Study of field driven electroluminescence in colloidal quantum dot solids

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Semiconductor nanocrystals, or quantum dots (QDs), promise to drive advances in electronic light generation. It was recently shown that long range transport of charge, which is typically required for electric excitation and which is inherently limited in nanosized materials, can be avoided by developing devices that operate through local, field-assisted generation of charge. We investigate such devices that consist of a thin film of CdSe/ZnS core-shell QD placed between two dielectric layers and that exhibit electroluminescence under pulsed, high field excitation. Using electrical and spectroscopic measurements, we are able to elucidate the dynamics of charge within the QD layer and determine that charge trapping and field-induced luminescence quenching are the main limitations of device performance. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4720377]

I. INTRODUCTION

Colloidal quantum dot based light emitting devices (QLEDs) have shown potential for displays and large area lighting applications. To date, most QLEDs involve a monolayer or thin film of quantum dots (QDs) sandwiched between hole and electron transport layers of organic, inorganic, or hybrid materials. Air stable QLEDs that would lower costs due to the elimination of packaging use ceramic charge transport layers. However, the efficiency of these devices has so far been limited by difficulties in controlling charge injection into the QD film.

A variety of schemes have been developed to manage charge transport and generation more effectively in LED structures. One method uses charge generation layers (CGLs) that inject charge into a semiconductor by field assisted charge separation, and induce electroluminescence (EL) even when external charge injection is suppressed by dielectric layers on one or both sides. Due to the blocking of charge injection, the excitation of such devices is achieved by applying an alternating voltage. These approaches originated as modifications to traditional pn-type light emitting diodes, however, they exhibit striking similarities to alternating current thin-film electroluminescent (ACTFEL) devices, which are an alternative display and lighting technology that has been commercially available for several decades.

We recently reported the development of a structure in which electroluminescence from QDs is achieved without the need for charge injection. The structure sandwiches a QD thin film between two dielectric layers as depicted in Fig. 1(a). We hypothesized that this QD device operates by means of field-ionization of electrons from one QD valence band to the conduction band of a neighboring QD, providing a local mechanism for bipolar charge generation that obviates the need for charge injection. In order to develop guidelines for rational optimization of these devices, this work aims to provide a quantitative understanding of the different charge generation, transport, and recombination processes that occur in these field-driven quantum dot light emitting devices (FD-QLEDs).

Sections II–IV describe the materials characterization, device fabrication, and device operation. The remaining sections describe the optoelectronic measurements used to elucidate the charge related processes studied, which are depicted schematically in Figs. 1(c) and 1(d). Sections V–VII describe time resolved electrical measurements performed as a function of temperature and photoillumination (to generate charge uniformly within active layer) that indicate the important role of charge trapping in QLED performance. In particular, the electrical measurements confirm that above a threshold voltage, free charges are generated through field-ionization (depicted by green arrows). A majority of the free charges created by field-ionization are trapped and recombine slowly (red arrows). Contrary to initial expectations, the trapping process is only weakly dependent on temperature up to room temperature (indicative of deep trap states) and photoillumination (suggestive of a spatial separation between the exciton generation region and the trap locations). In agreement with studies on QD solids, charge trapping is identified as one of the dominating processes and limitations to light generation.

In Sec. VIII, we describe the concurrent electrical and photoluminescence (PL) measurements we developed to probe the importance of exciton dissociation (blue arrows) under the high field conditions. While strong field-dependent luminescence quenching is recorded, only minor charge separation is observed simultaneously, suggesting that exciton dissociation is not responsible for the luminescence quenching. Due to suppression of charge injection in the capacitive structure, we can control charge carrier densities, and exclude Auger-type processes as the source of the reduced luminescent efficiency. We successfully explain our data using a model of electric field-dependent coupling of the exciton to surface states, which was observed and explained previously in Ref. 15.

