Highly-Efficient Thermoelectric-Pumped Light-Emitting-Diodes Based on Colloidal Quantum Dots

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Pumped by sub-bandgap electric work and Peltier heat, thermoelectric-pumped light-emitting diodes (TEP-LEDs) can achieve a power-conversion-efficiency greater than 100%¹⁻³. However, cost-effective and high-efficiency TEP-LEDs are not readily accessible for the epitaxially grown III-V LEDs due to the high chip cost and efficiency droop at sub-bandgap voltages⁴. Photoluminescence with power-conversion-efficiency above unity through phonon-assisted excitation has been realized in high-quality colloidal quantum dots (QDs), owing to their defect-free nature⁵. Here, we show that solution-processed QD-LEDs (QLEDs) can achieve high power-conversion-efficiency and high brightness, circumventing the deficiency faced by conventional LEDs. The optimal red-emitting device exhibits internal power-conversion-efficiency of 93.5% at 100 cd m⁻². At this brightness, the driving voltage (V) of 1.89 V is much lower than the photon voltage ($V_p = h\nu/q = 1.96$ V). Our results highlight that TEP-LEDs can be constructed by integrating large-scale solution processing techniques^{6,7} and chemical-grade materials, towards cost-effective display and lighting applications.

Increasing external power conversion efficiency (EPE) would reduce the energy cost and extend operating lifetime of devices by relieving heat dissipation problems. Phosphor-converted light-emitting-diodes (LEDs) based on GaN have substantially advanced lighting and display technologies. Conventional LEDs are usually driven with voltage much larger than V_p to get a maximized output power, minimize the expensive chip area, and avoid internal quantum efficiency (IQE) droop at low current densities. EPE consists of three terms, IQE, V_p/V , and light extraction efficiency (LEE)

$$39 \quad \text{EPE} = \text{IQE} \times \frac{V_p}{V} \times \text{LEE} = \text{IPE} \times \text{LEE}. \quad (1)$$

40 LEE depends on optical design of the devices, which reached 94% for the state-of-art
 41 technologies^{4,8}. Simultaneously attaining high IQE and small V is the intrinsic key to
 42 pursuing high EPE. For bulk-size semiconductor crystals including quantum wells, IQE
 43 can be approximately given by the ABC model⁹

$$44 \quad \text{IQE} = \frac{Bn^2}{An+Bn^2+Cn^3} \quad (2)$$

45 where A , B , and C are the Shockley-Read-Hall (SRH), radiative, and Auger recombination
 46 constants, and n is the carrier density in active region (the electrons and holes
 47 concentrations are assumed to be equal). Even though can be reduced with costly and
 48 delicate vacuum-based epitaxy techniques, defect-related SRH processes can never be
 49 eliminated. Equation (2) indicates that IQE decreases sharply at low charge carrier densities.
 50 By inducing asymmetric band offset of the quantum well, the radiative part becomes linear
 51 to n , enhancing IQE at low voltages¹⁰, while EQE is limited to ~7% due to LEE issues.
 52 Another route to realize TEP-LEDs is to drive LED under a forward bias much below $k_B T/q$,
 53 where IQE becomes voltage-independent¹¹, which has only been demonstrated for mid-
 54 infrared bandgap material¹² with picowatts-level optical intensity.

55 Colloidal QDs are solution-processable semiconductor nanocrystals presenting carrier
 56 quantum confinement in three dimensions^{13,14}. Photo- and electro-excitation of a QD forms
 57 an exciton (electron-hole pair bonded by electrostatic interaction), instead of free carriers,
 58 which thus results in a linear dependence of radiative term on exciton population (n)

