All-Quantum-Dot Infrared Light-Emitting Diodes

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ABSTRACT Colloidal quantum dots (CQDs) are promising candidates for infrared electroluminescent devices. To date, CQD-based light-emitting diodes (LEDs) have employed a CQD emission layer sandwiched between carrier transport layers built using organic materials and inorganic oxides. Herein, we report the infrared LEDs that use quantum-tuned materials for each of the hole-transporting, the electron-transporting, and the light-emitting layers. We successfully tailor the bandgap and band position of each CQD-based component to produce electroluminescent devices that exhibit emission that we tune from 1220 to 1622 nm. Devices emitting at 1350 nm achieve peak external quantum efficiency up to 1.6% with a low turn-on voltage of 1.2 V, surpassing previously reported all-inorganic CQD LEDs.

KEYWORDS: colloidal quantum dots · light-emitting diodes · infrared light emission · carrier transport layers
materials. Their Fermi energies were controlled using impurity doping and surface ligand exchanges. Benefits such as tunability of the CTLs' bandgaps and high charge carrier mobilities were demonstrated by integrating a CQD-based HTL in planar perovskite photovoltaics. Independent energy band modification of the doping type via ligand engineering was shown to improve CQD photovoltaic performance by enhancing carrier collection. Even with these significant steps forward for all-inorganic CTLs, only CQD HTLs have been shown. CQDs as ETL materials are so far unexplored, principally because the insufficient charge carrier blocking provided by relatively small-bandgap CQDs. Further, previous CQD CTL work has employed a non-CQD active layer: as a result, the CQD:ETL configuration has, until now, been unexplored in the CTL context.

Herein, we fabricate the first CQD-active-layer infrared LEDs that employ a distinct CQD solid for each CTL material. The active layer and CTLs are each CQD solids having the same underlying semiconductor composition, with only nanoparticle size and ligand choice varied to produce the heterointerfaces. These all-CQD devices feature emission wavelengths tunable from 1220 to 1622 nm. Metal halide-based surface treatments improve the CQD ETL in particular, and we use this to reduce the device turn-on voltage. We report EQE values that reach 1.6%. This is over seven times higher than previously reported all-inorganic CQD-based LEDs.

RESULTS AND DISCUSSION

We fabricated devices with CQD-based CTL and active layers directly on a prepatterned indium-doped tin oxide (ITO)-coated glass substrate using solution processing and solid-state surface treatment. PbS CQDs of various sizes were synthesized following an established procedure in which lead(II) oleate and bis(trimethylsilyl) sulfide were used as precursors. CdCl₂ treatment was selectively applied during post-processing and solid-state surface treatment. PbS CQDs using mercaptopropionic acid (MPA) and tetrabutylammonium iodide (TBAI) solutions, respectively. MPA-treated small CQDs (∼1.90 eV) used in the HTL have shallower energy band gaps of CQDs were confirmed using absorption spectra (Figure 1c). No obvious shift of λ(abs) was observed after the ligand exchange and purification processes for any of the CQDs. A cross-sectional scanning electron micrograph (Figure 2a) shows the total thickness of the stacked PbS layers is about 200 nm (HTL, ∼100 nm; active layer, ∼50 nm; ETL, ∼50 nm; Ag cathode, 220 nm). The emission peak can be widely tuned from 1220 up to 1622 nm by changing emissive CQD size (Figure 2b). No significant EL wavelength shift of the devices was observed with respect to the CQD PL spectra. We did not observe EL from devices that used smaller-diameter CQDs as emissive materials (i.e., PL maxima below 1100 nm). This is consistent with the view that Auger recombination increases in smaller dots; meanwhile, a sufficient CTL/ emissive layer bandgap offset is required for efficient charge carrier blocking by the CTLs.