II. SAMPLE PREPARATION

For all measurements presented here, we use FD-QLEDs fabricated concurrently using the same materials...
and conditions. A 70 nm layer of Al₂O₃ is deposited by RF magnetron sputtering at 3.0 W/cm² in 4 mTorr of Argon on an ITO coated glass substrate. CdSe/ZnS core-shell QDs with oleic acid capping ligands, provided by QD-Vision Inc., are spin-cast from octane at 2000 rpm (6000 rpm/s) to achieve a thickness of 29 ± 1 nm as determined by atomic force microscopy (AFM). The top Al₂O₃ layer is prepared using the same procedure as the bottom Al₂O₃ layer. 150 nm thick Al top electrodes are deposited by RF magnetron sputtering at 0.77 W/cm² in 5 mTorr of Argon to define an active device area of 2 x 10⁻² cm². In order to characterize the dielectric properties of our materials, we simultaneously prepare a reference device that includes all layers except the spin-cast QD film.

III. DIELECTRIC CHARACTERIZATION

To enable accurate calculation of the electric fields and charge present within our FD-QLED, we first characterize the capacitance of the dielectric layers by temperature dependent impedance spectroscopy. Using the reference sample, we find a capacitance of \( C_{\text{ox}}/2 = 69.7 \text{nF/cm}^2 \) (1.80 nF) at 300 K and 5 kHz. This capacitance is found to decrease linearly with temperature from room temperature down to 40 K with a coefficient of 0.031 nF/cm²K⁻¹. This effect is well characterized in oxides and can be attributed to the decrease in ionic motion with decreasing temperature.¹⁶,¹⁷

The complete FD-QLED structure has a capacitance of 41.5 nF/cm² (1.07 nF), from which we calculate a QD film capacitance of \( C_{\text{qd}} = 102 \text{nF/cm}^2 \) and a QD film dielectric constant of \( \varepsilon_{\text{qd}} = 3.35 \). Unlike the oxides layers, the capacitance of the QD thin film shows a negligible temperature dependence from 50 K to 300 K (data not shown).

Using the effective medium theory by Maxwell and Garnett, we can use these impedance spectroscopy results to obtain an independent confirmation of the number of QDs within the active layer of our device. Assuming that the QD film consists of semiconductor particles with dielectric constants \( \varepsilon_{\text{se}} = 10 \) and organic surfactants with \( \varepsilon_{\text{org}} = 2.2 \), we determine a semiconductor volume fraction of 27.4%. Furthermore, if we assume a close packed configuration of QDs with a 6.5 nm diameter, we calculate a distance between the center of two QD cores to be 9.1 nm, which is in reasonable agreement with an interQD distance of 9.6±1.4 nm determined independently by AFM. This configuration of QDs implies a QD volume density of \( \rho_{\text{3D}} = 2.1 \times 10^{19} \text{cm}^{-3} \).

IV. DEVICE OPERATION

We characterize the efficiency of our FD-QLED by measuring the electroluminescence response \( (I_{\text{EL}}) \) to a sinusoidal voltage as a function of peak-to-peak voltage \( V_{\text{pp}} \) and frequency \( v \). A representative \( I_{\text{EL}} \) versus voltage measurement taken at 100 kHz is shown in Fig. 1(b). The voltage where the device turns on (emits EL) is indicated by the vertical line.

Simultaneously the dielectric loss is measured using the Sawyer-Tower circuit depicted in Fig. 1(a). By measuring the voltages \( V_0, V_1, V_s \), we calculate the current and the voltage over the device using \( i = (V_0 - V_1)/R_s \) and \( v = (V_1 - V_s) \). The dielectric loss is then determined by \( P_{\text{loss}} = \frac{1}{T} \int_0^T i(t)v(t)dt \). As shown in Fig. 2(a), the dielectric loss in the device exhibits a \( v^{0.5} \) dependence as a function of frequency for all voltages. We attribute the features around 30 kHz to insufficient calibration of the measurement setup.

