Supporting Information to

Quantum Dots with Highly Efficient, Stable and Multicolor Electrochemiluminescence

Zhiyuan Cao†, Yufei Shu†, Haiyan Qin, Bin Su* and Xiaogang Peng*

Center for Chemistry of High-Performance & Novel Materials, Institute of Analytical Chemistry, Department of Chemistry, Zhejiang University, Hangzhou 310058, China

†These authors contributed equally to this work.

*e-mail: subin@zju.edu.cn; xpeng@zju.edu.cn
Table of Contents

Experimental Procedures

Chemicals and materials .................................................. S-3
Synthesis and purification of CdSe core QDs ....................... S-3
Synthesis and purification of CdSe/CdS core/shell QDs .......... S-3
Synthesis and purification of CdSe/CdS/ZnS core/shell/shell QDs S-4
Surface ligand exchange ................................................... S-4
Preparation of SNM/FTO electrodes ..................................... S-4
Characterization of QDs .................................................... S-4
Determination of the concentrations of QDs ....................... S-5
Determination of the thicknesses of epitaxial CdS and ZnS shells S-5
PL decay dynamics ........................................................... S-5
ECL measurements ............................................................ S-5

Supplementary Figures

S1. TEM images of QDs ..................................................... S-7
S2. PL and ECL of CdSe/CdS QDs with 8 monolayers of CdS shells S-8
  S2.1. PL properties ........................................................ S-8
  S2.2. ECL-potential spectra ............................................. S-9
S3. ECL efficiency of CdSe/CdS/ZnS QDs ............................ S-10
S4. Experimental proof of direct electron injection for ECL generation S-12
  S4.1. Characterization of SNM/FTO electrodes .................... S-12
  S4.2. ECL generation from CdSe/CdS/ZnS QDs at SNM/FTO electrodes S-15
S5. Size-dependent ECL generation from CdSe/CdS/ZnS QDs .... S-16
  S5.1. TEM images ........................................................ S-16
  S5.2. ECL-potential spectra ............................................. S-17
  S5.3. Comparison of the ECL efficiency of CdSe/CdS/ZnS QDs S-18

References
Experimental Procedures

Chemicals and materials. All chemicals of analytical grade or higher were used as received without further purification. Ultrapure water (18.2 MΩ cm) was used to prepare all aqueous solutions. NaH$_2$PO$_4$$\cdot$2H$_2$O (99%), K$_2$S$_2$O$_8$ (99.99%), and sodium hydroxide (96%) were purchased from Aladdin. Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)$_2$Cl$_2$), triethoxysilane (TEOS, >99.0%), hexaammineruthenium(III) chloride (Ru(NH$_3$)$_6$Cl$_3$, 98%), ammonium hydroxide solution (NH$_3$$\cdot$H$_2$O, ~25% wt.%), cadmium oxide (CdO, 99.99%), cadmium acetate dihydrate (Cd(AC)$_2$$\cdot$2H$_2$O, >98%), zinc acetate dihydrate (Zn(AC)$_2$$\cdot$2H$_2$O, >99%), selenium powder (Se, 200 mesh, 99.999%), sulfur powder (S, 200 mesh, 99.999%), 1-octadecene (ODE, 90%), capric acid (HCA, 98%), oleic acid (OA, 90%), mercaptopropionic acid (MPA, >99%) and tetramethylammonium hydroxide (TMAH, 25% w/w in methanol) were purchased from Sigma-Aldrich. Hexadecyl trimethyl ammonium bromide (CTAB, >99%) was purchased from Acros Organics. Stearic acid (HSt, >90%) was supplied by Tokyo Chemical Industry. Ethyl acetate, toluene, hexane, methanol, ethanol and chloroform were purchased from Sinopharm Reagents. Fluorine-doped tin oxide (FTO, <15 ohm/sq) coated glasses were purchased from Zhuhai Kaivo Electronic Components.

