



A “Turn-On” thiol functionalized fluorescent carbon quantum dot based chemosensory system for arsenite detection



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HIGHLIGHTS

- Environmental friendly carbon quantum dots grafted with thiol moieties.
- The functionalized CQDs demonstrated for optical detection of arsenite in water.
- High analytical performance in terms of sensitivity, selectivity and detection limit (0.086 ppb).

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ABSTRACT

Carbon quantum dots (CQDs) have emerged out as promising fluorescent probes for hazardous heavy metals detection in recent past. In this study, water soluble CQDs were synthesized by facile microwave pyrolysis of citric acid & cysteamine, and functionalized with dithierithritol to impart thiol functionalities at surface for selective detection of toxic arsenite in water. Microscopic analysis reveals that the synthesized CQDs are of uniform size (diameter ~5 nm) and confirmed to have surface –SH groups by FT-IR. The functionalized probe is then demonstrated for arsenite detection in water by “Turn-On” read out mechanism, which reduces the possibility of false positive signals associated with “turn off” probes reported earlier. The blue luminescent functionalized CQDs exhibit increase in fluorescence intensity on arsenite addition in 5–100 ppb wide detection range. The probe can be used for sensitive detection of arsenite in environmental water to a theoretical detection limit (3s) of 0.086 ppb ($R^2 = 0.9547$) with good reproducibility at 2.6% relative standard deviation. The presented reliable, sensitive, rapid fCQDs probe demonstrated to exhibit high selectivity towards arsenite and exemplified for real water samples as well. The analytical performance of the presented probe is comparable to existing organic & semiconductor based optical probes.

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1. Introduction

Inorganic arsenic, which exists as arsenite (As(III)) and arsenate (As(V)), in water has intrigues lots of global concern due to its toxic and carcinogenic effects [1,2]. Amongst these states, arsenite is likely thought to be relatively more mobile and toxic over other inorganic and organic states. Owing to its complex formation ability with various enzymes/co-enzymes involved in human metabolism

through As–O or As–S linkages [3–8] it leads to acute and chronic physiological health effects such as cancer, liver and kidney damage, pigmentation, acute renal failure, neuropathy, abdominal pain, cell dysfunction, etc. [9,10]. Therefore the acceptance level of arsenite in drinking water is laid down below 10 ppb by World Health Organization (WHO) [11].

Due to well recognized importance of arsenite detection, plethora of conventional techniques including chromatography, mass spectrometry, atomic absorption/emission spectroscopy, etc., are reported for its determination, however, they have been limited to laboratory sphere in view of expensive & sophisticated instrumentation requirement, longer analysis time, tedious sample preparation, personnel training and poor stability limits [12].

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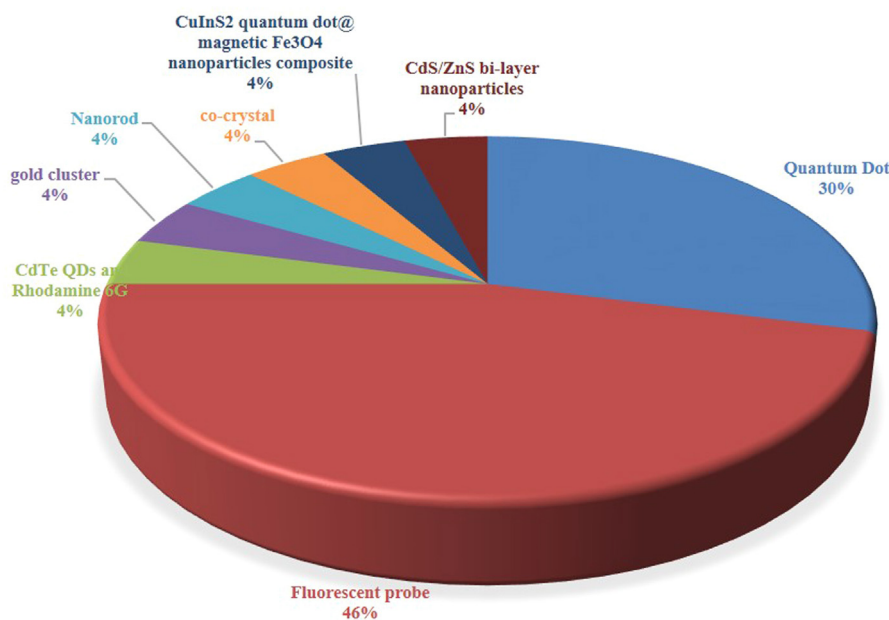


Fig. 1. Pie chart of reported materials for optical detection of arsenite (Year 2010–2016).

