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## Quantum dot-based photoelectric conversion for biosensing applications



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## ABSTRACT

As semiconductor nanocrystals, quantum dots (QDs) have attracted great interest in recent years in chemical and biological detection due to their attractive optoelectronic characteristics. Biosensing of QD-based photoelectric conversion mainly includes electrochemiluminescence (ECL) and photoelectrochemical (PEC) sensing. Different authors have published overviews of bioanalytical applications of QDs. However, there has been no specific review on the use of QD-based systems for ECL and PEC bioanalysis. In this overview, we review novel methods and sensing principles based on using QDs for ECL and PEC sensing. We then provide an outlook on the future of the QD-based ECL and PEC biosensors.

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## 1. Introduction

Quantum dots (QDs), as one kind of semiconductor nanocrystal, comprise a new type of luminescent nanomaterial, which has been very popular in recent years. The range of this nanoparticle (NP) size is usually 2–20 nm. QDs have unique, superior physical and chemical properties, which are widely used in optics, electronics, catalysis and biology [1–6]. Based on these properties, applications of QDs in electrochemiluminescence (ECL) and photoelectrochemical (PEC) biosensing attracted great interest in recent years [7–11].

ECL is a technique using optical emissions from the excited states of luminescent substances generated from electrode surfaces through an applied potential [12–14]. Since the first ECL phenomena from silicon-QDs was reported in 2002 [15], QD-based ECL-sensing strategies have been developed. Many QD-based ECL emitters (e.g., II-VI, III-V and IV-VI nanocrystalline) have been employed to fabricate many ECL biosensors to detect biomolecules.

ECL converts electrochemical energy into luminous energy around the electrode surface. Conversely, the process of PEC detection is just the reverse of ECL: the light is used as the excitation source and the photocurrent as the detection signal. Under illumination, charge separation and transfer of the photoelectroactive species on the surface of the electrode will occur and hence generate electric signal in the electrolyte solution consisting of the specific electron donor or acceptor. Thus, the photoelectroactive materials are one of the most crucial factors in the performance of PEC sensors.

QDs with unique photoelectric features have also attracted considerable attention in PEC sensing. Attributed to the separated energy form between the excitation source and the resulting signal, ECL and PEC sensors possess excellent sensitivity with low background signals. Moreover, by integrating the advantages of electrochemistry and optical methods, ECL and PEC have been extensively used in immunoassay, DNA analysis, biomolecule detection, clinical diagnosis, cell analysis, and environmental monitoring [7–9,16–19].

We discuss the application of QDs as emitters or photoactive materials in construction of ECL and PEC biosensors. We focus attention on the principles and the demonstration of intriguing applications of QD-based ECL and PEC. Finally, we give a brief outlook on the future development of ECL and PEC sensors based on QDs.

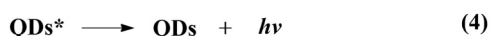
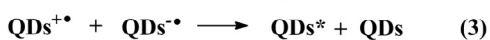
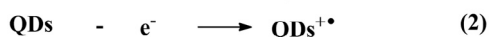
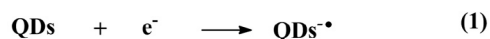
## 2. Fundamentals of QD-based ECL and PEC

### 2.1. Mechanism of ECL emission of QDs

In the QD-ECL process, species produced at the electrode surface involve high-energy electron-transfer reactions and form excited states that emit light. Two kinds of mechanism are mainly involved in ECL emission (i.e., annihilation mechanism and coreactant mechanism).

#### 2.1.1. Annihilation ECL

In the annihilation courses are shown in Scheme 1, both oxidized and reduced QD (radical ions) are produced around the electrode surface during potential sweeping or pulsing [13]. These



Scheme 1. The mechanism of annihilation ECL.

species [radical cation ( $\text{QD}^{\bullet+}$ ) and anion ( $\text{QD}^{\bullet-}$ )] are temporary and can quickly form the excited state ( $\text{QD}^*$ ), which then emits light.

In order to generate efficient annihilation ECL, some conditions are necessary for the radical QDs, including chemical stability and maintenance of their charged states for a long time in order to transfer charge when facing conflict with oppositely-charged QDs. Also, the applied electrode potential must be suitable for the electron-transfer reaction for producing ECL emission via the excited state. Thus, although the annihilation ECL requires no additional reagent, current applications of QDs in ECL are particularly based on coreactant ECL.

#### 2.1.2. Coreactant ECL

In the coreactant courses, the coreactant species are oxidized or reduced at the surface of the electrode and then radicals are formed and react with the oxidized or reduced QDs, generating the excited states and emitting light during one-directional potential scanning. Unlike annihilation ECL, which demands oxidized and reduced ECL species, coreactant ECL usually occurs by a potential sweep in a single direction around the electrode and containing the QDs as a luminophore and a deliberately added coreactant in solution.

Coreactant ECL not only breaks the limit of the potential window, improving the stability of radical anions or cations, but also can generate higher ECL signal than the annihilation process. Thus, the coreactant courses are widely used in constructing biosensors.

A good ECL coreactant requires the following properties – chemical stability, good solubility, low background and quick response. ECL reactions can be classified into oxidative-reduction and reductive-oxidation, according to the generated intermediate species being reducing or oxidizing during an electrochemical process. In general, commonly-used ECL coreactants include oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) [15], tri-n-propylamine (TPrA) [20], dibutylaminoethanol (DBAE) [21], and sulfite ( $\text{SO}_3^{2-}$ ) [22], which belong to the “oxidation–reduction” reaction mechanism, and hydrogen-peroxide ( $\text{H}_2\text{O}_2$ ) [23],  $\text{O}_2$  [24], and peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ) [25], which are “reductive–oxidative” coreactants.

Table 1 shows the corresponding mechanisms of the “oxidation–reduction” reaction. During the oxidation process, an agent is produced with strong reduction properties, reacts with luminophore QDs and generates light from an excited state.

Table 2 shows “reductive–oxidative” coreactants, which can also produce ECL signal through a negative potential. The reduction of coreactants forms an oxidation agent, which initiates the interaction with the negatively-charged QDs, and an ECL signal appears.

### 2.2. PEC mechanism of QDs

As a popular PEC active material, QDs are used extensively in biosensors due to their excellent PEC properties. Fig. 1 shows the photocurrent-generation mechanism of the QDs, which is as follows. When the QDs absorb photons with higher energies than that of their band gaps, electrons are excited from the valence band (VB) to the conduction band (CB). Then electron–hole pairs are formed. The generated electron–hole pairs recombine or charges transfer when the charge separation occurs. An anodic photocurrent occurs when the electrons are ejected to the electrode, following with the electron from an electron donor D in solution (Fig. 1A). If the electrons transfers to electron acceptor A, complementary electrons can neutralize the holes, and then yield a cathodic photocurrent (Fig. 1B). Thus, generally speaking, unlike the optical detection signals of ECL originating from the spontaneous emission of the electron–hole recombination, during the process of PEC, the trapped excited electron in the surface states would generate the electron–hole pairs with sufficiently long life, and electron–hole pairs allow the transfer of CB electrons close to the electrode or electron acceptor in solution and then anodic or cathodic photocurrents are generated [11,17,19].

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