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Quantum Dots with Highly Efficient, Stable, and Multicolor Electrochemiluminescence

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Title: Quantum nuts: two shells are better than one to achieve highly efficient electrochemiluminescence

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Dek: Rational design of core/shell/shell quantum dots to meet the specific requirements of electrochemiluminescence

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Developing bright and multicolor electrochemiluminescence (ECL) nano-emitters is widely pursued to achieve high sensitivity and multiplexing in bioassays and microscopy operating in physiological conditions. It is a particularly challenging task considering the specific requirements of charge injections and surface traps occurring in water during the ECL process. In this issue of *ACS Central Science*, Su, Peng, and coworkers rationalize the criteria of QDs architecture for ECL generation.¹ In an exciting report, they present elegantly designed water-soluble QDs with an impressive ECL efficiency.

ECL is the light emitted by the excited state of a luminophore upon an electrochemical reaction (i.e. without photoexcitation).² The initial electron-transfer reaction at the electrode surface triggers a cascade of reactions involving energetic intermediates that leads *in fine* to the formation of the excited state. It relaxes to the ground state and emits a photon. It is a powerful analytical technique with an extremely low background because it combines the orthogonal modalities of electrochemical stimulation and optical detection. **Thus, ECL crystallizes the beauty and complexity from both electrochemistry and photophysics. ECL is successfully commercialized for a large number of immunoassays, such as for cardiac and infectious diseases, thyroid, tumor markers, etc. Almost 2 billion ECL-based assays for clinical diagnostics run worldwide each year.**¹ Since it is based on an optical readout, ECL has also evolved into a powerful imaging method.³ Most of the applications still rely on the model $[\text{Ru}(\text{bpy})_3]^{2+}$ or cyclometalated Ir(III) luminophores with a sacrificial coreactant species.⁴ Many works have been carried out to improve the ECL efficiency in water.⁵ Indeed, brighter ECL emitters and various emission colors are highly desirable due to the increasing demand for accuracy and multiplexing in microscopy and diagnostics.

Colloidal quantum dots (QDs), which are semiconductor nanocrystals (NCs) exhibit unique quantum size effects. Their electronic, optical, and electrochemical properties depend strongly on their size, shape and surface chemistry due to their very high surface area-to-volume ratio that may lead to various heterogeneous redox reactions with the surrounding environment. In a seminal work in the early 2000's, Ding et al. reported the ECL from silicon QDs.⁶ After that, a large variety of semiconductor materials such as Ge, CdTe, CdSe, and PbSe have been explored to generate ECL. But, in most cases, surface reactivity can lead to the formation of electronic traps for electrons and holes, which strongly inhibit the ECL process by translating into poor efficiency. Indeed, depending on the semiconductor and its intrinsic surface chemistry, the QDs' chemical reactivity can result in either disastrous characteristics or original useful performances.⁷ As nicely discussed in the article,¹ ECL of QDs corresponds to a very different situation in comparison to photoluminescence (PL) and electroluminescence. In the ECL process (Figure

1a), the QDs diffuse freely in solution during the sequential injection events of electrons (heterogeneously, from the electrode) and holes (homogeneously, from the electrogenerated coreactant radical). Therefore, trapping of such injected charges by the QDs' surfaces might be very effective and lasts much longer than in PL or electroluminescence. Therefore, specific criteria for the design of water-soluble ECL-active QDs should be considered to avoid such surface traps for charge carriers.

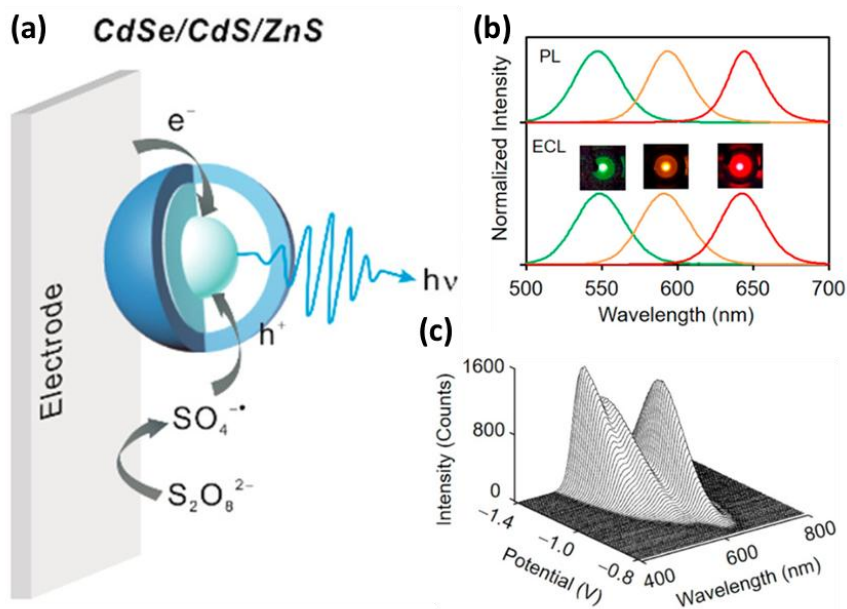


Figure 1. (a) Schematic representation of the ECL process with the charge injection from the electrode and the sacrificial persulfate coreactant. (b) Spectrally-resolved multicolor ECL generation from CdSe/CdS/ZnS QDs with different core sizes. (c) 3D graphs of ECL-potential spectra of the ternary mixture of green-, yellow-, and red-emitting QDs. Reprinted with permission from ref 1. Copyright 2020 American Chemical Society.

