

## Review

## Quantum dots-enhanced chemiluminescence: Mechanism and application

Hui Chen, Ling Lin<sup>1</sup>, Haifang Li, Jin-Ming Lin\*

Department of Chemistry, Beijing Key Laboratory of Microanalytical Methods and Instrumentation, The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Tsinghua University, Beijing 100084, China

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## ABSTRACT

Quantum dots (QDs) with excellent optical and electronic properties have been the potential alternatives of chemiluminescence (CL) emitters. CL generates from the excited QDs which is formed by electron- and hole-injection after direct oxidation. We successfully realize the QDs-enhanced CL from different ultraweak CL systems, such as hydrogen peroxide mixing with NaHCO<sub>3</sub>, NaHSO<sub>3</sub>, NaNO<sub>2</sub>, NaClO, NaIO<sub>4</sub>, and so on. Mechanisms and applications of these QDs-enhanced CL were discussed, and we found that QDs can also participate in CL reactions as catalysts or energy acceptor, or a direct QDs oxidation and energy transfer taking place simultaneously to enhance the CL intensity. In this paper, the recent advance in QDs-based chemiluminescence resonance energy transfer (CRET) is comprehensively summarized and their applications in the detection of small biological molecules, the analysis of DNA and protein, cell imaging and immunoassays are reviewed. The challenges and future prospects of this field are also discussed.

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## 1. Introduction

Quantum dots (QDs) have attracted much attention due to their unique and excellent optical and electronic properties, and have been widely applied as multicolored photoluminescent probes [1] and biological luminescent labels [2,3] since two works were introduced in 1998 [4,5]. Compared to conventional dyes, QDs shows the advantages of large Stokes shifts, broad excitation spectra, good photo stability, high quantum yield, and size-dependent

\* Corresponding author. Tel.: +86 10 62792343; fax: +86 10 62792343.

E-mail address: [jmlin@mail.tsinghua.edu.cn](mailto:jmlin@mail.tsinghua.edu.cn) (J.-M. Lin).<sup>1</sup> Present address: Faculty of Engineering, The University of Tokyo, Tokyo Daigaku, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan.

emission-wavelength tunability. Excitons are easily generated when QDs are exposed to light of higher energy than that of the bandgap of the composing semiconductor. These excitons return to their lower energy level generating emission of a narrow and symmetric energy band [6–8]. The nanocrystal size, morphology and surface-ligands are very important factors to influence the optical properties of QDs in their applications [9]. Apart from the well-known photoluminescent properties, QDs show catalytic properties for redox reactions, size-dependent catalytic action, controllable charge- and electron-transfer events, and biocompatibility. Such properties could be employed to increase the selectivity or the kinetics of a given chemical reaction or even to implement new reaction schemes, as well as to enhance the response signals of instruments improving detection sensitivity [10,11].

Chemiluminescence (CL) in aqueous phase system is generated mainly by redox reactions with proper reaction conditions and CL reagents. Unstable products are created from intermediate radicals in the CL reaction process. They decompose to form electronically-excited molecules that deactivate with CL emission in batch or flow reactors [12]. The CL can take place by direct oxidation of target compound to produce emitting species or by indirect enhancing or inhibitory effects of certain luminescence compounds [13,14]. The CL produced from reactions of inorganic molecules is relatively weak due to low quantum yield. Therefore, it is necessary to enhance the CL intensity for analytical applications. Compounds or reaction strategies, such as nanomaterials, transition elements, catalytic process and energy transfer process, have been proposed for an enhanced CL [15–20]. In that sense, QDs, due to their reactivity, brightness and continuous band gap tunability, have attracted great attentions as the CL emitters or as a novel alternative to catalyze redox CL reactions, enhancing the CL emission under proper conditions [21].

Nowadays, high quality semiconductor QDs, composed of atoms from groups II–VI, III–V, or IV–VI, can be easily synthesized and have been widely used in CL systems, such as CdTe QDs [22,23], ZnSe QDs [24], CdSe QDs and InP QDs [25], etc. Core-shell structured CdSe@CdS QDs produce a highly improved CL performance in the stability and quantum yield because non-radiative dissipation derived from the surface traps can be inhibited by surface passivation [26]. New properties can be found by doping conventional QDs with other ions [27–29]. For example, the doping of a trace amount of Mn<sup>2+</sup> in ZnS QDs produces a catalysis-assisted CL emission [30]. Recently, the luminescence property of the emerging carbon nanomaterials, carbon QDs, has been explored [31–34]. Carbon QDs are discrete nanoparticles (NPs) with sizes below 10 nm in near spherical shape; they generate fluorescence in the visible regions upon light excitation [35]. Compared to fluorescent semiconductor nanocrystals, photoluminescent carbon QDs have advantages of chemical stability, biocompatibility, and low toxicity [36], and have been applied in chemiluminescence [37,38].