Synthesis and purification of CdSe core QDs. The Se-suspension (Se-SUS) was prepared by dispersing Se powder (1 mmol) in ODE (10 mL). In a typical synthesis, CdO (0.2 mmol) and stearic acid (0.5 mmol) were loaded into a 50 mL three-neck flask with 4 mL of ODE. The mixture was heated to 280 °C to obtain a colorless solution. The temperature was reduced to 250 °C, and then 1 mL of the Se-SUS was injected swiftly into the solution. The reaction was allowed to proceed at 250 °C. After 5 min, the Se-SUS was instilled into the solution with the speed of 0.2 mL/min until CdSe QDs with a targeted size were obtained. The reaction process was monitored by taking aliquots for UV-vis measurements. The purification of CdSe core QDs was performed as reported previously, which consists of two steps.\textsuperscript{[S1]} In the first step, 2 mL of original reaction mixture with CdSe core QDs was mixed with 2 mL of ethyl acetate. After vortex and centrifugation at 4000 rpm, the supernatant was removed. Another 2 mL of ethyl acetate was added to repeat the above operation once again. In the second step, 1 mL of toluene was used to dissolve the precipitate, and the resulting mixture was heated at 110 °C until a clear solution was formed. Then, 1 mL of methanol was added and the mixture was centrifuged at 4000 rpm. The supernatant was removed, and the resulting precipitate was re-dissolved in 1 mL of toluene to repeat this cycle once again. Particularly, cadmium compounds are toxic and must be handled carefully.

Synthesis\textsuperscript{[S2]} and purification of CdSe/CdS core/shell QDs. In a typical synthesis, Cd(AC)$_2$$\cdot$2H$_2$O (0.7 mmol), capric acid (0.7 mmol), oleic acid (2.1 mmol), purified CdSe core QDs (0.1 μmol) and ODE (4 mL) were loaded in a 50 mL three-neck flask. Then the mixture was heated to 260 °C and sulfur dissolved in ODE (0.1 M) was instilled into the solution with the speed of 2 mL/h until CdSe/CdS core/shell QDs with a targeted size were obtained. The reaction process was monitored by taking aliquots for UV-vis measurements. The purification scheme of CdSe/CdS core/shell QDs is similar to that of CdSe core QDs with a slight modification. Firstly, 3 mL of original reaction mixture was mixed with 9 mL of ethanol. After vortex and centrifugation at 4000 rpm, the supernatant was removed. Secondly, 2 mL of toluene was used to dissolve the precipitate. Then 2 mL of methanol was added and the mixture was kept at 110 °C for 1 minute. After that, the centrifugation was carried
out at 4000 rpm for 3 minutes. The supernatant was removed and the procedure above was repeated once again.

**Synthesis and purification of CdSe/CdS/ZnS core/shell/shell QDs.** Typically, Zn(Ac)$_2$·2H$_2$O (0.5 mmol), capric acid (0.4 mmol), oleic acid (1.2 mmol), purified CdSe/CdS core/shell QDs (0.05 μmol) and ODE (4 mL) were loaded in a 50 mL three-neck flask. Then the mixture was heated to 290 °C and sulfur dissolved in ODE (0.1 M) was instilled into the solution with the speed of 2 mL/h until CdSe/CdS/ZnS core/shell/shell QDs with a targeted size were obtained. The reaction process was monitored by taking aliquots for UV-vis measurements. The purification process of CdSe/CdS/ZnS core/shell/shell QDs is described as follows. Firstly, 2 mL of reaction mixture was mixed with 6 mL of ethyl acetate, which was heated at 50 °C for 3 minutes. After vortex and centrifugation at 4000 rpm, the supernatant was removed. 0.5 mL of toluene was added to dissolve the precipitate to repeat the procedure above once again.

**Surface ligand exchange.** The original ligands of all QDs in this paper are only carboxylates, which are essential in the ligand exchange procedure (eq. S1). If L-type ligands such as amine, tri-n-octylphosphine (TOP) and tri-n-octylphosphine oxide (TOPO) exist in the reaction mixture, L-type promoting Z-type ligand exchange will take place. As a result, the number of carboxylates on the surface of QDs will decrease, leading to poor solubility of QDs in water.

$$\text{QD-}[\text{Cd(OOCR')}_2] + \text{RSH} \rightarrow \text{QD-}[\text{Cd(SR)}_2] + \text{R'COOH}$$  \hspace{1cm} (S1)

A typical procedure of ligand exchange with MPA is described below. ~0.5 μmol of purified QDs was dissolved in 1 mL of chloroform, and then 0.2 mL of MPA was added to the solution. After vortex for 5 minutes and centrifugation at 4000 rpm, the supernatant was removed and the precipitate was washed twice with hexane. The precipitate was dried under vacuum at room temperature to completely remove organic solvent. Finally, the precipitate was dissolved in 1 mL of water and 200 μL of TMAH.