$$59 \quad \text{IQE} = \frac{k_r n}{k_r n + k_{nr} n + k_a n^2} \quad (2)$$

where k_r , k_{nr} , and k_a are rate constants for radiative recombination, non-radiative recombination—equivalent to SRH recombination in the ABC model, and Auger recombination. Under targeted excitation conditions, Auger recombination can be ignored, implying a constant IQE ($\frac{k_r}{k_r+k_{nr}}$) for a specific sample. Because QD sizes are usually smaller than the free diffusion length of impurities at elevated synthetic temperatures^{15,16}, high-quality QDs can be defect-free within their lattices, eliminating internal non-radiative recombination. With engineered ligand passivation, surface traps can be removed almost completely. Altogether, the photoluminescence quantum efficiency can practically reach unity under moderate excitation conditions⁵, surpassing conventional epitaxially-grown semiconductors. Recently, it has been demonstrated that phonon-assisted up-conversion photoluminescence can take place with power-conversion efficiency above unity for colloidal QDs, holding great potential in applications such as optical cooling and white lighting⁵. These features make colloidal QD a competitive candidate for realizing TEP-LEDs.

CdSe/CdS core/shell QDs applied for fabrication of TEP-QLEDs are with excellent photoluminescence properties, i.e., 95% photoluminescence quantum efficiency and mono-exponential photoluminescence decay dynamics (Supplementary Fig. 1). Figure 1a illustrates schematic structure and energy-level diagram of TEP-QLEDs. To minimize voltage lose in charge transport, our TEP-QLEDs use one monolayer of QDs as emissive layer¹⁷, which is closely-packed in between electron transport layers (ETLs) and hole transport layers (HTLs), as shown in the high-angle annular dark-field (HAADF) image and energy dispersive X-ray (EDX) image in Fig. 1b. Figure 1c shows the voltage-dependent EPE, EQE and luminance of the optimal TEP-QLEDs. In particular, the

operating voltages at display-relevant luminance (100 cd m^{-2}) is 1.89 V. Giving a V_p/V value of 104%, EPE (21.5%) surpasses EQE (20.5%). The LEE of the device is determined to be 23% following the literature method^{18,19} (Supplementary Fig. 2). Thus, the peak IPE is close to unity (93.5%) and the peak IQE is 89%. These results indicate behavior of efficient TEP-LEDs. As shown in Fig. 1d, the normalized electroluminescence spectra of a device driven under 1.86, 1.96 and 2.20 V overlap with each other, eliminating the possible emission from lower-energy defect states. With a narrow and symmetric electroluminescence peak at 1.96 eV, nearly all electroluminescence obtained at sub-bandgap bias voltage of 1.86 V and half of it obtained at 1.96 V are Peltier heat-assisted emission.

In comparison with previously reported QLEDs^{6,7}, we remove the polymeric insulator thin layer and limit the thickness of emissive layer to one monolayer of QDs in order to eliminate unnecessary voltage losses. Figure 2a and b show the comparisons of EQE-voltage and EPE-luminance characteristics between different devices. Removal of the insulating PMMA and reducing the thickness of QD layer is found to shift the device operating voltage downward step by step, while maintaining good performance. This strategy enhances the performance of devices using different type of QDs as well. We take CdSe/CdZnSeS alloy/ZnS dots as an example which have been demonstrated to have better performance at high injection level^{20,21}. With the thickness of QD layer decreases from 4 to 2, the device operating voltage decrease by 0.15 V (Fig. 2c). Compared with thicker QD layer, device with 2-monolayer QD holds the highest EPE in $100\text{-}10,000 \text{ cd m}^{-2}$ range.

