Analytica Chimica Acta xxx (2018) 1–8

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Halobenzoquinone-mediated assembly of amino acid modified Mn-doped ZnS quantum dots for halobenzoquinones detection in drinking water

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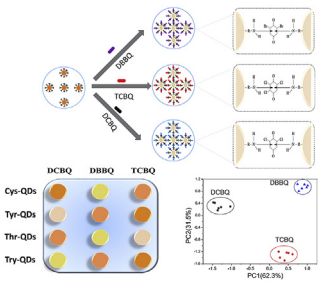
HIGHLIGHTS

- The detection method was based on HBQ-mediated assembly of QDs.
- Discrimination of HBQs was based on characteristic responses of QDs to different HBQs.
- The proposed method was convenient and also had high selectivity and sensitivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 November 2017
Received in revised form
12 April 2018
Accepted 14 April 2018
Available online xxx

Keywords:
halobenzoquinones
Quantum dots
Sensor array

ABSTRACT

Halobenzoquinones (HBQs) were reported as disinfection byproducts (DBPs) which had potential risk of bladder cancer. In this paper, a highly selective analytical method for HBQs was developed by HBQs-mediated assembly of amino acid modified Mn-doped ZnS/Quantum Dots (Mn: ZnS QDs). In the presence HBQs, a charge-transfer complex (CTC) was formed between aromatic rings of HBQs and the primary amino groups on the surface of the QDs. The formation of CTC led to the aggregation of QDs, as a result fluorescence decreasing occurred. The decrease was correlated with the concentration of HBQs. Then a fluorescence sensor array for discrimination of three kinds of HBQs including 2,6-Dichloro-1,4-benzoquinone (DCBQ), 2,6-Dibromo-1,4-benzoquinone (DBBQ) and 2,3,6-trichloro-1,4-benzoquinone (TCBQ) was developed. Four kinds of amino acids including cysteine, threonine, tyrosine and tryptophan were embellished on the Mn: ZnS QDs. The different extents of aggregation led to different fluorescence decreasing effect, thus distinct fluorescence patterns were created. It showed that three kinds of HBQs could be discriminated successfully by fluorescence sensor array at a range of concentrations through principal component analysis (PCA). The unknown samples were predicted by with a stepwise linear discriminant analysis (SLDA) using Mahalanobis distance as a selection criterion with accuracy of 100%. Remarkably, the practicability of the proposed sensor array was further validated by identification of three kinds of HBQs at different concentrations in real drinking water samples. Compared to LC/MS/

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https://doi.org/10.1016/j.aca.2018.04.017

MS, this fluorescent sensor array-based method was proved to be more convenient since the nanoparticles can be prepared flexibly according to the property of the target.

1. Introduction

Disinfection byproducts (DBPs) arise from unintentional reactions of disinfectant (e.g. chlorine) with natural organic matter in water [1–4]. Exposure to DBPs has been found adverse to human health, primarily as an increased risk of bladder cancer [5–7]. Therefore, it is imperative to develop suitable analytical method for determination of DBPs in drinking water. Up to now, LC/MS/MS combined with solid phase extraction method and electrochemical methods have been so far developed for the determination of DBPs, offering high sensitivity [8–10]. However, it relies on complex instruments, well equipped laboratories and costly analytical procedures. Therefore, it is necessary to develop selective, as well as cost-effective system for detection and discrimination of DBPs. Integration of nanomaterials into optical or electrochemical sensors has been reported as an alternative analytical method due to its convenient synthesis, adjustable surface decoration and less dependence on complex instruments. Metal nanoparticles, quantum dots (QDs), etc. are recently employed sensors due to their excellent photoluminescence property [11,12].

The conventional lock-and-key such as molecular recognition technology has been found not particularly useful for analyzing complex samples of relatively similar compounds. To solve this problem, sensor arrays were generated. On the basis of cross-responsive sensing elements rather than specific receptor-analyte binding reactions, sensor arrays generate composite responses unique to different analytes. It is similar to the olfactory systems of animal and therefore called “chemical nose/tongue” [13]. The diverse response patterns generated by different analytes can be differentiated by linear discriminant analysis (LDA) or principal component analysis (PCA), where versatile systems can be “trained” to identify different analytes. Functional nanomaterials including gold nanoparticles, quantum dots, etc. have been adapted as colorimetric [14], fluorescent and colorimetric [15] and fluorescent nanoprobes for discrimination of metal ions, organic matter and protein in various samples [16–18].