**Preparation of SNM/FTO electrodes.** The SNM/FTO electrodes were prepared by the Stöber-solution growth approach as reported previously. Briefly, the bare FTO electrodes were firstly immersed in 1 M NaOH aqueous solution for 12 h and then cleaned sequentially under ultrasonication in acetone, ethanol, and water for 20 minutes. Subsequently, they were immersed in a mixture containing 30 mL of ethanol, 70 mL of water, 10 μL of concentrated ammonia aqueous solution, 80 μL of tetraethoxysilane (TEOS) and 0.16 g of cetyltrimethylammonium bromide (CTAB). The growth of SNM on FTO electrodes were carried out in water bath at 60 °C for 8 h, 10 h, 12 h and 24 h, respectively, which yielded SNM with different thickness. Finally, the prepared SNM/FTO electrodes were rinsed with water and further aged at 100 °C for 12 h. Prior to electrochemistry and ECL experiments, the SNM/FTO electrodes were immersed in 1 M HCl ethanol solution to remove CTAB micelles. Thus prepared SNM/FTO electrodes possess silica nanochannels vertically oriented on the electrode surfaces.

**Characterization of QDs.** TEM images were obtained on a transmission electron microscopy (SU-8020, Hitachi, Japan) at 100 kV. The absolute PLQY was measured on an integrating sphere (Ocean Optics FOIS-1) coupled with a spectrophotometer (QE65000). Measurements were performed at room temperature using toluene as the solvent. Transient PL decay curves were measured on a time-correlated single-photon counting (TCSPC) spectrofluorometer (FLS920, Edinburgh Instrument,
UK) at room temperature. The samples were diluted by toluene and excited by a 405 nm picosecond diode laser with a repetition rate of 2 MHz.

**Determination of the concentrations of QDs.** The concentration of CdSe cores was estimated from their extinction coefficients reported by Peng group\(^{[S1]}\), which was assumed to be constant after the epitaxial growth of CdS or ZnS. Therefore, the concentrations of core/shell and core/shell/shell QDs were determined according to the concentration of CdSe plain cores. For instance, 100 mmol of CdSe cores was employed for the epitaxial growth of CdS, then the amount of CdSe/CdS was 100 mmol as well.

**Determination of the thicknesses of epitaxial CdS and ZnS shells.** The number of CdS and ZnS monolayers of CdSe/CdS core/shell and CdSe/CdS/ZnS core/shell/shell QDs were determined by TEM measurements. Briefly, for the case of CdSe/CdS core/shell QDs, the radii of CdSe core QDs \(R_{\text{CdSe}}\) and CdSe/CdS core/shell QDs \(R_{\text{CdSe/CdS}}\) at a given epitaxial growth stage could be calculated by TEM. Given the QDs remaining monodisperse in size in epitaxial growth, the number of CdS monolayers \(x\) could be calculated according to its lattice constant \(d\) by the following equation,

\[
x = \frac{R_{\text{CdSe/CdS}} - R_{\text{CdSe}}}{d} \tag{S2}
\]

The number of ZnS monolayers of CdSe/CdS/ZnS core/shell/shell QDs was determined by the same method in which the lattice constant of ZnS was used. For faceted QDs with well-defined facets (in this work and ref. S2), one can replace radii of the spherical QDs by the height of faceted QDs\(^{[S2]}\).