Sub-bandgap electroluminescence has been repeatedly observed for solution-processed LEDs²²⁻²⁵, which is usually suggested as a result of Auger-mediated hole

injection. The upper limit of IQE of an Auger-mediated processes is 50% (Supplementary Note 1). However, the IQE of our device biased at 1.86 V reaches greater than 90% (Fig. 1c), disapproving the Auger-mediated mechanism. Another argument comes from electroluminescence measurement at low voltage regime (1-1.5 V). We determine the luminance ideality factor—a measure of the slope of the current or luminance versus voltage on a semi-logarithmic plot—by numerical differentiation²⁶

$$n_{\text{lum}} = \left(\frac{k_B T}{q} \frac{d \ln L}{d V} \right)^{-1} \quad (3)$$

where L is luminance and V is driven voltage (current ideality factor is provided in Supplementary Fig. 3). At the voltage regime where current is not limited by space charge effect, the diode ideality factor is smaller than 2/3 for Auger process, while electron-hole recombination is characterized by a diode ideality factor of 1^{27,28}. At 1.2-1.4 V, luminance ideal factor of our QLED is close to 1 (Fig. 3a inset), inferring that electron-hole band-to-band radiative recombination occurs. When voltage approaches 1.4 V and higher, luminance-voltage dependence deviates from ideal exponential-like form (Fig. 3a dashed line), which means the applied voltage drops across charge transport layers due to resistance. Electroluminescence spectra (Fig. 3b red) at this very-low bias range shows that there is a blue-shift of 8 meV when driven voltage increases from 1.2 V to above 2.0 V, which could be attributed to non-uniformity of QD sizes or alleviating of build-in field induced Stark effect. Sub-bandgap electroluminescence can be demonstrated at single-dot level as well (Supplementary Fig. 4 and Note 2), which shows that both up-conversion and down-conversion electroluminescence originates from the same emissive states.

The operating mechanism of TEP-LEDs relies on thermally assisted charge diffusion at the hetero-junction(s) by absorbing lattice phonons. Thus, a temperature-enhanced EQE at a given voltage should be expected. Fig. 3c clearly shows that, at a given bias voltage, EQE of a device increases sharply upon increasing the operating temperature from -40 to 50 °C. Results (Supplementary Fig. 5) further show that such temperature-enhancement occurs for both current and brightness. Figure 3e illustrates that, at a given EQE (11.5%), V_p/V steadily increases from 99% at -40 °C to 112% at 50 °C, indicating enhanced contribution of Peltier heat to electroluminescence upon increasing temperature. For typical GaN LEDs, the rate of SRH-type recombination is known to increase with operating temperature due to the thermal activation of trap centers, which results in a leftward and downward shift of their IQE versus forward voltage upon increasing operating temperature^{4,29}. Because of QD's practically defect-free nature, the IQE curves of TEP-QLEDs shifts in an ideal manner (Fig. 3d), i.e., leftward and upward, which results in significantly increased EPE of the device at a certain brightness level.

The electroluminescence peak shifts 29 meV upon increasing the operating temperature from -40 to 50 °C (Supplementary Fig. 5). However, within the same operating-temperature range, the forward bias at several key points, i.e., with fixed EQE/IQE, current density and brightness, all steadily down-shift for 250-300 mV (Fig. 3e). Figure 3f (Supplementary Fig. 6) illustrates temperature-dependent voltages at a given current density (0.5 mA cm^{-2}) of the devices with the specific hetero-junction(s). Evidently, neither injection of electrons into the ETL nor the interface between ITO and PEDOT:PSS causes noticeable voltage drop at all temperatures. Thus, majority of voltage drops should be contributed by the PEDOT:PSS/Poly-TPD or (Poly-TPD/PVK)/QD interfaces and the

resistance of Poly-TPD/PVK layers. By applying MoO₃ between ITO and Poly-TPD, the electronic characteristics of the Poly-TPD/PVK layers with their interface can be isolated, which shows a medium temperature dependence contributed by the temperature-dependent mobility of Poly-TPD. In comparison, when the MoO₃ layer is replaced by PEDOT:PSS, a strong temperature dependence is evidenced, indicating the thermally activated crossing of the holes through the interface between PEDOT:PSS and Poly-TPD. These results confirm that temperature-dependent performance of the devices reflects both the carrier transport and thermal-assisted carrier injection (see also Supplementary Fig. 7), specifically for holes.

