



Ligand displacement-induced fluorescence switch of quantum dots for ultrasensitive detection of cadmium ions



Xianyun Hu^{a,b,1}, Kao Zhu^{a,1}, Qingsheng Guo^a, Yuqian Liu^a, Mingfu Ye^a, Qingjiang Sun^{a,*}

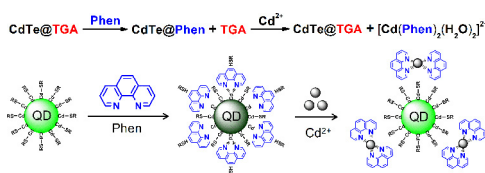
^a State Key Laboratory of Bioelectronics, School of Biological Science & Medical Engineering, Southeast University, Nanjing 210096, China

^b Qiannan Medical College for Nationalities, Duyun 558000, China

HIGHLIGHTS

- A simple CdTe QD–Phen sensor is constructed for detecting Cd²⁺.
- The sensor is operated with a ligand-displacement induced PL switch strategy.
- The detection limit of 0.01 nM for Cd²⁺ is achieved.
- This sensor features to discriminate Cd²⁺ versus Zn²⁺, and succeeds in real water samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 October 2013

Received in revised form

31 December 2013

Accepted 5 January 2014

Available online 11 January 2014

Keywords:

Quantum dot

1,10-Phenanthroline

Photoluminescence

Sensor

Ligand displacement

Cadmium ions

ABSTRACT

This paper reports the construction of a simple CdTe quantum dots (QDs)-based sensor with 1,10-phenanthroline (Phen) as ligand, and the demonstration of a novel ligand displacement-induced fluorescence switch strategy for sensitive and selective detection of Cd²⁺ in aqueous phase. The complexation of Phen at the surface quenches the green photoluminescence (PL) of QDs dominated by a photoinduced hole transfer (PHT) mechanism. In the presence of Cd²⁺, the Phen ligands are readily detached from the surface of CdTe QDs, forming [Cd(Phen)₂(H₂O)₂]²⁺ in solution, and as a consequence the PL of CdTe QDs switches on. The detection limit for Cd²⁺ is defined as ~0.01 nM, which is far below the maximum Cd²⁺ residue limit of drinking water allowed by the U.S. Environmental Protection Agency (EPA). Two consecutive linear ranges allow a wide determination of Cd²⁺ from 0.02 nM to 0.6 μM. Importantly, this CdTe QDs-based sensor features to distinctly discriminate between Cd²⁺ and Zn²⁺, and succeeds in real water samples. This extremely simple strategy reported here represents an attempt for the development of fluorescent sensors for ultrasensitive chemo/biodetection.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

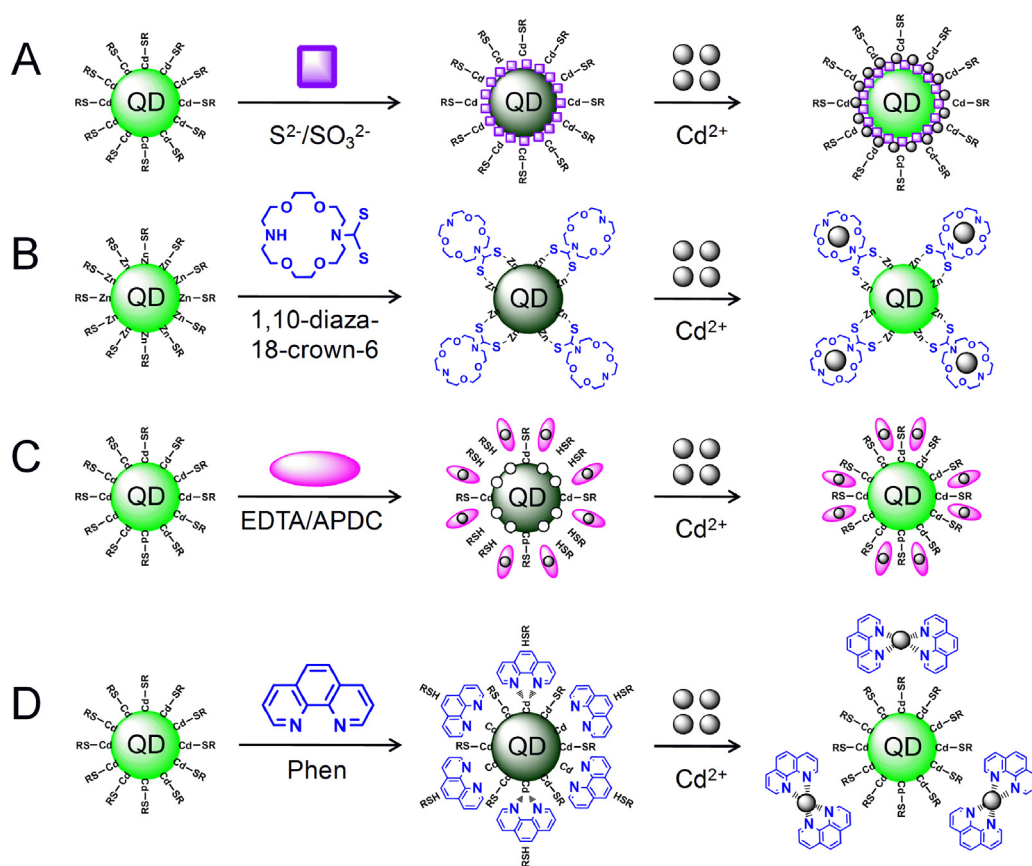
Agricultural activities such as the excessive use of fertilizers and pesticides, irrigation with waste water, industrial applications (nickel–cadmium batteries, dyes and pigments, coating of steel, various alloys) and urban life increase the content of cadmium in soils and waters. As a consequence of food chain system, cadmium exposure can cause anemia, abdominal pain, neurological