The polynomial frequency dispersion is known to be a universal feature of electron transport in disordered materials and is often related to a broad distribution of hopping rates.¹⁹ This suggests that energy consumption in the device is predominantly due to movement of charge in the QD film which is limited by the availability and mobility of charge carriers. Fig. 2(a) shows a strong increase in energy consumption with only small increases in voltage, which indicates that more charge becomes available through field-ionization. At the same time, the dissipated power increases sub-linearly in frequency, which implies that for increasing frequencies a decreasing fraction of the charge is able to follow the excitation.

The EL intensity \( (I_{\text{EL}}) \), measured with a Si photo detector, exhibits the same \( v^{0.5} \) dependence for all voltages (see Fig. 2(b)) as the dielectric loss. We conclude that the EL signal is dominated by the dynamics of charge within the QD film. Our pulsed measurements described in Secs. V and VII confirm this. Similar results were reported in Ref. 3.
While the $I_{\text{EL}}$ increases with frequency, we find the EL efficiency ($I_{\text{EL}}/P_{\text{loss}}$) to be frequency independent in the observed range up to 100 kHz. At the same time, the EL efficiency goes down by 50% when the voltage is increased from 83V_{pp} to 90V_{pp}. In Sec. VIII, we show that the loss in efficiency can be understood as an increase of the non-radiative recombination rate in the QDs due to high fields.

V. INTERNAL ELECTRIC FIELD AND CHARGE

To identify the internal field and charge within the QD film as a function of time, we employ characterization techniques introduced by Wager and Keir\textsuperscript{7} for ACTFEL devices. As depicted in Fig. 1(a), the device is placed in series with a sense resistor ($R_s$) and a sense capacitor ($C_s$), which enables extraction of information about the current flowing into the device and the charge in the device, respectively. The values $R_s = 3.3 \Omega$ and $C_s = 387 \text{nF/cm}^2$ (10 nF) are chosen such that most of the applied voltage drops over the device. Based on the equivalent circuit in Fig. 1(a), we can relate the measured voltages $V_{1}(t)$, $V_{s}(t)$ to the electric field ($F_{qd}$) and the polarization charge ($Q_{qd}$) in the QD film\textsuperscript{7} through

$$F_{qd}(t) = \frac{1}{d_{\text{film}}} \left[ \left( \frac{2C_s}{C_{\text{ox}}} + 1 \right) V_s(t) - V_1(t) \right],$$

$$Q_{qd}(t) = \left( C_{qd} + C_s + 2 \frac{C_s C_q}{C_{\text{ox}}} \right) V_s(t) - C_{qd} V_1(t).$$

We apply bipolar voltage pulses, as shown in Fig. 3(a), with a length of 100 $\mu$s. The data for a 40V_{pp} pulse (shown in black) are representative of all subthreshold voltage pulses. In this case, $F_{qd}$ which is plotted in Fig. 3(c) is proportional to the applied voltage. In particular, we note that the electric field at the beginning of the pulse ($F_{\text{init}}$) and the electric field at the end of the pulse ($F_{\text{final}}$) are the same. This means that no free charge moves in the QD film during the applied voltage pulse. This is also reflected by the fact that $Q_{qd}(t)$ stays close to zero. This is the characteristic of a good dielectric and is consistent with the expectation that no mobile charge carriers are available in the material.\textsuperscript{12}

From this data, we can estimate the dielectric constant of the QD film using

$$\varepsilon_{r,\text{qd}} = \frac{C_s V_s}{\epsilon_0 F_{qd}},$$

where $\epsilon_0$ is the vacuum permittivity. During the pulse, we find $\varepsilon_{r,\text{qd}} = 3.05$, which is in good agreement with the value determined by impedance spectroscopy discussed in Sec. III. As suggested in Ref. 7, we use the value $\varepsilon_{r,\text{qd}} = 3.05$ for the following data analysis.