The corresponding results of peak EQE vs current density are shown in Figure 2c. The record peak EQE performance of this architecture is 1.58%, achieved by the champion device emitting at 1350 nm. This is over 7 times higher than the best previously published all-inorganic CQD based LEDs. The peak EQE values are 0.79%, 0.37%, and 0.14% for devices emitting at 1220, 1450, and 1622 nm, respectively. The current density values at which the peak EQE appears are only slightly different (ranging between 10⁻⁴ and 10⁻³ A/cm²) because all active layer CQDs were passivated using the same type of ligand. Similar trends of size-dependent EQE and power conversion efficiency (PCE) performance are noticeable in the average peak EQE values (Figure 2d). Similar to the results reported by Sun et al., our LEDs with MOA-treated emissive dots have much higher efficiency.
higher peak EQE than devices using CQDs treated with shorter MPA ligands in the same architecture (higher peak EQE values by factors of \(\sim 20\) to \(\sim 60\), depending on the sizes of emissive CQDs), indicating the
The peak radiance of all devices is between $10^7$ $\text{A/cm}^2$ while providing sufficient EQEs as well as turn-on voltages. Table 1 shows the energy gaps, maximum EQEs, and turn-on voltages of LEDs with different CQDs as CTLs (Devices Emit at 1350 nm).

For all particle sizes, the HTL CQDs (i.e., MPA-treated CQDs) were treated using CdCl$_2$ in a postsynthesis step to improve surface passivation and stability against oxidation during low-temperature annealing in air (see Experimental section). We noticed that devices that use larger-diameter CQD-based HTLs had smaller turn-on voltages but lower peak EQEs. This is consistent with the inferior electron-blocking properties provided by larger CQDs due to their smaller bandgap. For ETL preparation, both CQD size and surface passivation were investigated. Devices using ETLs with TBAI-only ligand treatment (i.e., without the addition of CdCl$_2$ during postsynthesis) have higher peak EQE values compared with their counterparts treated using both TBAI and CdCl$_2$. This may be due to the surfaces of CQDs without CdCl$_2$ pretreatment, which have more sites available for iodine incorporation, providing stronger band edge downshifting, and are more beneficial to electron injection and hole blocking. When the ETL is treated using TBAI only, the conduction band offset between the ETL and active layer is smaller; a slightly higher turn-on voltage is consequently observed from such devices. ETLs constructed using slightly larger CQDs have higher EQE values, opposite to what is observed in the HTL study. This may again result from better alignment between the valence bands of the ETL and active layer, which is consistent with the considerably lower turn-on voltages observed in the corresponding devices. To verify the details of recombination modes within these all-inorganic CQD devices, we performed optoelectronic modeling. The simulations (using the SCAPS software suite) are presented in Figure 4 and use material parameters, e.g., trap densities and mobilities, explored previously for CQD photovoltaic devices (see Table S1 for more details). Auger and radiative recombination are included via their respective coefficients coupled to quadratic and linear carrier concentrations. Figure 4a shows the band diagram of the device emitting at 1350 nm, above the turn-on voltage, reaching a flat-band condition for efficient carrier injection. The corresponding carrier concentrations are shown in Figure 4b. Some asymmetry in carrier concentration is observed owning to the choice of the electrode.

**Table 1. Summary of the electrical Properties of LEDs with Different CQDs as CTLs (Devices Emit at 1350 nm)**

<table>
<thead>
<tr>
<th>$E_g$ of ETL CQDs (eV)</th>
<th>$E_g$ of HTL CQDs (eV)</th>
<th>max EQE (%)</th>
<th>turn-on voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.90 (CdCl$_2$ treated)</td>
<td>1.90</td>
<td>1.12</td>
<td>1.32</td>
</tr>
<tr>
<td>1.90 (CdCl$_2$ treated)</td>
<td>1.90 (CdCl$_2$ treated)</td>
<td>0.85</td>
<td>1.26</td>
</tr>
<tr>
<td>1.90 (CdCl$_2$ treated)</td>
<td>1.60</td>
<td>1.58</td>
<td>1.20</td>
</tr>
<tr>
<td>1.90 (CdCl$_2$ treated)</td>
<td>1.60 (CdCl$_2$ treated)</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td>1.60 (CdCl$_2$ treated)</td>
<td>1.60</td>
<td>1.08</td>
<td>1.11</td>
</tr>
<tr>
<td>1.60 (CdCl$_2$ treated)</td>
<td>1.60 (CdCl$_2$ treated)</td>
<td>0.71</td>
<td>1.08</td>
</tr>
</tbody>
</table>

*:Turn-on voltage is the applied voltage when the EL is detected by the infrared photodetector.
propose that in our devices, recombination is dominated by Auger processes, with Shockley–Read–Hall (SRH) recombination being secondary and radiative recombination consuming only ~5% of the injected current. This is expected as Auger recombination is fast in CQDs (~100 ps) under high-injection conditions. We note that LEDs that use core–shell CQDs as the active material provide a means of decreasing the Auger rate.40 Changing the mobility of the active layer to reflect the change of the ligand length affects mostly the SRH recombination, with higher mobilities (~10^{−2} cm²/V s) favoring SRH over Auger and PL (Figure S1). When mobility is reduced to ~10^{−5} cm²/V s, carrier transport slows, allowing higher carrier accumulation in the active layer, increasing both radiative and Auger recombination, providing more opportunity for carriers to recombine radiatively or via Auger, rendering the relative importance of SRH appreciably lower (Figure 4b,c).

