown in the plot. At 2.5 V, the dramatic change in PL intensity can be readily observed by eye in the video as the QD film becomes dimmer and reaches similar intensity as background. The dotted lines highlight the luminescent area in the dark state.

Acknowledgements

This work was funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 (EMAT program KC1201). Device fabrication part of this work was funded by Samsung Display. N.H. acknowledges support from Postdoctoral Fellowships for Research Abroad of the Japan Society for the Promotion of Science. The authors acknowledge A. Paul Alivisatos for stimulating discussions and Shogo Tajima for his support in device fabrication.

Author Contributions

R.R., S.Z.U. and A.J. conceived the idea for the project and designed the experiments. H.L and J.L synthesized quantum dots. R.R., S.Z.U., N.H., J.C.K., Q.L. and J.A. fabricated devices and performed optical measurements. R.R. K.L. H.K. performed the optical imaging. R.R., N.H., and A.J. analyzed the data and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing financial interests

The authors declare no competing financial interests

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