



Sensitive determination of hardness and fluoride in ground water by a hybrid nanosensor based on aggregation induced FRET on and off mechanism

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ABSTRACT

Sensitive detection and determination of hardness and fluoride in the ground water is an important issue for the water safety. The present work reports a sensitive, selective, rapid and visual hybrid fluorescent nanosensor by hybridizing carbon dots and hexametaphosphate capped gold nanoparticles through intrinsic interactions of the two components. The hybrid nanosensor can be used for hardness (Ca^{2+} , Mg^{2+}) detection with the fluorescence intensity decreasing at 439 nm and increasing at 608 nm via the aggregation induced fluorescence resonance energy transfer on mechanism. In addition, the hybrid nanosensor mixed with calcium ions can detect fluoride in water with a lower detection limit of 0.339 ppm with the fluorescence color recovery based on the precipitation induced fluorescence resonance energy transfer off process. Experimental results indicate that the as-synthesized hybrid nanosensor has shown efficient feasibility and practicality for hardness and fluoride detection in actual groundwater samples. Furthermore, a paper-based analytical device has been fabricated by immobilizing the hybrid nanosensor on the cellulose filter paper for the visual and on-site detection of fluoride in water. The hybrid nanosensor would provide new sensing materials and mechanisms for the determination and detection of hardness and fluoride in the groundwater.

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1. Introduction

Ground water is the important and even the only source of drinking water in many areas, especially in the remote agricultural regions. However, the arbitrary discharge of various pollutants into the environment has resulted in serious pollutions to deteriorate the ground water quality, thus greatly endangered the environmental safety and human health [1,2]. Among the micropollutants, the detection of fluoride (F^-) in ground water has padded increasing public attention due to the serious fluorosis, acute gastric and kidney problems induced by the high take of F^- [3–6]. In addition, an interesting phenomenon can be noticed that high-fluoride in ground water usually accompanies with high hardness which may lead to trouble in home and industry for the formation of the deposits called lime scale. Additionally, those alkaline ions especially calcium and magnesium ions are the main cause of cardiovascular disease and would affect the health of humans and animals [7,8]. So the development of novel materials and meth-

ods to recognize and sense hardness and F^- in ground water has received considerable attentions due to their important roles in the environmental, chemical and biological process [9–11].

Despite the increasing interest and endeavors, few methods have ever been reported on hardness and F^- determination. The traditional EDTA titration method for hardness determination suffers from the sophisticated operation process, time consuming and vulnerable to operational errors [7]. Besides, the titration end point is hard to judge when interference ions exists, and the reagents used such as potassium cyanide are highly toxic to generate harms for operators and environment. Some other instrumental approaches, such as UV–vis spectrophotometry, atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectrometry et al. have also been proposed for determining total hardness, but these methods are tedious and complicated [7,8]. In addition, the previous F^- detection methods rely heavily on the fragile and expensive instrumentations, their endogenous tedious sample pretreatments and low selectivity greatly hinder the field applications [12–17]. As a result of these deficiencies, the fluorescent sensors with high specificity and sensitivity, visual ability, ease and safety of handling have attracted considerable attentions, and a number of fluorescent sensors have ever been reported for F^-

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detection [18–23]. These sensors are indeed innovative and sensitive, most of which are mainly based on the organic dyes with special ion recognition units containing rich amino, hydroxyl and carboxyl groups that can bind strongly to F^- [16,24–26]. However, these dye-based probes for F^- are faced with the poor water solubility which severely restricts their application in water environment systems. And also the synthesis of the organic dyes is complex and expensive. More importantly, these organic probes are significantly influenced by the environmental factors and are not suitable for the direct visual observation with the naked eye [27]. Compared with traditional fluorescent probes for F^- , quantum dots (QDs), as a kind of inorganic nanomaterials, have attracted more attentions owing to their unique optical properties including size tunable fluorescence, narrow and symmetric emission peak with a broad excited wavelength, and excellent photo stability [28,29]. For example, carbon dots (CDs) with a size of less than 10 nm have attracted extensive attentions due to their low toxicity, good water solubility and excellent photo stability, and have been used for ions detection [30,31]. Gold nanoparticles (Au NPs) have also been intensively reported due to their applications in the detection field [32–34]. And the construction of fluorescence resonance energy transfer (FRET) channel from CDs and Au NPs is the efficient solution for various analytes detection [35–37]. So it may be a suitable candidate to construct a novel nanosensor via CDs and gold nanoparticles for F^- detection.

Herein, we have designed and prepared a novel fluorescent hybrid nanosensor by integrating the blue emissive CDs and orange emissive Au NPs capped with hexametaphosphate groups which can chelate with Ca^{2+} and Mg^{2+} . The novel hybrid nanosensor has shown dual characteristic emissions at 439 nm and 608 nm, which can be ascribed to CDs and capped Au NPs. With the presence of Ca^{2+} or Mg^{2+} , the fluorescence intensity decreased at 439 nm and increased at 608 nm accompanying with the fluorescence color transfer from blue violet to orange based on the aggregation induced FRET on mechanism. When F^- was added into the hybrid nanosensor mixed with Ca^{2+} , the fluorescence intensity increased at 439 nm and decreased at 608 nm with the fluorescence color recovery due to the FRET off effect. Furthermore, the paper-based analytical device based on the hybrid nanosensor has also been developed for the on-site and visual sensing of F^- in water, and the new nanosensor can also be used for hardness and F^- determination in the real ground water samples.