QDs have attracted extensive research interest due to their excellent photophysical properties, such as size-dependent tunable photoluminescence, continuous absorption profiles, robust signal intensity and high photochemical stability. QDs-based analytical methods achieved the sensitive detection by electron transfer (ET) or fluorescence resonance energy transfer (FRET), which utilized QDs as donors of energy or electrons. The fabrication of these conjugates to keep the proximity of QDs donors to the acceptors is essential for the high efficiency of ET or FRET. Most of these methods involved modification process, such as labeled with antibody for FRET process [19]. Apart from ET or FRET, analyte-guide self-assembly of QDs has been reported. Self-aggregation through non-covalent interactions, such as hydrogen bonding interaction, π-π interaction, electrostatic forces, van der Waals forces and so on, have been proved to be an efficient mechanism for nanoparticle assembly, which is often accompanied by fluorescence decreasing. Mediation of the assembly of QDs by a small molecular analyte, yield a facile means of fabricating QD sensor arrays in response to concentration changes of the analyte. Recently, Wu et al. demonstrated that a simple glucose probe could be designed on the basis of the glucose mediated assembly of phenylboronic acid modified CdTe/ZnTe/ZnS QDs [20]. Wang and co-workers developed substitution-triggered disaggregation of fluorescent QDs for fluoride ions detection by hydrogen bonding [21]. Xu et al. presented a label-free fluorescent assay for monitoring the activity and inhibition of protein kinases based on the aggregation behavior of CdTe QDs [22]. Liu et al. has developed a sensor array for discrimination of different nucleobases through target nucleobase-triggered self-assembly of QDs [23].

The strong charge-transfer interaction between the electron deficient aromatic ring of quinone and the electron-rich amino group of amino acid has been reported, and charge transfer complex (CTC) was formed with a new ultraviolet absorbance peak appeared. However, this method has been employed for determination of amino acids with unsatisfactory sensitivity [24]. Therefore, we reason that if the amino acids were anchored on the surface of QDs, the target HBQs would also form complex with amino acids which induced aggregation of QDs and subsequently fluorescence decreasing. Notably, regardless of the different surface properties, the as-prepared QDs showed similar fluorescence characteristics. The different analyte response behaviors, as well as similar fluorescence characteristics of these QDs, encourage us to design and synthesize a series of amino acid functionalized QDs for detecting various HBQs.

Therefore, in this work, we designed a fluorescence sensor array of Mn-doped ZnS/Quantum Dots (Mn: ZnS QDs) with different capping agents including cysteine, threonine, tyrosine and tryptophan. 2,6-Dichloro-1,4-benzoquinone (DCBQ), 2,6-dibromo-1,4-benzoquinone (DBBQ), and 2,3,6-trichloro-1,4-benzoquinone (TCBQ) were chosen as discriminant targets. The ability to form complex led to the assembly of QDs, thus gave a readily detectable fluorescence decreasing effect. The fluorescence response patterns of QDs upon addition of three HBQs were obtained, and data matrix were discriminated by principal component analysis (PCA), linear discriminant analysis (LDA), etc. Finally, the applicability of the sensor array for discrimination of HBQs at various concentrations in real water samples was investigated.

2. Materials and methods

2.1. Chemicals

2,6-Dichloro-1,4-benzoquinone (DCBQ, >98%) and 2,3,6-trichloro-1,4-benzoquinone (TCBQ, >98%) were purchased from Tokyo Chemical Industry. 2,6-Dibromo-1,4-benzoquinone (DBBQ, >98%) was purchased from Toronto Research Chemicals (>98%). Anthraquinone (99%), 1,4-benzoquinone (99%), 1,4-naphthoquinone (98.5%), were purchased from Dr. Ehrenstorfer (Germany). 9,10-phenanthraquinone (99%) and 1,2-napthoquinone (95%) were purchased from CNW Technologies (Germany). 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, 98%), N-Hydroxysulfosuccinimide sodium salt (NHS, 98%), L-cysteine (Cys), L-threonine (Thr, 99%), L-tyrosine (Tyr, 99%), and L-tryptophan (Try, 99%) were bought from Shanghai Makclin Biochemical Co., Ltd (China). $Zn(Ac)_2 \cdot 2H_2O$, $Mn(Ac)_2 \cdot 2H_2O$, Na_2S, sodium dihydrogen phosphate, potassium dihydrogen phosphate ammonium, 3-mercaptopropionic acid (MPA, 98%), formic acid, methanol, ethanol, acetone and NaOH were purchased from Tianjin Damao

Please cite this article in press as: Z. Jiao, et al., Halobenzoquinone-mediated assembly of amino acid modified Mn-doped ZnS quantum dots for halobenzoquinones detection in drinking water, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.04.017