The article published now in *ACS Central Science* investigated the effects of the architecture and surface of QDs on the PL quantum yield (Φ_{PL}) in water, which impacts directly the ECL efficiency.¹ The authors present a systematic PL and ECL study by preparing CdSe core QDs, CdSe/CdS core/shell QDs and finally CdSe/CdS/ZnS core/shell/shell QDs. They selected CdSe as the core material for the QDs because it has been reported to behave as a trap-free QDs with near-unity Φ_{PL} in toluene and monoexponential PL decay dynamics. But, when converted to the water-soluble form through ligand exchange, CdSe core QDs became barely emissive in water. By contrast, the CdSe/CdS core/shell QDs with five monolayers of CdS shells show much larger Φ_{PL} in water but still with surface trap issues. Therefore, the authors used the epitaxial ZnS shells with a very wide bandgap to isolate these traps from the photogenerated excitons in the QDs. The authors developed a new epitaxy scheme to eliminate possible defects and the resulting CdSe/CdS/ZnS QDs with three monolayers of the ZnS shells exhibit near-unity Φ_{PL} and monoexponential PL decay dynamics in both toluene and water. The inner CdS shell is necessary because it functions as a buffer layer to relieve the lattice mismatch between CdSe and ZnS.

This stepwise comparative structure-ECL activity study demonstrates that the CdSe/CdS/ZnS core/shell/shell QDs are extremely bright ECL nano-emitters in PBS. Nowadays, the metal coordination complex, $[Ru(bpy)_3]^{2+}$, remains the gold standard in ECL, even if some cyclometalated Ir(III) luminophores challenge its performances.⁸ The significance of this work is further emphasized by the

fact that the optimized QDs with two tightly controlled shells show exceptional ECL performances. Indeed, **their ECL efficiency is 6 orders of magnitude larger than that of the reference $[\text{Ru}(\text{bpy})_3]^{2+}$** . This remarkably high value is due to several key factors: high Φ_{PL} , short luminescence lifetime, center-localized charges, and large size of the QDs (*i.e.* from 5.9 nm up to 9.0 nm). In addition, by controlling the size of the CdSe core of the QDs, the ECL emission was tuned precisely from green to yellow and red when increasing the QDs size (Figure 1b). **Finally, concomitant multicolor ECL emission from multiple QDs was readily achieved in aqueous media** (Figure 1c). Such an ability to tune the ECL emission color(s) has recently generated a wide interest due to potential multiplexing applications.^{9,10}

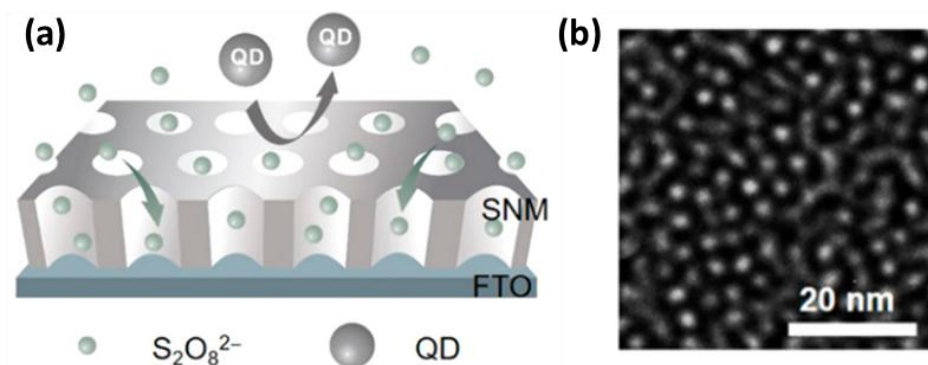


Figure 2. (a) Blocking effect of the electron injection from the FTO electrode to the QDs by the ultrathin SNM. (b) Top-view TEM image of the SNM. Reprinted with permission from ref 1. Copyright 2020 American Chemical Society.

This study also demonstrated clearly a key mechanistic element that has been proposed to enable the ECL process. Since ECL starts with an initial electron-transfer reaction, it was essential to prove the direct reduction of the QDs at the electrode surface (*i.e.* direct electron injection from the electrode to the conduction band of the QDs). For this, an original approach using fluoride-doped tin oxide (FTO) electrode surface modified with an ultrathin insulating silica nanochannel membrane (SNM) was elaborated (Figure 2). The diameter of the channels was in the range of 2–3 nm whereas the diameter of the QDs was ~ 8 nm. Therefore, the QDs cannot reach the electrode surface and be reduced directly at the FTO surface. Only the persulfate coreactant, which is much smaller can diffuse through the channels of the SNM and reacts at the electrode surface. With the SNM, ECL intensity of the QDs was extremely low in comparison to the bare FTO electrode. This smart experiment demonstrates unambiguously the essential role of the direct electron injection from the electrode into the QDs to generate ECL.

In a *nutshell*, the understanding of the ECL process with the crucial role of the charge injection allowed the authors to design water-soluble CdSe/CdS/ZnS core/shell/shell QDs. Such a structure with a CdSe core and a chemically-engineered double shell generates ECL light very efficiently (*i.e. two shells are better than one*). The reported approach provides a general methodology opening enticing perspectives for spectrally distinct detection of several analytes with improved sensitivity in multiplexed bioassays and ECL microscopy.

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TOC Graphic