For voltage pulses above threshold, the electrical behavior of the QD film changes. At the onset of the voltage pulse, we observe a large increase of $Q_{qd}(t)$ in Fig. 3(e), which corresponds to the generation of free charge that provides the carriers for the electroluminescence observed in Fig. 3(g). As described in the Introduction, we attribute this free charge generation to field-ionization of electrons from the valence band of a QD to the conduction band of a neighbouring QD.\textsuperscript{10} The total charge which is transported during the voltage pulse will be denoted by $Q_{\text{cond}}$. This charge screens part of the field in the QD film and we find that the field at the end of the pulse is smaller than in the beginning, i.e., $F_{\text{final}} < F_{\text{init}}$. 

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FIG. 2. a) Measured dielectric loss ($P_{\text{loss}}$) vs frequency when applying a sinusoidal voltage with 77V_{pp} (purple circles), 83V_{pp} (red squares), and 90V_{pp} (orange diamonds). The dashed line shows a polynomial with exponent 0.5. (b) Electroluminescent intensity ($I_{\text{EL}}$) vs frequency for the same voltages as in panel (a). The dashed line is again a polynomial with exponent 0.5.

FIG. 3. Time-dependence of key parameters in response to electrical pulses with peak-to-peak voltages of 40V_{pp} (black), 70V_{pp} (purple), 80V_{pp} (red), and 90V_{pp} (orange). Right column is a zoomed-in view of the data on the left. (a and b) Applied voltage pulse (only 40V_{pp} plotted) (c and d) Electric field in the QD-layer. Initial field ($F_{\text{init}}$) and the field at the end of the pulse ($F_{\text{final}}$) are extracted from this graph. (e and f) Polarization charge in QD-layer. Charge transported during the pulse ($Q_{\text{cond}}$) and charge recombining between pulses ($Q_{\text{rec}}$) are extracted from this graph. (g and h) Electroluminescent response ($I_{\text{EL}}$) recorded with an ultra fast photodetector.
Between the voltage pulses (when the applied voltage is 0), some charge recombines ($Q_{\text{rec}}$), resulting in a reduction of $Q_{\text{el}}$. Immediately after the applied voltage goes to zero, there is a fast reduction, followed by a reduction with a long time scale (see Fig. 3(e)). The fast time scale change in $Q_{\text{el}}(t)$ is attributed to the recombination of free electrons and holes driven by the built up polarization. This is supported by a concurrent peak in EL intensity (Figs. 3(g) and 3(h)). The long time scale recombination is associated with trapped charges and can be quantified by $Q_T = (Q_{\text{cond}} - Q_{\text{rec}})$. This trapped charge does not recombine between the pulses and is only transported in the beginning of the next pulse. This rearrangement of charge leads to the EL intensity peak at the rising edge of the voltage pulse as shown in Figs. 3(g) and 3(h).

We performed the pulsed experiments for different pulse voltages and extracted the values of $F_{\text{init}}$, $F_{\text{final}}$ and $Q_{\text{cond}}$, $Q_{\text{rec}}$. In Fig. 4(a), we plot the electric field value ($F_{\text{init}}$) versus the applied voltage and find a linear relationship. The electric field at the end of the pulse ($F_{\text{final}}$) follows $F_{\text{init}}$ closely until ~72Vpp, which we identify as the voltage above which there is rearrangement (generation, transport, and recombination) of charge. We note that this threshold voltage, which is extracted from purely electrical measurements, is in good agreement with the turn-on voltage extracted from optical measurements (Fig. 1(b)).

We plot $Q_{\text{cond}}$ and $Q_{\text{rec}}$ versus the applied voltage (gray lines in Fig. 4(b)) to facilitate understanding of device operation below and above the threshold voltage. Below the threshold voltage, we expect that mobile charge is not available nor generated during the applied voltage pulse. Indeed, the conduction charge during the pulse and the recombination charge between the pulses are comparably small. The measured value of 0.03 $\mu$C/cm² for both $Q_{\text{cond}}$ and $Q_{\text{rec}}$ represents the measurement uncertainty, and should therefore be interpreted as an upper limit on the free charge present in the QD film. To provide a value for reference, we consider the hypothetical situation in which every QD has an electron and a hole on its surface forming a dipole. In this case, we calculate a polarization of 0.22 $\mu$C/cm².