Besides, voltammetric approach has been widely investigated for ppb level arsenic detection, wherein a range of bulk and modified working electrodes including, noble metals, metal oxides, carbon nanostructures, etc., have been employed [13–18]. On the other hand, fluorometric methods have also gained tremendous attentions for heavy metal/metalloid ions including arsenic detection owing to their simplicity, easy operation, tunability and fast response. Yet the sensitivity and selectivity characteristics of optical probe decides their fate for field translation. Over the years, semiconductor QDs (CdTe, CdS), conventional organic dyes, gold nanoparticles, gold nanoclusters, fluorescent polymers, organic fluorophores, etc., have been reported for optical detection of arsenite, as shown in Fig. 1. [19]. Wang et al. reported glutathione capped CdTe QDs for ultra trace arsenic detection to $2 \times 10^{-8} \text{ mol L}^{-1}$ level [20]. In another work, Villiers and co-workers demonstrated glutathione capped CdSe/ZnS core-shell QDs for mobile arsenic(III) measurement in surface waters [21]. Recently, Ensafi et al. reported a simple and sensitive fluorimetric aptasensor for the ultrasensitive detection of arsenite based on cysteamine stabilized CdTe/ZnS QDs aggregation [22]. But, irrespective of excellent optical and chemical stability of semiconductor QDs over existing organic fluorophores for arsenite determination, their real world application realization is still a challenge due to their toxicity in terms of their heavy metals based composition. Further, their poor aqueous solubility, low quantum yield in water, presence of the surface trap sites and complex synthesis from expensive & toxic precursors remains a considerable challenge for researchers. In view of these facts, the development of an alternative environment friendly and cost effective probe for trace arsenite detection remains an insight of research for peer group.

Of late carbon quantum dots (CQDs), an emerging class of zero dimensional nanomaterials have been widely employed in the field of catalysis, bio-imaging, fuel cells, optoelectronics, etc., due to their superior chemical stability, low toxicity, tunable surface functionalities, high aqueous solubility and resistivity to photo-bleaching [23,24]. In recent past, they have been used for sensing of several cations, anions and organic molecules [25]. Liu and coworkers have reported a novel carbon dots (CDs) based fluorescent probe for fluoride detection [26]. Copper ions detection has been demonstrated by Dong and co-workers using polyamine functionalized CQDs [27].

Similarly, CQDs have been demonstrated for detection of mercury and silver ions [28,29]. These reports projects CQDs as leading and promising alternatives for the existing organic fluorescent markers and toxic semiconductor probes for optical sensing.

Therefore, fascinated by recent past application of CQDs in sensors and motivated by the need to design an alternative optical probe for arsenite detection, herein, we report dithioetheritol (DTT) functionalized CQDs for its detection in water by 'turn-on' mechanism, which is still not investigated to the best of our knowledge. The turn-on mechanism allows ease of measuring low concentration contrast relative to a dark background, which reduces the possibility of false positive signals. The presented probe utilize As-S bond (strength = 379 kJ mol^{-1}) chemistry for selective detection of arsenic. A vast number of sulfur containing ligands such as glutathione, dithioetheritol, cysteine, mercapto-acetic acid, mercapto-propionic acid, etc., have been demonstrated for the arsenic detection in the recent past utilizing As-S bond strength in aqueous solution [23,36–38]. In our work, in view of available surface chemistry, we have used DTT, which possess free sulfhydryl groups, for functionalization on synthesized CQDs surface to selectively detect arsenite in water.

2. Experimental

2.1. Materials/Chemicals

All chemicals procured were of analytical grade and used directly without any purification. CQDs were synthesized and functionalized using citric Acid [SRL, SISCO Research Laboratory], cysteamine hydrochloride (Avra Synthesis) and dithioetheritol (DTT, Himedia). TRIS buffer (TRIS [tris(hydroxymethyl)aminomethane] powder, Fisher scientific) and arsenite stock solution (1000 ppm) obtained from inorganic ventures were used to conduct all sensing experiments. Standard stock solutions (1000 ppm) of various ions (NO_3^- , NO_2^- , Br^- , PO_4^{2-} , F^- , Co^{2+} , Ni^{2+} , Li^{2+} , Fe^{2+} , Cu^{2+} , Rb^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , K^+ , As(V) and Se(IV)) purchased from Merck & Inorganic Ventures were used for interference study. Deionized water obtained from Millipore corporation grade water system (Milli-Q) was used to prepare all solutions and subsequent dilutions.

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