**PL decay dynamics.** The number of PL decay channels of QDs and the corresponding lifetimes were determined based on transient PL decay curves. Generally, the PL intensity is assumed to decay as the sum of individual single-exponential decay components,

\[
I(t) = \sum_i \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \tag{S3}
\]

where \(\tau_i\) stands for the lifetime of each individual single-exponential decay component and \(\alpha_i\) the amplitude of the component at \(t = 0\). The goodness of fit is tested by the reduced-\(\chi^2\), which is given by

\[
\chi^2 = \frac{1}{m} \sum_{k=1}^{m} \frac{[I(t_k) - I_c(t_k)]}{I(t_k)} \tag{S4}
\]

where \(m\) is the total number of data points for PL decay curves. \(I(t_k)\) and \(I_c(t_k)\) are the measured and calculated PL intensities. The value of \(\chi^2\) should be less than 1.3. Fitting the measured PL decay curves by eq. S3 and testing the fitting results by eq. S4, one could determine the number of PL decay channels. The PL decay lifetime could also be calculated based on the fitting results of eq. S3. In this work, the PL decay curves with maximum intensity of 1000 counts could be well fitted by single or double-exponential decay function. For single-exponential decay, there was only one exponential decay component with the lifetime of \(\tau\) in eq. S3. For double exponential decay, the PL decay curves were fitted by the sum of two exponential components with the lifetimes of \(\tau_1\) and \(\tau_2\).

**ECL measurements.** All ECL measurements were conducted using a classical three-electrode configuration. For ECL intensity measurements, an MPI-E ECL analytical system (Remex Analysis Instrument, Xi’an, China) consisting of a photomultiplier tube (PMT) and an electrochemical
workstation was used, which allowed simultaneous record of ECL intensity and current upon sweeping the potential. The PMT was biased at 300 V unless otherwise specified. To acquire ECL-potential spectra, a custom-built system consisting of CHI440A electrochemical workstation (Chenhua, Shanghai, China) and optic fiber spectrophotometer (QE-Pro, Ocean Optics) was used to supply the potential sweeping control and simultaneously record ECL spectra. The potential sweep rate was 100 mV/s and the integration time of each ECL spectrum was 100 ms.
Supplementary Figures

S1. TEM images of QDs

Figure S1. TEM images of CdSe core QDs (a), CdSe/CdS core/shell QDs with five monolayers of the CdS shells (b), CdSe/CdS core/shell QDs with eight monolayers of the CdS shells (c), and CdSe/CdS/ZnS core/shell/shell QDs with five monolayers of the CdS inner shells and three monolayers of the ZnS outer shells (d). The average diameters of four types of QDs are 3.1 nm, 5.6 nm, 8.1 nm, and 7.1 nm, respectively. Number of the CdS (or ZnS) monolayers of core/shell (or core/shell/shell) QDs were calculated by dividing the increased height after epitaxial growth of the CdS (or ZnS) shells by the lattice constant of CdS (or ZnS).
S2. PL and ECL of CdSe/CdS QDs with 8 monolayers of CdS shells

S2.1. PL properties

CdSe/CdS core/shell QDs with 8 monolayers of CdS shells were also synthesized to compare with CdSe/CdS/ZnS core/shell/shell QDs with 5 monolayers of CdS transition shells and 3 monolayers of ZnS outer shells. This type of QDs have a monodisperse size distribution (8.1 nm in diameter, Figure S1c). However, their PLQY decreased significantly from near-unity (>90%) in toluene to ~38% in water (Figure S2a), although the mono-exponential decay dynamics in transient PL spectra almost remained before and after transfer (Figure S2b). These results suggest that even 8 monolayers of CdS shells cannot efficiently isolate excitons of QDs and surface traps in water.

Figure S2. Steady state (a) and transient PL spectra (b) of CdSe/CdS core/shell QDs with 8 monolayers of CdS shells before and after transfer from toluene to water.
S2.2. ECL-potential spectra

ECL-potential spectra of CdSe/8CdS QDs are shown in Figure S3. The ECL intensity of CdSe/8CdS QDs is ~40 times weaker than that of CdSe/5CdS/3ZnS QDs (Figure 2d). The results confirm that the excellent ECL properties of CdSe/5CdS/3ZnS QDs does not originate from the size effect and that the outer ZnS shells offer efficient protection for ECL generation. The PL and ECL properties of CdSe/CdS/ZnS core/shell/shell QDs with other thicknesses of CdS and ZnS shells were also investigated (data not shown). Because CdSe and ZnS have a large lattice mismatch (12%), 3 ~ 8 monolayers of the CdS intermediate shells are found to function as the suitable buffer layer. The larger the core is, the thicker the CdS shells are needed. With the CdS buffer layer, the epitaxial growth of the ZnS shells is controlled to be 2 ~ 3 monolayers. Growth of the ZnS shells thicker than 3 monolayers would create strain-induced defects. Less than one monolayer would be insufficient for isolation of the excitons from the aqueous environment.