2. Experimental

2.1. Materials and instrumentation

Hydrogen tetrachloroaurate ($HAuCl_4$), L-glutathione, ethylenediamine, citric acid, calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), potassium chloride (KCl), sodium chloride (NaCl), aluminum chloride ($AlCl_3$), copper chloride ($CuCl_2$), ferric chloride ($FeCl_3$), manganese chloride ($MnCl_2$), zinc chloride ($ZnCl_2$), cadmium chloride ($CdCl_2$), cobalt chloride ($CoCl_2$), sodium fluoride (NaF), sodium hexametaphosphate ($Na_6P_6O_{18}$), sodium hydrogen sulfite ($NaHSO_3$), potassium iodide (KI), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), sodium acetate (CH_3COONa), sodium carbonate (Na_2CO_3), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), sodium phosphate (Na_3PO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Sinopharm Chemical Reagent Co, Ltd (Shanghai, China). All reagents and solvents of analytical grade and used without further purification. Ultrapure water ($18.25 M\Omega cm^{-1}$) was obtained from a Millipore water purification system and employed throughout the experiments.

All fluorescence measurements were recorded on a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) with excitation and emission slit width of 10 nm. Ultraviolet–visible (UV–vis) spectra were conducted on a Perkin Elmer Lambda 35 spectrophotometer. Fourier transform infrared (FTIR) spectra were collected by an EQUINOX 55 instrument using the diffuse reflectance scanning disc technique from $4000 cm^{-1}$ to $400 cm^{-1}$ at room temperature. Transmission electron microscopy (TEM) images were obtained with a JEOL 2000 EX transmission electron microscope operated at 200 kV (JEOL, Japan). High resolution transmission electron microscopy (HRTEM) images were obtained with a JEM-2100 FEF(UHR) high resolution transmission electron microscope. Powder X-ray diffraction (XRD) data were obtained on a Rigaku D/MAXRC X-ray diffractometer with a $Cu K\alpha$ radiation source (45.0 kv, 50.0 mA). The zeta potential was recorded on a zeta potential and particle size analyzer (Malvern, nano ZS 90).

2.2. Synthesis of fluorescent CDs

The fluorescent CDs were prepared by a simple one-pot hydrothermal method. Typically, 5.0 g of citric acid was dissolved in 50 mL of ultrapure water, followed by the introduction of 0.5 mL of anhydrous ethylenediamine agitating vigorously for 15 min to form a clear solution. The mixture solution was then heated for 7 h at $180^\circ C$ in the polytetrafluoroethylene autoclave. The obtained brown solution was cooled down to room temperature and filtered twice through $0.22 \mu m$ membrane filter. After that, the filtrate was purified by dialyzing with ultrapure water using membrane (MW = 500) to obtain the CDs solution. The purified solution was freeze-dried into powder and measured, and the obtained CDs powder was dissolved in water again with $10 \mu g/mL$ and stored for further use.

2.3. Synthesis of capped Au NPs

All the glasswares were firstly washed with aqua regia and then rinsed with ultrapure water several times before use. The hexametaphosphate-capped Au NPs were prepared via a thermal reduction method. Typically, 0.0737 g of L-glutathione was dissolved in a mixture solution of 50 mL of ultrapure water and $150 \mu L$ of 1 M $HAuCl_4$. After vigorous stirring for 30 min, the mixture solution was heated and refluxed for 30 min at $95^\circ C$, and the solution color transferred to yellow. The pH values of the obtained yellow solution was adjusted to 3–4, followed by the addition of 5 mL of ethanol. Then Au NPs can be obtained by centrifugation, and dissolved in phosphate buffer solution for further functionalizations. 10 mL of 20 mM sodium hexametaphosphate was added into the Au NPs buffer solution with vigorous stirring for 12 h at ambient temperature. The hexametaphosphate-capped Au NPs solution was transferred into the dialysis bag (MW = 500), and the dialysis of solution lasted over 48 h to obtain the functionalized Au NPs solution. The purified solution was freeze-dried into yellow powder, which was dissolved in water with $17.3 mg/mL$ for further use.

2.4. Synthesis of hybrid nanosensor

The hybrid nanosensor was prepared following the below procedures. Briefly, $20 \mu L$ of CDs ($10 \mu g/mL$) and $10 \mu L$ of hexametaphosphate-capped Au NPs ($17.3 mg/mL$) solution were thoroughly mixed in 1.97 mL ultrapure water. The mixture solution was kept under vigorous stirring for 10 min for the surface hybridization through reaction and interaction, and then the hybrid nanosensor was obtained and stored for further use. The fluorescence spectra of the hybrid nanosensor were collected, and

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