



Fluorescence “turn on” probe for bromide ion using nanoconjugates of glutathione-capped CdTe@ZnS quantum dots with nickel tetraamino-phthalocyanine: Characterization and size-dependent properties



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ABSTRACT

In this paper, three differently sized glutathione (GSH)-capped CdTe@ZnS quantum dots (QDs) have been successfully conjugated to nickel tetraamino-phthalocyanine (NiTAPc) to form different QDs-NiTAPc nanocomplexes. Several techniques such as TEM, FT-IR, time-resolved fluorescence measurement and electronic spectroscopy were employed to characterize the nanocomplex. Bromide ion was chosen as a model anion to test the efficacy of the nanoprobe. The fluorescence of the nanoconjugate was “turned off” upon binding but was progressively “turned on” upon interaction with varying concentrations of bromide ion. Experimental results showed that the quantum size effect of nanocrystal QD determined the overall sensitivity and selectivity of the nanoprobe and followed the order QD₅₆₃-NiTAPc > QD₆₀₅-NiTAPc > QD₆₂₁-NiTAPc. The mechanism of reaction is proposed.

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1. Introduction

The unique properties of colloidal semiconductor nanocrystal quantum dots (QDs) such as broad absorption, size-tunable narrow emission wavelength and high fluorescence quantum yields have elicited a great deal of research in optical sensor technology [1–5]. In order to fine-tune their luminescence properties, surface modification of QDs with proteins [6] and macrocyclic compounds such as calixarenes [7,8], cyclodextrins [9,10], crown ether [11] and porphyrins [12] has been reported. The surface modified QDs have been used for the recognition of ions and small molecules [8,10–12].

Coordination of QDs to macrocyclic compounds such as nickel tetraamino-phthalocyanine (NiTAPc) has been reported to provide stability of the former [13]. Triggered by the above efforts, we have recently reported that metal tetraamino-phthalocyanine (MTAPc) can be covalently linked to QDs (via amide bond formation) for the fluorescence recognition of superoxide ion [14]. We proposed a fluorescence “off/on” sensing system [14]. As a continuation to our research on the development of novel QDs-MTAPc nanosensors, herein we report on the chemical coordination of differently-sized glutathione (GSH)-capped CdTe@ZnS QDs to

NiTAPc and its application as a fluorescence-based sensor for bromide ion.

Even though significant strides have been accomplished in the area of fluorescence sensing using QDs, fluorescence “turn on” probes for anions have not received much attention [15–20]. Our group has reported on a nanoprobe for bromide ion based on fluorescence “turn on” of GSH-capped CdTe QD-4-amino-2,2,6,6-tetramethylpiperidine-N-oxide (QDs-4AT) system [20]. Using electron paramagnetic resonance studies, the interaction between QDs-4AT and bromide ion was suggested to be electron transfer from the latter to the nitrosyl moiety of 4AT [20]. In this work, the enhancement of the QDs fluorescence is observed in the presence of bromide ion when QDs are linked to NiTAPc, and the effect of the QDs size on the fluorescence enhancement will be discussed. The central metal (Ni) was chosen as an example. Studies have shown that the enhancement of QDs fluorescence occurs in the presence of the analytes regardless of the central metal within the Pc ring [21].

Development of probes for bromide ion is vital, since this ion is naturally present in ground water and in untreated waters from coastal cities due to salt water intrusion. It has been reported that brominated organic compounds are more toxic and mutagenic when compared with their chlorinated counterparts [22,23].

ZnS was used to passivate the core CdTe surface with the sole aim of improving the photophysical properties of the QDs and to obtain enhanced sensitivity and selectivity as previously

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