Overall, by excluding internal impurities and lattice defects, excitonic emission of high-quality colloidal QDs can offer near-unity quantum efficiency for up-conversion electroluminescence at mild excitation conditions, which makes TEP-QLEDs with near-unity IPE under ambient temperatures feasible. Given the extremely low fabrication cost of large-area devices, TEP-QLEDs with near-unity IQE demonstrated here are already sufficiently bright for display and applications requiring relatively low power consumption. By applying well-known optical engineering techniques^{8,30,31}, the LEE of TEP-QLEDs can be greatly increased from low twenty percent to low ninety percent, implying high-brightness TEP-QLEDs for lighting and applications with relatively high emission power. Given internal quantum efficiency of TEP-QLEDs is near-unity at relatively low carrier densities, it is fully possible to achieve electroluminescence cooling devices^{1,2} with more stable QDs and charge transport layers that can operate at elevated temperatures.

Methods

Materials:

CdSe/CdSeS/ZnS core/shell/shell quantum dots were purchased from Najing technology Co., Ltd. Poly-TPD (average molecular weight, $\sim 60,000 \text{ g mol}^{-1}$) was purchased from Xi'an polymer light technology Corp. Tetramethylammonium hydroxide (TMAH, 98%), zinc acetate dihydrate (98%), magnesium acetate (98%), and PVK (average molecular weight, $25,000\text{--}50,000 \text{ g mol}^{-1}$) was purchased from Sigma Aldrich. Ethanol (extra dry, 99.5%) and ethyl acetate (HPLC grade) were purchased from Acros. Dimethyl sulfoxide (DMSO, HPLC grade) was purchased from Alfa-Aesar. Myristic acid (98%), stearic acid (>90%), lauric acid (99.5%), cadmium oxide (CdO, 99.998%), selenium power (Se, 200 mesh, 99.999%), 1-octadecene (ODE, 90%), oleic acid (99% or 90%), sulfur powder (S, 99.98%), oleylamine (>98%) and polymethyl methacrylate (PMMA, >98.0%) were purchased from either Aldrich or Alfa-Aesar. Tributylphosphine (TBP) was purchased from Acros. Cyclopentane (>98.0%) were purchased from TCI. Toluene, methanol, chloroform, acetone, and acetonitrile were obtained from Sinopharm Reagents. All chemicals were used directly without any further purification unless otherwise stated.

Synthesis of QDs and ZnMgO nanocrystals:

The CdSe/CdS core/shell QDs (ten monolayers of CdS shell) were synthesized according to reference³² with some modifications. Cadmium acetate (0.7 mmol), decanoic acid (0.7 mmol), oleic acid (2.1 mmol) and ODE (4 mL) were mixed and raised to 150°C with degassing for 20 min. Then purified CdSe (0.1 μmol) were injected, followed by raising temperature to 260°C. A solution of sulfur in ODE (0.1 mol L^{-1}) was introduced

into reaction at a rate of 2 mL h⁻¹ for 90 min. The QDs were precipitated by adding acetone and then purified twice by using toluene and methanol for dissolution and precipitation, respectively. The resulting CdSe/CdS core/shell QDs, i.e., CdSe/CdS-Cd(RCOO)₂ QDs, were dissolved in toluene.

The Zn_{0.9}Mg_{0.1}O nanocrystals were synthesized by a solution-precipitation process according to reference⁷ with some modifications. Typically, a DMSO solution (30 mL) of zinc acetate hydrate (2.7 mmol) and magnesium acetate hydrate (0.3 mmol) mixed dropwise with an ethanol solution (10 mL) of TMAH (5 mmol). The mixture was stirred for 1 hour in a water bath at 50 °C under ambient conditions. The resulting Zn_{0.9}Mg_{0.1}O nanocrystals were precipitated by adding ethyl acetate, further purified by dispersing/precipitating twice using the combination of ethanol/ethyl acetate, and re-dispersed in ethanol.