Figure S3. ECL-potential spectra of 0.3 μM CdSe/CdS core/shell QDs with 8 monolayers of CdS shells in 0.1 M PBS containing 10 mM K2S2O8 (pH = 7.4).
S3. ECL efficiency of CdSe/CdS/ZnS QDs

The relative efficiency of ECL generation from CdSe/CdS/ZnS core/shell/shell QDs was estimated with respect to Ru(bpy)$_3^{2+}$ according to the following equation:[55]

$$
\Phi_{\text{ECL}} = \frac{\int_{0}^{t} \frac{ECL}{dt}}{\int_{0}^{t} \frac{I}{dt}}_{\text{QD}} \div \frac{\int_{0}^{t} \frac{ECL}{dt}}{\int_{0}^{t} \frac{I}{dt}}_{\text{Ru}}
$$

(S5)

where $ECL$ represents the ECL intensity and $I$ the voltammetric current. QD stands for CdSe/CdS/ZnS core/shell/shell QDs, and Ru denotes Ru(bpy)$_3^{2+}$. Under the same experimental condition, ECL intensity and current curves are shown in Figure 3a-b. The integrals of ECL intensity and current over time were substituted into eq. S5 to calculate $\Phi_{\text{ECL}}$. As calculated, the efficiency of ECL generation from CdSe/CdS/ZnS core/shell/shell QDs is $6.9 \times 10^5$ times higher than cathodic Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ system.

To further illustrate the outstanding PL and ECL properties of CdSe/CdS/ZnS core/shell/shell QDs, the optical property and ECL efficiency of the as prepared QDs were compared with other QDs and ECL-active nanoparticles reported previously. As summarized in Table S1, most cadmium chalcogenide QDs reported in literatures possess poor optical properties characterized by their low PLQY and multi-channel PL decay dynamics. As a result, the ECL generation from those QDs cannot be efficient and are barely compared with Ru(bpy)$_3^{2+}$ to calculate the ECL efficiency. Recently, ECL generations from various types of metal clusters were reported and the ECL efficiencies of them were found to be 1 ~ 2 orders of magnitude higher than that of Ru(bpy)$_3^{2+}$. However, there is still a significant room for improvement on their optical properties.[613-15] By contrast, CdSe/CdS/ZnS core/shell/shell QDs exhibited nearly ideal optical properties with near-unity PLQY and mono-exponential PL decay dynamics. And the ECL efficiency of the QDs was 6 orders of magnitude higher than that of Ru(bpy)$_3^{2+}$. The ideal PL properties and highly efficient ECL of CdSe/CdS/ZnS core/shell/shell QDs suggest that the efficient gap between ECL and PL of QDs can be removed by judiciously designing the synthetic strategies.
Table S1. Comparison of the optical properties and ECL efficiencies (versus the standard Ru(bpy)$_3^{2+}$) of different ECL emitters.