and adverse developmental effects, kidney damage, hypertension, changes in vitamin D metabolism, and even increased risk of cancer [1–3]. The International Agency for Research on Cancer has classified cadmium as category 1 carcinogens [4]. In the United States, the acute and chronic exposure criteria for dissolved cadmium (Cd²⁺) in drinking water are 3.7 and 1.0 μg L⁻¹ (32.9 and 8.9 nM), respectively. Therefore, in view of its toxic effects on environment as well as human health, the monitoring of chemical safety through Cd²⁺ analysis of the most widely used resources, especially drinking water, is of paramount importance. Of various analytical methods [5–10], the most common one still remain the use of fluorescence, which indicates the presence of an analyte by fluorescent changes that can be observed by naked eye or by simple measurements.

* Corresponding author. Tel.: +86 25 83790920; fax: +86 25 83792349.

E-mail address: sunqj@seu.edu.cn (Q. Sun).

¹ The authors contribute equally.



Scheme 1. QDs based surface complexation ((A)–(C)) and proposed ligand displacement (D)-induced PL switch strategies for Cd^{2+} detection.

While a variety of synthetic organic-fluorophore receptors for Cd^{2+} assay have been designed [11], they often suffer from low solubility in water, low sensitivity, and poor photostability, which restricts their practical applications.

Quantum dots (QDs) are a recently developed class of inorganic fluorophores with unique spectral properties including high PL quantum yields and exceptional resistance to photobleaching [12–16]. Recent advances in surface modification of QDs with appropriate receptors, able to interact selectively with an analyte, allow for greater analytical sensitivity in a wide variety of sensing schemes [17,18]. In the past few years, researchers have made efforts toward the development of QDs-based fluorescent sensors for detecting heavy metal ions including Cd^{2+} [19–22]. Of the fluorescent sensors, a PL switch-on mode, with the reduced chance of false positives, is more preferable than a PL switch-off mode [23]. So far, only a few of the QDs-based PL switch-on sensors for detecting Cd^{2+} have been reported, which can be classified into three strategies by the analyte-receptor complexation reactions, namely, “surface passivation” [24–28], “host–guest reaction” [29], and “chemical etching” [30,31], as shown in Scheme 1A–C. In these sensors, different Cd^{2+} receptors such as anions (sulfur or sulfite), *N*-containing crown ethers (1,10-diaza-18-crown-6), and chelating reagents (ethylene diamine tetraacetic acid, EDTA, or ammonium pyrrolidine dithiocarbamate, APDC) are appended onto the QDs surface, quenching the PL of QDs. Upon exposure to Cd^{2+} , the analyte-receptor complexation reactions occur at the surface of QDs, which block the non-radiative recombination pathway, inducing the restored PL of QDs. These sensors have achieved the lowest detection limit of 6–10 nM for Cd^{2+} [30]. However, the detection limit needs to be further lowered for quantitative assay of Cd^{2+} in drinking water, according to the standards of EPA. In addition, the QDs-based Cd^{2+} sensors all suffer from the interference of Zn^{2+} . The

formation of a ZnS passivation layer, or complexation of Zn^{2+} with *N*-containing crown ether, EDTA or APDC at the QDs surface can also restore the PL of QDs to some extent [24–31]. The ability of a sensor to distinctly discriminate between Cd^{2+} and Zn^{2+} is important because these ions are often found together in nature [32,33]. Therefore, there is an urgent demand to develop novel fluorescent sensors based on QDs for sensitive and selective detection of Cd^{2+} .

Herein, we report an extremely simple PL switch strategy for ultrasensitive detection of Cd^{2+} , with CdTe QDs as the fluorescent reporter and Phen as the Cd^{2+} receptor as well as the QDs ligand. Phen is chosen to construct the fluorescent sensor primarily because it is a classic chelating bidentate ligand whose nitrogen atoms are beautifully placed to act cooperatively in binding with metals [34,35]. As illustrated in Scheme 1D, the CdTe QD–Phen sensor is proposed to operate with a novel ligand (receptor) displacement-induced PL switch strategy. In the absence of Cd^{2+} , the quenched PL of CdTe QDs is mainly ascribed to a PHT process from QDs to the Phen ligand [22,29,36]. Only in the presence of Cd^{2+} , the chelation of Phen with Cd^{2+} detaches the Phen ligand from the QDs surface, interrupting the PHT process and switching on the PL of QDs. On basis of this strategy, this sensor has demonstrated to feature excellent selectivity for Cd^{2+} over Zn^{2+} .

2. Experimental

2.1. Materials and reagents

All the starting materials of synthesis of Thiolglycolic acid (TGA)-capped CdTe QDs and mercaptopropionic acid (MPA)-capped CdSe/ZnS core/shell QDs were used without further purification. Chloroform (AR) and anhydrous ethanol (AR) were purchased from NCR and used for purification of QDs. Various metal salts (>99.99%)

Download English Version:

<https://daneshyari.com/en/article/1164151>

Download Persian Version:

<https://daneshyari.com/article/1164151>

[Daneshyari.com](https://daneshyari.com)