Device fabrication:

The ITO-coated glass substrates (~40 Ω per square in sheet resistance) were cleaned with acetone, deionized water, and ethanol in an ultrasonic bath. Oxygen plasma treatment was undertaken for 8 min using an ultraviolet ozone cleaner (Harrick Plasma, PDC-32G-2). A PEDOT:PSS solution (Baytron PVP Al 4083) was spin-coated onto the substrates at 3,500 r.p.m. for 45 s and baked at 150 °C for 30 min. The PEDOT:PSS-coated substrates were subjected to an oxygen plasma for 4 min and then transferred to a nitrogen-filled glove box (O₂ < 1 ppm, H₂O < 1 ppm) for subsequent processes. Poly-TPD solutions (in chlorobenzene, 8 mg mL⁻¹) were spin-coated at 2,000 r.p.m. for 45 s and baked at 150 °C for 30 min. PVK solutions (in m-xylene, 8 mg mL⁻¹) were spin-coated at 2,000 r.p.m. for

45 s, followed by baking at 150 °C for 30 min. QD solutions (in octane, ~12 mg mL⁻¹) and Zn_{0.9}Mg_{0.1}O nanocrystals (in ethanol, ~30 mg/mL) were layer-by-layer spin-coated onto the substrates at 2,000 r.p.m. for 45 s. Next, Ag electrodes (100 nm) were deposited by a thermal evaporation system (Trovato 300C) under a high vacuum (~2×10⁻⁷ torr). For devices in Fig. 2c and d, QD solutions with different concentrations of 15, 20, and 24 mg mL⁻¹ were used for devices with 2, 3, and 4 monolayers of QDs, respectively.

The structure of the single-dot EL device is similar to a previous report³³. The ITO-coated glass used was 0.18 mm in thickness. PEDOT:PSS solutions, poly-TPD solutions, QD solutions (in octane, 15 mg mL⁻¹, diluted 20,000-folds before use), PMMA solutions (in acetone, 1.5 mg mL⁻¹) and Zn_{0.9}Mg_{0.1}O nanocrystals (in ethanol, 30 mg mL⁻¹) were layer-by-layer deposited onto the substrate by spin-coating and then the Ag electrodes were deposited by thermal evaporation.

Electron- and hole-only devices studied in Fig. 3f were fabricated by following procedures similar to TEP-QLED. MoO₃ was deposited on ITO-coated glass substrate by thermal evaporation.

Characterizations of TEP-QLEDs:

Devices were characterized under ambient conditions (room temperature 20-24°C) unless specified otherwise. The current density-luminance-voltage (J-L-V) characteristics of the TEP-QLEDs were measured on a system consisting of a Keithley 2400 source meter and a QE-Pro spectrometer coupled with an integration sphere (Ocean Insight FOIS-1). The devices were swept from zero bias to forward bias with a scanning rate of 0.01 V s⁻¹.

For the characterizations at the very-low bias range, the electroluminescence intensity was detected by an avalanche photodetector (PicoQuant τ -SPAD APD) through a multimode fiber (core diameter 62.5 μm). Photon counts were recorded by a time-correlated single-photon counting module (Becker & Hickl DPC-230). The devices were swept from 1.10 V to 1.66 V with a 10-mV step and the residence time for each voltage was set as 1 s. To obtain absolute luminance, photon counts recorded by APD were calibrated by a factor to give the same luminance in the 1.5-1.6 V voltage range as the one acquired with integration sphere method mentioned above. For the measurement to produce Fig. 3b, a spectrometer (Princeton Instrument SP2750) equipped with a liquid nitrogen cooled charge coupled device (PyLoN:800BR) was used. Optical signals were collected by a multimode fiber (62.5 μm in diameter) and directed to the entrance of spectrometer. The devices were swept from 1.20 V to 2.0 V (20 mV step). Residence and exposure time for each voltage varied from 3600 s to 0.01 s depending on the signal intensity.