According to our understanding of FD-QLED operation, above the threshold voltage, charge is generated in the QD film by the voltage pulse. Indeed, we see that $Q_{\text{cond}}$ grows exponentially with voltage. At 90Vpp, the charge transported during one voltage pulse is 0.60 $\mu$C/cm². As more charge is generated, both the amount of charge that recombines ($Q_{\text{rec}}$) and the amount of trapped charge ($Q_T$) increase; however, the amount of trapped charge increases at a faster rate than the amount of charge that recombines. In other words, only a small fraction of the charge that is generated and transported during the pulse is able to recombine between pulses. This highlights one of the current limits to device efficiency.

VI. PHOTOCONDUCTION EXPERIMENTS

To better understand the generation and recombination of charge within our FD-QLED, the bipolar pulse electrical experiments are also performed while illuminating the sample. The illumination is supplied by a 475 nm collimated LED source at an intensity of approximately 1.5 W/cm². Fig. 4(b) plots the charge that recombines between the voltage pulses ($Q_{\text{rec}}$) and the charge that is shuttled within the QD film during the voltage pulse ($Q_{\text{cond}}$) as a function of voltage with and without illumination. Although excitons in QDs have large polarizabilities, 20,21 we estimate that our illumination intensity produces only a small average exciton density ($<10^{-2}$ excitons/dot), the polarization of which cannot be detected in our charge measurements. Therefore, the measurement reported here shows primarily separated charge (i.e., charge that is field-ionized or that stems from dissociation of the photogenerated excitons).

We note two key trends: (1) illumination increases $Q_{\text{cond}}$ only for low voltages and (2) illumination increases the $Q_{\text{rec}}$ by 27%±4% for all voltages.

We established that no mobile carriers are available in the dark below the threshold voltage, so we attribute the increase of $Q_{\text{cond}}$ under illumination at low voltages to the creation of free charge carriers through dissociation of the photogenerated excitons. We estimate from the incident photon flux and absorption coefficient that for the observed change in $Q_{\text{cond}}$, 1 in every 2000 excitons is dissociated during the voltage pulse. Due to the availability of charge from illumination, traps are now populated even at low voltages ($Q_{\text{cond}} > Q_{\text{rec}}$). In the high field regime, the effect of the illumination on the conducted charge vanishes. In this regime, charge generation and the available charge is dominated by the field-ionization process.

The enhanced recombination (increase in $Q_{\text{rec}}$) is similarly attributed to the fact that the photogenerated excitons can dissociate into free charge carriers, move in the field of trapped charges, and neutralize occupied traps. We find that only 1 in every $10^4$ excitons needs to dissociate and neutralize a trap for the observed effect.

The effect of illumination on the recombinant behavior is small and is probably due to the mismatch of the exciton lifetime which is on the order of 20 ns (Ref. 22) and the comparatively slow charge transfer processes. It remains...
open, if the minimal impact of illumination indicates that charge trapping likely occurs away from the exciton generation region (i.e., traps are located at the QD film/dielectric interface rather than on the QD surface).

VII. TEMPERATURE DEPENDENCE

For the transport of charge in disordered materials, it is often times assumed that thermal processes play an important role. Detrapping of charge is also usually described by a thermal process. We therefore perform the bipolar pulse experiments for 10 temperatures between 50 K and 300 K. In the analysis, we use the results from dielectric spectroscopy measurements described in Sec. II to account for the temperature dependence of the oxide capacitances.

In Fig. 5(a), we plot the conducted charge ($Q_{\text{cond}}$) with and without illumination. Both traces show small variations for the different temperatures which are indicated by the error bars, but no systematic temperature trend is observed. We conclude from this data that thermal processes do not play a role in the transport of the charge during the applied voltage pulse. This regime is dominated by high field transport.\textsuperscript{13}

In contrast, the charge recombining between pulses ($Q_{\text{rec}}$) is constant between 50 K and 230 K and increases above 260 K for all voltages (Fig. 5(b)). Fig. 5(c) shows the temperature dependence for a representative voltage (90V$_{pp}$). We attribute the increase in $Q_{\text{rec}}$ to the enhanced thermal detrapping of charge. However, the enhancement of $Q_{\text{rec}}$ of $\sim$0.05 $\mu$C/cm$^2$ at room temperature is small compared to the total amount of trapped charge $Q_T \sim 0.5$ $\mu$C/cm$^2$, so we conclude that thermal-ionization of traps does not play a dominant role in our devices. This is consistent with the presence of deep traps with trapping energies larger than the available thermal energy.