Based on the light emission of the excited state of QDs, fluorescence resonance energy transfer (FRET) and chemiluminescence resonance energy transfer (CRET) coupled with QDs have been rapidly developed for applications in analytical chemistry [39–42]. The excited state of QDs can be produced by photoexcitation, electron injection, electron impact, or chemical reaction. Compared with FRET, QDs based-CRET occurs by the oxidation of a luminescent substrate without an exciting light source. Hence it can reduce the autofluorescence background and the fluorescence bleaching, and will be a promising technique in biochemical applications. Finding new QDs with a high CL efficiency to improve the sensitivity and stability is the constant driving force of this area.

The advances of QDs-based CL not only open a new field for the development of novel CL emitting species, but also expand the conventional optical utilizations of QDs. In the present article, we highlight the mechanism of QDs in CL reactions, discuss the typical

QDs-enhanced ultraweak CL systems, and summarize the applications of QDs-based CRET in detection of small biological molecules, DNA and protein analysis, cell imaging and immunoassays.

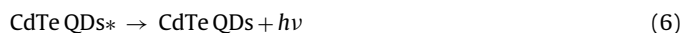
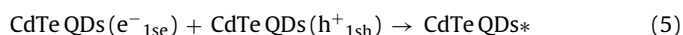
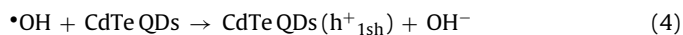
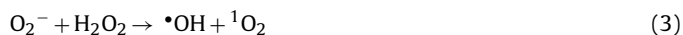
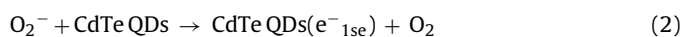
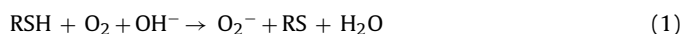
## 2. Mechanisms of QDs in chemiluminescence

There are three possible mechanisms for QDs in an enhanced CL: (i) QDs are emitter species after direct oxidation. (ii) QDs are catalysts of a reaction involving others luminophores. (iii) QDs are emitter species after CRET. It can be definitely presumed as a direct oxidation when QDs is the only luminescent compound in a CL system. When more than one luminophore exist in a CL system, the mechanism can be either CRET when the final emitter is the QDs, or a catalytic process by QDs when the final emitter is the luminophore. Sometimes, it is also possible that direct oxidation and CRET take place simultaneously.

### 2.1. Direct chemiluminescence

In QDs-based CL reactions, an electron can be injected into the conduction band and a hole can be injected into the valence band of QDs. Excitons are produced by the recombination of the injected electrons and holes. Direct QDs CL happens when chemically generated excitons relax with radiant energy emitting.

Wang et al. found CdTe QDs capped with thioglycolic acid (TGA) synthesized via a microwave-assisted method could be directly oxidized by oxidants, especially hydrogen peroxide and potassium permanganate [43]. The CdTe QDs CL emission has size-dependent effect and was enhanced with increasing sizes of QDs. Moreover, surfactants cetyltrimethylammonium bromide (CTAB) and  $\beta$ -cyclodextrin can also enhance this CL intensity, which is mainly contributed to the formation of aggregate nanostructure and the micellar micronanoenvironment, respectively. The mechanism proposed for the CdTe QDs–H<sub>2</sub>O<sub>2</sub> system is presented in Reactions 1–6.



By employing the same CL reaction, Han et al. found Ag<sup>+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> could inhibit the emission from TGA capped-CdTe QDs–H<sub>2</sub>O<sub>2</sub> system [44]. Based on the reactions, they developed a CL method for the selective determination of Ag<sup>+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> with detection limit of 3.0 × 10<sup>−8</sup>, 4.0 × 10<sup>−8</sup> and 6.7 × 10<sup>−8</sup> mol L<sup>−1</sup>, respectively.

Li et al. reported that the water-soluble CdTe QDs capped with three different thioalkyl acids (i.e. mercaptoacetic acid (MAA), cysteine and glutathione) could be directly oxidized by K<sub>3</sub>Fe(CN)<sub>6</sub> producing strong and stable CL emission in basic media [45]. CdTe QDs were the CL emitters. They found that the capping ligands and the size of CdTe QDs have a profound effect on the CL intensity of the QDs system. The CL emission from glutathione-coated CdTe system was stronger than that from MAA- and cysteine-coated CdTe QDs system. The possible mechanism of the modified CdTe QDs CL system can be simply explained as the following Reactions. In the basic media, ligand (glutathione) was oxidized by K<sub>3</sub>Fe(CN)<sub>6</sub> producing the excited intermediate M\*. Then CdTe QDs was excited

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