After characterization at room-temperature, the device is transferred onto a temperature-controlled metal holder. The Schematic view is shown in Supplementary Fig. 8. The metal holder is attached to a thermoelectric cooling (TEC) element whose bottom side temperature is kept at 0 $^{\circ}\text{C}$ by icy-water recycling system. To avoid condensation and freeze of moisture which would scatter out-light, the setup is put into an imperfectly-sealed box with dry N_2 filling the volume. Optical intensity acquired by QE-pro spectrometer were corrected by a factor to give the same luminance at room temperature as the one acquired with integration sphere method mentioned above. The same correction factor was used for measurement under different temperatures. The voltage source driving TEC element was

set at different target values to reach desired holder temperatures. We wait at least 5 min before acquiring J-L-V data for each test point to let the temperature stabilize.

Characterizations of Single-QD LED:

Optical measurements of single QDs were conducted on a home-built fluorescence microscopic system equipped with a 60× oil immersion objective (N.A. = 1.46) at room temperature (22-24 °C). The sample holder was a piezoelectric XYZ stage, allowing precise position control. A direct-voltage source (Keithley 2400) was used for electrical excitation. Photons from a single QD were directed through a single-mode fiber (9-um core diameter) pinhole and detected by avalanche photodetectors (SPCMs, PerkinElmer). Photon correlation measurements were performed using a time-correlated single-photon counting module (PicoHarp 300) with a 50:50 beam splitter. Single-dot electroluminescence spectra were recorded by a spectrometer (Andor Shamrock 303i).

Data Availability

All relevant data that support the findings of this study are available on request from the corresponding author.

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Author contributions

X.P. conceived the idea and supervised the project. Y.S. synthesized the QD samples. X.D. fabricated the high-performance QLED devices. X.L., Z.Y. and X.D. designed the experiment, carried out the room-temperature, temperature-dependent and low-voltage characterizations and completed data analysis. X.P., X.L., X.D. and Z.Y. wrote and revised the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

The authors declare no competing interests. Correspondence and requests for materials should be addressed to xpeng@zju.edu.cn (X.P.).

Figure 1 | TEP-LED structure and performance. **a**, Device structure with enlarged sketch showing carrier distribution at interface. **b**, A cross-sectional HAADF image (left, scale bar 60 nm) and a color-coded elemental mapping image produced by EDX spectroscopy (right, scale bar 20 nm). **c**, EQE/EPE and luminance versus driving voltage for the device with the best efficiency. The crossing point of EPE and EQE curves corresponds to the electroluminescence energy peak (1.96 eV). **d**, Electroluminescence spectrum at driving voltage of 1.86, 1.96 and 2.29 V. Inset: a photograph of a device working under 1.86 V driving voltage.

Figure 2 | Comparison of devices performance with varied structures. a, Comparison of EQE versus driving voltage between the optimal device and our previous work. **b,** Comparison of EPE versus luminance between the optimal device and our previous work. **c,** Voltage-dependent EQE of devices with 2-4 layer of QDs. **d,** Luminance-dependent EPE of devices with 2-4 layer of QDs.

Figure 3 | TEP-QLED characterization under low driving voltage and varied temperatures. **a**, Luminance versus driving voltage with a straight dashed guide line for eye. Inset: luminance ideality factor versus driving voltage. **b**, Electroluminescence spectrum peak versus driving voltage. Inset: spectrum acquired at voltage of 1.2 V. **c**, EQE versus bias under various temperatures. **d**, IQE versus bias normalized by photon energy V_p under various temperatures. The region above dashed line indicates where internal power conversion efficiency $> 100\%$ happens. **e**, Driven voltages, under which the devices reach 11.5% EQE, 100 cd m^{-2} luminance and 0.5 mA cm^{-2} current density, versus temperature. **f**, Driven voltages, under which controlled (electron and hole-only) devices reach a current density of 0.5 mA cm^{-2} , versus temperature.

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