Finally, we do not observe any systematic change in the EL between 300 K to 50 K (data not shown). This is consistent with the conclusion that EL is limited by the availability and movement of free charges, which shows a weak temperature dependence.

VIII. LUMINESCENCE QUENCHING

To better understand the effect of the high electric fields on the QD luminescence, we measure the QD PL intensity ($I_{\text{PL}}$) during the photoconduction experiments described in Sec. V. We observe that $I_{\text{PL}}$ is reduced during the applied voltage pulse even for voltages below threshold (Figs. 6(a) and 6(b)). However, our measurements of polarization indicate that below the threshold voltage, there is no mobile charge in the QD film even under photolumination, which suggests that Auger recombination and exciton dissociation cannot be responsible for the observed luminescence quenching. We therefore hypothesize that luminescence quenching is field-induced.

Field-induced PL quenching in CdSe/ZnS QDs was previously reported by Park \textit{et al.} and attributed to increased coupling of excitons to surface trap states with applied field, which decreased the QD quantum yield (QY).\textsuperscript{15} Other effects such as a decrease of the radiative rate\textsuperscript{22} and increasing

\[ Q_{\text{cond}} \text{ vs applied voltage for temperatures 50–300 K. No specific temperature dependence was found.} \]

\[ Q_{\text{rec}} \text{ vs applied voltage for temperatures 50–230 K. Between 50 and 300 K, there was no change with temperature. Above 230 K, an increase of a factor of 2 is observed.} \]

\[ Q_{\text{rec}} \text{ at 90V}_{pp} \text{ vs temperature.} \]
exciton-phonon coupling\textsuperscript{23,24} were shown to play a minor role in such systems. To verify that field is responsible for the luminescence quenching in our devices, we demonstrate that $I_{\text{PL}}$ is dependent on the field experienced by a QD. Under constant illumination, we expect the PL intensity to be proportional to the QY, such that

$$I_{\text{PL}} \propto \text{QY} = \frac{k_r}{k_{nr} + k_r} = \frac{1}{k_{nr}/k_r + 1},$$

where $k_r, k_{nr}$ are the radiative and non-radiative exciton decay rates, respectively. In accordance with Ref.\textsuperscript{15}, we assume that the non-radiative rate dominating the QY is linearly dependent on the field in the QD film ($F_{\text{qd}}$)

$$k_{nr}(t)/k_r = A + BF_{\text{qd}}(t),$$

where the free parameters $A$ and $B$ and the radiative decay rate are assumed to be constants.\textsuperscript{22} Figs.\textsuperscript{6(c) and 6(d)} plots QY($t$) using the values of $F_{\text{qd}}(t)$ from the electrical measurements and parameters $A = 5.0$ and $B = 3.5\text{MV/cm}^{-1}$. This simple model for the QY that includes only field-induced quenching quantitatively matches all major features of $I_{\text{PL}}$ (Figs.\textsuperscript{6(a) and 6(b)} including the increase that occurs at the end of the pulse. This increase is a consequence of the zero-crossing of the electric field in the film at the point where the externally applied field and the internal polarization cancel out.

