



Novel fluorescent polymeric nanoparticles for highly selective recognition of copper ion and sulfide anion in water



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ABSTRACT

In the present study, a fluorescence resonance energy transfer (FRET)-mediated multifunctional sensor based on fluorescent polymeric nanoparticles was synthesized via a combination of a facile one-pot miniemulsion polymerization and subsequently by surface modification technology. Firstly, fluorescent polymeric nanoparticles were obtained by copolymerization of styrene, vinylbenzylchloride and the fluorescent vinylic crosslinking monomer (fluorescein-O,O-bis-propene: FBP) in oil-in-water miniemulsion stabilized with a cationic surfactant (dodecyltrimethyl ammonium bromide: DTAB). Then, 1,4,7,10-tetraazacyclododecane (Cyclen) was selected as ligand to graft onto the surface of nanoparticles. Due to the specific FRET effect between FBP and the Cu²⁺-Cyclen complex, the as-prepared nanoparticles display highly sensitive (detection limit: 340 nM) on-off-type fluorescence change with high selectivity toward Cu²⁺ among 11 metal ions (such as K⁺, Na⁺, Co²⁺, Ni²⁺, Zn²⁺, Hg²⁺, Mn²⁺, Ca²⁺, Mg²⁺, Fe²⁺ and Pb²⁺) in 100% aqueous solution. Moreover, it is worth to note that the in situ generated nanoparticle-Cu²⁺ ensemble could recover the quenched fluorescence upon addition of sulfide anion resulting in an off-on-type sensing with a detection limit of 2.1 μM in the same medium. No obvious interference was observed from other familiar anions such as Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, Br⁻, F⁻, S₂O₃²⁻, ClO₄⁻ and HPO₄²⁻. Furthermore, the nanoparticle-based dual-ion sensor can be reversibly switched for multi-times by alternative addition of adequate Cu²⁺ or S²⁻, was also applicable in a relatively wide pH range (pH 4–10), and exhibited excellent long-term photostability for Cu²⁺ detection (≥40 days) in aqueous media. Thus, this approach may reveal a new pathway for selective detection of multiplex analyst in environmental and biological applications.

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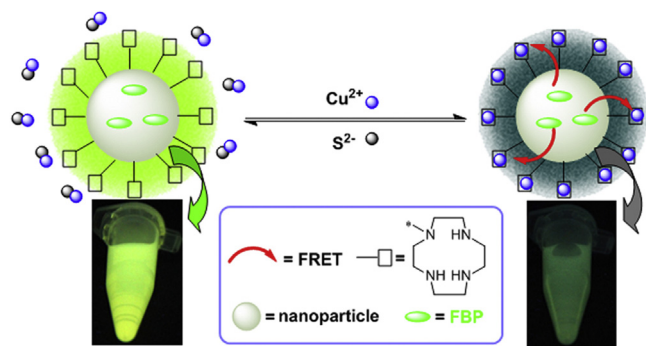
1. Introduction

The development of fluorescent sensors for selective detection of a chemical and biological analyst has attained increasing attentions because of their potential applications in chemistry, life sciences, medicine and environmental monitoring [1–5]. As one of the candidates, sulfide anion is widespread in the environment via generation from industrial processes and biological metabolism [6]. As a well-known toxic pollutant, sulfide anion can cause gradual and cumulative damage to life, such as loss of consciousness and irritation of mucous membranes [7]. Once protonated, sulfide becomes even more toxic as it turns into HS⁻, and further converts to H₂S under acidic pH [8]. Recent studies have shown that

protonated sulfide is linked to diseases like Alzheimer's disease [9], Down's syndrome [10], diabetes [11], and liver cirrhosis [12]. Thus, developing a strategy for sulfide anion measurement is very important for treatments and environmental requirements.

Compared with other traditional detection techniques including titration [13], inductively coupled plasma atomic emission spectroscopy [14], ion chromatography [15] and electrochemical method [16] etc., usage of fluorescent sensor to detect sulfide anion reveals a more promising strategy for its easy detection together with high sensitivity and selectivity. To date, some of the talented fluorescent sensors have been fabricated for sulfide anion detection [6,14,17–42]. However, most of the sensors often involve time-consuming organic synthesis or need harmful organic co-solvent system, which strongly limits their commercial applications in many fields like water quality monitoring and in vitro or in vivo detection of sulfide anion. Nevertheless, among these sensing platforms, a unique strategy like utilization of copper sulfide affinity

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Scheme 1. Schematic illustration of novel Cyclen-functionalized FPNs for Cu^{2+} and S^{2-} selective recognition.

attracted our highest attention. Sulfide ions are known to quickly react with copper ions in aqueous media to form a stable CuS species with low-solubility ($K_{\text{sp}} = 6.3 \times 10^{-36}$) [43]. Therefore, this method can be employed to sulfide anion detection at physiological environment. More importantly, this strategy can be given to produce multifunctional sensors for sequential recognition of copper ion and sulfide anion [24]. Although several fluorescent sensors which are built on sulfide ions affinity with Cu^{2+} have been successfully designed [23–25,28–34], multifunctional probes are quite scarce and still highly desirable.