| ECL emitters                        | PLQY | PL decay dynamic and lifetime (τ) $^a$ | ECL efficiency (versus Ru(bpy)$_3^{2+}$) | Ref. |
|-------------------------------------|------|----------------------------------------|------------------------------------------|------|
| MPA and HMP capped CdSe QDs         | 29%  | -                                      | -                                        | [S6] |
| CdTe/CdS core/shell QDs             | 74.6%| Bi-exponential decay (τ = 136 ns)       | -                                        | [S7] |
| Co$^{2+}$ doped CdTe QDs            | 6.7% | Multi-exponential decay (τ = 98.6 ns)   | -                                        | [S8] |
| CdSeTe/CdS/ZnS core/shell QDs       | 63%  | Multi-exponential decay (τ = 67 ns)     | -                                        | [S9] |
| CuInS$_2$/ZnS Nanocrystals          | 18.9%| Tri-exponential decay (τ = 401 ns)      | -                                        | [S10]|
| Halide perovskite CsPbBr$_3$ Nanocrystals | -    | Tri-exponential decay (τ = 95.9 ns)    | -                                        | [S11]|
| Silole-containing Polymer nanodots   | 38%  | -                                      | 0.39 times                               | [S12]|
| Au$_{13}$Ag$_{13}$ NCs              | 40%  | -                                      | 10 - 400 times                           | [S13]|
| L-methionine capped Au NCs          | -    | -                                      | 13.2 times                               | [S14]|
| ARG/ATT-capped Au NCs               | 67.02%| Multi-exponential decay (τ = 48.18 ns)  | -                                        | [S15]|
| CdSe/CdS/ZnS core/shell QDs         | >90% | Mono-exponential decay $6.9 \times 10^5$ times | This work                                |      |

$^a$ the average lifetimes (τ) were given for ECL emitters with multi-exponential PL decay dynamics

$^-$ data not shown in the literatures

HMP = Sodium hexametaphosphate, ARG = L-arginine, ATT = 6-aza-2-thiothymine
S4. Experimental proof of direct electron injection for ECL generation

S4.1. Characterization of SNM/FTO electrodes

The thickness and pore structure of SNM were characterized by transmission electron microscopy (SU-8020, Hitachi, Japan) at 100 kV. To prepare the TEM specimens, SNM was mechanically scraped from FTO electrodes, dispersed in ethanol and deposited on carbon-coated copper grids. The thicknesses of SNM after growing for 8 h, 10 h, 12 h, and 24 h are 51 nm, 63 nm, 93 nm and 161 nm, respectively (Figure S4). The SNM exhibits a uniform pore size of 2 ~ 3 nm (Figure S5).

![Figure S4. Cross-sectional TEM images of SNM after growing for 8 h (a), 10 h (b), 12 h (c), and 24 h (d). The thickness of SNM is annotated in each figure.](image)

Figure S5. Top-view TEM images of SNM after growing for 8 h (a), 10 h (b), 12 h (c), and 24 h (d).
Apart from TEM characterization, electrochemical experiments were also carried out to prove the integrity of SNM on the FTO electrodes. Figure S6 compares cyclic voltammograms of 0.5 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> at the bare FTO and SNM/FTO electrodes before and after removal of CTAB micelles. Due to the hydrophobic repulsion between hydrophobic CTAB micelles and charged Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, no faradaic current was observed with the SNM/FTO electrode before removal of CTAB micelles (black, dashed line), indicating SNM on the FTO electrode from a compact layer without cracking or leakage. After removal of micelles, reversible voltammetric peak was observed (red line) and the peak current of SNM/FTO electrode was almost the same with that of bare FTO electrode (black, solid line), suggesting the good permeability of SNM.

Figure S6. (a) Schematic illustration of mass transport of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in silica nanochannels before and after removal of CTAB micelles. (b–e) Cyclic voltammograms of the bare FTO (black, solid line) and SNM/FTO electrode before (black, dashed line) and after (red line) removal of CTAB micelles in 0.1 M KCl containing 0.5 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>. From b to e, the growth times of the SNM were 8 h, 10 h, 12 h, and 24 h, respectively.
S4.2. ECL generation from CdSe/CdS/ZnS QDs at SNM/FTO electrodes

Voltammetric behavior and ECL generation from CdSe/CdS/ZnS core/shell/shell QDs at SNM/FTO electrodes with different thickness of SNM were investigated and shown in Figure S7. In agreement with the results in Figure 4, the reduction current of K$_2$S$_2$O$_8$ was always displayed whereas no ECL signal was observed. The results confirm that the direct electron injection from electrode to QDs is necessary for ECL generation.