To further confirm field-quenching of the luminescence, we perform time-resolved optical spectroscopy on the device during application of the bipolar pulses at a range of voltages. We collected the time-resolved spectra of the photoluminescence using a Hamamatsu streak camera system (Model C5680) and fit each temporal slice of the spectra with a Gaussian of the form $A_0/\sigma \cdot \exp(-(\lambda - \lambda_0)^2/\sigma^2)$. Above the threshold voltage, we collect both photo- and electroluminescence; however, our Gaussian function remains a good fit to the data. Figs.\textsuperscript{6(e) and 6(f)} plot the peak emission wavelength ($\lambda_0(t)$) and the PL intensity ($A_0(t)$). The PL intensity ($A_0(t)$) dependence with voltage is consistent with the measurements presented in Figs.\textsuperscript{6(a) and 6(b)}.

From the peak emission wavelength ($\lambda_0(t)$), we can (independently of electrical measurements) estimate the values of the electric field within the QD layer. We observe an increasing red shift in $\lambda_0(t)$ as a function of voltage. This red shift can be attributed to the quantum confined Stark effect (QCSE), which has been well characterized for single CdSe/ZnS QDs.\textsuperscript{26} Using the results in Ref.\textsuperscript{20}, we relate our experimentally measured 24 meV red shift close to the threshold voltage to a field of approximately 1.0 MV/cm. From our independent electrical measurements in Fig.\textsuperscript{4(a)}, we determined an average field across the QD film of 4.7 MV/cm at threshold. Taking into account that the field experienced by an individual QD in a heterogeneous film (in this case QDs and ligands) is reduced by approximately $1/\varepsilon_{r,\text{qd}} = 0.29$ from the value of the average field, we expect individual QDs to experience a field of 1.39 MV/cm, which is in good agreement with the electric fields predicted from the PL measurement of the Stark shift.

However, during voltage pulses that exceed the threshold voltage (70V\textsubscript{pp} and 90V\textsubscript{pp} lines in Fig. 6(e)), the Stark shift decreases, which is visually seen by $\lambda_0(t)$ returning to its near zero-field value. We attribute this to the fact that above the threshold voltage, field-ionization generates charge that can locally screen the field experienced by some of the QDs. The screening effect is particularly pronounced because luminescence from QDs that experience the unscreened field is quenched.

**IX. CONCLUSIONS**

In summary, we fabricated and characterized FD-QLEDs, which are promising LED structures because they eliminate the need for band alignment engineering or finely tuned charge transport layers. We confirmed that field-ionization is responsible for providing the free charge carriers that recombine and enable FD-QLED operation without direct charge injection. We also identified the two limitations to device performance: charge trapping and field-induced luminescence quenching.

Charge trapping was observed through time-resolved, capacitative electrical measurements. Charge density within the QD film was controlled through the applied voltage and photo-illumination intensity, while the shape and frequency of the applied field and temperature were used to control the motion of the charge within the QD film. We find that over 90% of the charge becomes trapped over long timescales ($\gg$ 1 ms) with weak dependence on illumination or temperature. Field-induced luminescence quenching was explored by simultaneous, time-resolved optical and electrical measurements. Our ability to control and measure charge density within the QD film, enabled us to infer that exciton dissociation and Auger recombination do not play a significant role in the luminescence quenching. Instead, we suggest that field-induced coupling to surface states may be the cause of the luminescence quenching in agreement with Ref.\textsuperscript{15}.

These observations clarify the steps for improving the efficiency of next generation FD-QLEDs and other types of QLEDs, which also incorporate QD films that experience electric fields larger than 1 MV/cm. In particular, the development of surface treatments to reduce charge trapping at interfaces will be critical to higher performance light emitting devices. In the specific case of FD-QLEDs, our results also suggest two other avenues for higher performance. Higher frequency operation could enhance charge generation without a loss in efficiency, or novel materials could enable reduced field-quenching and field-ionization at lower voltages.

Finally, the phenomena we observe also demonstrate that the FD-QLED architectures provide a platform with which to investigate QD solids in the mesoscopic regime, in particular, the intricate interdependence between dielectric and conductive effects can be investigated from a new perspective due to the absence of charge injecting interfaces.

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9V. Wood, J. Halpert, M. Panzer, M. Bawendi, and V. Bulovic, Nano Lett. 9, 2367 (2009).