CONCLUSIONS

In this study, we report the first CQD-based infrared LEDs to employ CQD solids for each carrier-transporting layer as well as in the light-emitting active material. Band engineering via joint control of surface ligand passivation and quantum size tuning of the bandgap enables PbS nanoparticles to multiple key roles in a single LED. Device emission peaks are tailored between 1220 and 1622 nm by changing the emissive dot sizes. The best devices used CQDs emitting at 1350 nm and provided peak EQE reaching 1.58%. Despite significant Auger recombination losses in the shell-free PbS CQDs used here, EQE values and turn-on voltages comparable to the best reported architectures with core–shell CQDs and organic CTLs are achieved. This confirms the best-in-class carrier-transporting and blocking performance of CQD-based CTLs. The simplified material requirements (i.e., single type of material for different functions) and facile solution-based process offer a promising pathway to prepare low-cost and highly efficient CQD-based LEDs.

METHODS

Materials. All chemicals used are commercially available from Sigma-Aldrich (or otherwise specified) and were used without any additional purification steps: lead(II) oxide (99.99%, from Alfa Aesar), cadmium chloride (99.99%), bis(trimethylsilyl)sulfide (synthesis grade) oleic acid (OA, tech. 90%), 1-octadecene (ODE, ≥95%), oleylamine (≥98%), tetrabutylammonium iodide (TBAI, ≥98%), 3-mercaptopropionic acid (MPA, ≥99%), 8-mercaptooctanoic acid (MOA, 95%) toluene anhydrous, methanol anhydrous, and acetone, distilled in glass (Caledon).

PbS CQD Synthesis and Cadmium Chloride Treatment. Small-diameter PbS CQDs (absorption maximum <785 nm) were synthesized using a well-established hot injection method with some modifications:34 0.45 g of PbO, 1.5 mL of OA, 18 mL of ODE, and 0.5 mL of oleylamine were loaded in 250 mL 3-neck round-bottom flask, and then the mixture was pumped at 100 °C for 60 min. After the solution turned optically clear, the temperature was set to the predesigned reaction temperature (60 and 110 °C for dots with absorption peak at 650 and 775 nm, respectively). Then, bis(trimethylsilyl)sulfide ODE solution (0.083 M) was rapidly injected into reaction flask. The heating mantle was turned off (but was not removed) to provide slow cooling. The dots were isolated by addition of 80 mL of acetone and redispersed in anhydrous toluene.

Large PbS dots (absorption maximum >1100 nm) were synthesized according to a recently published method using lead(II) oleate as precursor.34 Sizes of particles were controlled by the growth time. The solution phase CdCl₂ treatment was carried out following a published optimized method.35 Briefly, 1 mL of CdCl₂ (0.06 M) oleyamine solution was injected into the
CQD reaction flask during the slow cooling process. At the temperature below 40 °C, CQDs were precipitated by the addition of ∼50 mL of acetone and separated by ultracentrifugation. The supernatant was decanted, and the nanoparticles were redispersed in 2 mL of toluene and transferred into a glovebox. Inside the glovebox, the CQDs were reprecipitated by the addition of an ethanol/methanol mixture (1:1 volume ratio). After the centrifugation, the supernatant was decanted and particles were dried in vacuum for 1 h and then redispersed in octane at a concentration of 50 mg mL−1.

**LED Fabrication.** The substrate, prepatterned indium tin oxide (ITO)-coated glass, was treated with oxygen plasma for 10 min immediately prior to use. Each functional layer was prepared on the substrate using layer-by-layer spin-coating deposition of CQD:octane solutions with different sizes under air atmosphere immediately prior to use. Each functional layer was prepared on (ITO)-coated glass, was treated with oxygen plasma for 10 min and connected to an NIR spectrophotometer (Ocean Optics, Dunedin, FL). The devices were connected with a Keithley 2410 source meter.

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