**Figure S7.** Cyclic voltammograms (a) and ECL intensity profiles (b) of CdSe/CdS/ZnS core/shell/shell QDs at SNM/FTO electrodes with different thickness of SNM. The solution was 0.1 M PBS (pH 7.4) containing 10 mM K$_2$S$_2$O$_8$ and 0.3 µM QDs. The scan rate was 100 mV/s.
S5. Size-dependent ECL generation from CdSe/CdS/ZnS QDs

S5.1. TEM images

Figure S8. TEM images of green- (a), yellow- (b), and red-emitting (c) CdSe/CdS/ZnS core/shell/shell QDs with different core sizes. The average diameters are 5.9 nm, 6.6 nm and 9.0 nm, respectively.
S5.2. ECL-potential spectra

ECL-potential spectra of above three types of CdSe/CdS/ZnS core/shell/shell QDs are shown in Figure S9. The onset potential of ECL generation for green, yellow, and red-emitting QDs was $-0.99$ V, $-0.98$ V and $-0.80$ V, respectively. The maximum ECL intensity was observed at $-1.38$ V, $-1.30$ V, and $-1.20$ V, respectively. Upon sweeping the potential up to the negative limit, ECL spectra exhibited similar lineshape without obvious shift or broadening for all three types of QDs.

Figure S9. ECL-potential spectra of 0.3 μM green- (a), yellow- (b), and red-emitting (c) CdSe/CdS/ZnS QDs in 0.1 M PBS containing 10 mM K$_2$S$_2$O$_8$ (pH = 7.4).
S5.3. Comparison of the ECL efficiency of CdSe/CdS/ZnS QDs

Figure S10a-c shows the current and ECL intensity curves of three types of QDs. The ECL intensity was maximum at −1.20 V, −1.30 V, and −1.38 V for red-, yellow-, and green-emitting QDs (Figure S9). Using the standard method (Supporting Information, Section S3) and setting ECL efficiency of red-emitting ones as reference (100%), ECL efficiency of green- and yellow-emitting CdSe/CdS/ZnS core/shell/shell QDs was 35% and 68%, respectively (Figure S10d). In comparison with the orange-emitting CdSe/CdS/ZnS core/shell/shell QDs in Figure 2d and 3b, the ECL efficiency of the red-emitting ones in this series is about 1.6 times higher. As epitaxial growth of CdS inner shells would red-shift the emission wavelength of the resulting QDs, the CdS shells for green- and yellow-emitting QDs might not be sufficiently thick to relieve the strain. As a result, their PLQY was relatively low. Nevertheless, the ECL efficiency of the green-, yellow-, and red-emitting CdSe/CdS/ZnS core/shell/shell QDs was approximately proportional to their PLQY, which was drastically different from the CdSe/CdS core/shell QDs. These results indicate the ZnS outer shells can isolate the surface traps from emissive core QDs equally efficiently for both PL and ECL.

Figure S10. Comparison of ECL generation efficiencies of red-, yellow-, and green-emitting CdSe/CdS/ZnS core/shell/shell QDs. (a-c) Current and ECL intensity curves of 0.3 μmol/L red- (a), yellow- (b), and green-emitting (c) QDs in 0.1 mol/L PBS (pH = 7.4) containing 10 mM K2S2O8. The PMT was biased at 500 V and a neutral filter (ND = 4) was positioned in the front of PMT to avoid light saturation. (d) Relative ECL efficiencies of yellow- and green-emitting QDs with respect to red-emitting QDs.
References

[S1] J. Li, J. Chen, Y. Shen, X. Peng, Extinction coefficient per CdE (E = Se or S) unit for zinc-blend CdE nanocrystals, *Nano Res.*, 2018, 11, 3991-4004.

[S2] J. Zhou, M. Zhu, R. Meng, H. Qin, X. Peng, Ideal CdSe/CdS core/shell nanocrystals enabled by entropic ligands and their core size-, shell thickness-, and ligand-dependent photoluminescence properties, *J. Am. Chem. Soc.*, 2017, 139, 16556-16567.

[S3] N. C. Anderson, M. P. Hendricks, J. J. Choi, J. S. Owen, Ligand exchange and the stoichiometry of metal chalcogenide nanocrystals: spectroscopic observation of facile metal-carboxylate displacement and binding, *J. Am. Chem. Soc.*, 2013, 135, 18536-18548.