Currently, FRET-based fluorescent polymeric nanoparticles (FPNs) acting as fluorescent sensors have attracted considerable attentions because of their exciting merits over traditional fluorescent probes, not only including water solubility/dispersibility, high brightness, excellent chemical stability and photostability, good biocompatibility and versatile structural design and functionalization capability, but also displaying the high internal self-calibration due to the principle of FRET [44–53]. For example, Larpent's group successively reported several types of FRET-based FPNs for highly sensitive and selective recognition of Cu^{2+} in water via a combination of miniemulsion polymerization and surface grafting technique [44–46,52]. Zeng's group utilized miniemulsion polymerization and surface grafting strategy to form ratiometric FRET-based FPNs sensor for Hg^{2+} in water [48]. Liu's group reported the fabrication of amphiphilic thermoresponsive diblock copolymer micelle-based multifunctional ratiometric fluorescent chemosensors for metal ions (Hg^{2+} and Cu^{2+}), pH, and temperatures via using FRET principle [47]. Our group also developed a class of stable FRET-based FPNs for sensing Cu^{2+} in 100% aqueous solution with high selectivity and sensitivity as well as prominent long-term stability [53]. However, although more and more sensors preferred to adopt FRET-based FPNs system, to the best of our knowledge, it seemed that there were no reports about the FRET-based FPNs sensors toward sulfide anions.

Herein, we report on the fabrication of novel FRET-based FPNs as a multifunctional sensor for highly selective and sensitive recognition of copper ion and sulfide anion in water via a combination of a facile one-pot miniemulsion polymerization and subsequently by surface modification technology (Scheme 1). In this sensor, fluorescent vinylic crosslinking monomer, fluorescein-O,O-bis-propene (FBP) acted as donor in FRET pair, and was covalently incorporated into polymeric nanoparticles via direct miniemulsion polymerization process. Obviously, this strategy can effectively avoid the dye leakage and greatly improve the structural and photic stability of prepared FPNs [54]. While effective Cu^{2+} ligand i.e. 1,4,7,10-tetraazacyclododecane (Cyclen) which served as a potential acceptor was selected to chemically graft onto the surface of polymeric nanoparticles. As the Cyclen exhibits high Cu^{2+} -binding affinities [24,25], and the Cyclen– Cu^{2+} complex have a specific FRET effect on FBP (donor), these ensured the sensor with

a highly sensitive and selective response to Cu^{2+} . Notably, other than the other azamacrocyclic Cu^{2+} ligands such as 1,4,7-triazacyclononane (TACN), 1,4,8,11-tetraazacyclotetradecane (Cyclam) etc., Cu^{2+} would be sensitively released from the Cyclen when a tiny sulfide anion is added to the system [25], resulting in fluorescence enhancement of as-prepared FPNs, which showed excellent properties as an off-on-type fluorescence sensor for sulfide anion. Moreover, this novel dual ion detection system also was applicable in a relatively wide pH range (pH 4–10) in water, and revealed outstanding long-term photostability (>40 days) in aqueous media. Overall, this work represents a proof-of-concept example of FRET-based FPNs as multifunctional fluorescent sensors for Cu^{2+} and S^{2-} , which bodes well for their potential applications in environmental monitoring and biological detection.

2. Experimental

2.1. Materials

The surfactant cetyltrimethylammonium bromide (DTAB, 99.5%, Aldrich), *n*-hexadecane (HD, 99%, Aldrich), Cyclen (98%, Alfa Aesar) and 4-vinylbenzyl chloride (VBCl, 97%, Aldrich), were used as received. Potassium peroxydisulfate (KPS, 99.99%, Aldrich) was recrystallized from purified water and dried under vacuum. Styrene (St, 99%, Aldrich) was purified by vacuum distillation. The water used throughout this work is the double-distilled water which was further purified with a Milli-Q system. Other reagents were analytical reagents and used without further purification. Nitrate salts of metal ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} and Hg^{2+}) and sodium salts of anion (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , Br^- , F^- , $\text{S}_2\text{O}_3^{2-}$, ClO_4^- and HPO_4^{2-}) were of analytic grade. FBP was prepared according to previously published procedures [54].

2.2. Preparation of the Cyclen-functionalized FPNs

A mixture containing the polymerizable dye, monomer, comonomer, hydrophobe and initiator (FBP, St, VBCl and HD) was added to a water solution with an emulsifier (DTAB) and stirred (1000 r/min) for 15 min; then, the mixture was ultrasonicated for 15 min (JY92-IIIN) to obtain a stable miniemulsion. The mixture was cooled in an ice-bath during ultrasonication to avoid being heated. The resulting miniemulsion was put into a 25 mL flask equipped with a condenser, which was immersed in an oil bath with a thermostat. The polymerization was initiated by water-soluble initiator KPS and proceeded at 75 °C for 180 min. After the polymerization, the as-prepared nanoparticle dispersions were percolated and filtered with a G2 sintered glass funnel. After that the dispersion was dialyzed by a porous cellulose membrane (MWCO 3500) against water for 48 h to remove the residual water-soluble molecules. Finally a stable halobenzyl-functionalized FPNs dispersion was obtained.

Subsequently, Cyclen-functionalized FPNs were obtained by adding 143 mg (0.83 mmol) of Cyclen to 10 ml of the crude suspension of halobenzyl-functionalized FPNs. The mixture was stirred at room temperature for 7 days. The excess of Cyclen was then removed by dialysis through a porous cellulose membrane (MWCO 3500) toward an aqueous solution of DTAB (15 wt%). A stable Cyclen-functionalized FPNs dispersion was obtained.

2.3. Characterization

The nanoparticle diameters were determined by a Malvern Nano-ZS90 instrument and their morphology was observed with an atomic force microscope (AFM, Bruker Dimension Icon) in the

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