[S4] X. Lin, Q. Yang, L. Ding, B. Su, Ultrathin silica membranes with highly ordered and perpendicular nanochannels for precise and fast molecular separation, *ACS Nano*, 2015, 9, 11266-11277.

[S5] R. Ishimatsu, H. Shintaku, Y. Kage, M. Kamioka, S. Shimizu, K. Nakano, H. Furuta, T. Imato, Efficient electrogenerated chemiluminescence of pyrrolopyrrole Aza-BODIPYs in the near-infrared region with tripropylamine: involving formation of S2 and T2 states, *J. Am. Chem. Soc.*, 2019, 141, 11791-11795.

[S6] S. Liu, X. Zhang, Y. Yu, G. Zou, Bandgap engineered and high monochromatic electrochemiluminescence from dual-stabilizers-capped CdSe nanocrystals with practical application potential, *Biosens. Bioelectron.*, 2014, 55, 203-208.

[S7] Y. He, S. Hou, L. Yang, F. Zhang, G. Zou, Adjustable electrochemiluminescence from highly passivated CdTe/CdS nanocrystals by simple surface decoration with counterions, *Chem. - Eur. J.*, 2018, 24, 9592-9597.

[S8] X. Gao, K. Fu, L. Fu, H. Wang, B. Zhang, G. Zou, Red-shifted electrochemiluminescence of CdTe nanocrystals via Co2+-doping and its spectral sensing application in near-infrared region, *Biosens. Bioelectron.*, 2020, 150, 111880.

[S9] L. Li, Y. Chen, Q. Lu, J. Ji, Y. Shen, M. Xu, R. Fei, G. Yang, K. Zhang, J. Zhang, J. Zhu, Electrochemiluminescence energy transfer-promoted ultrasensitive immunoassay using near-infrared-emitting CdSeTe/CdS/ZnS quantum dots and gold nanorods, *Sci. Rep.*, 2013, 3, 1529-1539.

[S10] L. Fu, B. Zhang, X. Long, K. Fu, X. Gao, G. Zou, Promising electrochemiluminescence from CuInS2/ZnS nanocrystals/hydrazine via internal Cu(I)/Cu(II) couple cycling, *Anal. Chem.*, 2019, 91, 10221-10226.

[S11] Y. Huang, X. Long, D. Shen, G. Zou, B. Zhang, H. Wang, Hydrogen peroxide involved anodic charge transfer and electrochemiluminescence of all-inorganic halide perovskite CsPbBr3 nanocrystals in an aqueous medium, *Inorg. Chem.*, 2017, 56, 10135-10138.

[S12] Y. Feng, C. Dai, J. Lei, H. Ju, Y. Cheng, Silole-containing polymer nanodot: an aqueous low-potential electrochemiluminescence emitter for biosensing, *Anal. Chem.*, 2016, 88, 845-850.

[S13] S. Chen, H. Ma, J. W. Padelford, W. Qinchen, W. Yu, S. Wang, M. Zhu, G. Wang, Near infrared electrochemiluminescence of rod-shape 25-atom AuAg nanoclusters that is hundreds-fold stronger than that of Ru(bpy)3 standard, *J. Am. Chem. Soc.*, 2019, 141, 9603-9609.

[S14] H. Peng, Z. Huang, Y. Sheng, X. Zhang, H. Deng, W. Chen, J. Liu, Pre-oxidation of gold nanoclusters results in a 66 % anodic electrochemiluminescence yield and drives mechanistic insights, *Angew. Chem., Int. Ed. Engl.*, 2019, 58, 11691-11694.

[S15] L. Yang, B. Zhang, L. Fu, K. Fu, G. Zou, Efficient and monochromatic electrochemiluminescence of aqueous-soluble Au nanoclusters via host–guest Recognition, *Angew. Chem.*, 2019, 131, 6975-6979.
Author Contributions

Bin Su and Xiaogang Peng conceived and designed the project. Zhiyuan Cao and Yafei Shu performed the bulk of the experimental work with help from Haiyan Qin. All authors analyzed the data, discussed the results, and took part in producing the manuscript. Zhiyuan Cao and Yafei Shu contributed equally to the work.