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On–off–on fluorescent silicon nanoparticles for recognition of chromium(VI) and hydrogen sulfide based on the inner filter effect

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ABSTRACT

A highly sensitive and selective fluorescence sensor for detection of chromium(VI) and hydrogen sulfide was developed by using silicon nanoparticles (SiNPs) as probe. The fluorescence of SiNPs was effectively quenched by Cr(VI) *via* the inner filter effect. Upon addition of hydrogen sulfide, the fluorescence of SiNPs was recovered due to the oxidation-reduction between Cr(VI) and H_2S. Under optimal conditions, the wide linear response ranges were obtained over the range of 0.1–200 μM and 0.1–200 μM with the low detection limits of 28 nM and 22 nM for Cr(VI) and H_2S, respectively. The sensing platform was successfully applied to determination of Cr(VI) and H_2S in real samples.

1. Introduction

During the last decades, industrial processes involving dyes, metallurgy, sewage treatment and petroleum have been constantly releasing heavy-metal ions and poisonous gas into the environment, such as hexavalent chromium and hydrogen sulfide [1–6]. Both of them are toxic pollutant in environment. Additionally, chromium contamination to ecosystem ranks the second among the pollutants as a result of human activities [7]. Aqueous chromium is most commonly found in two main stable states, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) is necessary for biological processes and mostly harmless [8–10]. However, Cr(VI) is hazardous due to its mutagenicity and carcinogenicity to living organisms, and its facile solubility in natural water provides both mobility and bio-accessibility [11–14]. The US Environmental Protection Agency limits Cr(VI) to 0.1 mg/L (1.9 μM) in drinking water [15]. On the other hand, hydrogen sulfide is also a well-known bad odor and poisonous gas that is generated as a by-product in many industrial processes, in particular petroleum-related industries [16]. The toxicity of H_2S is comparable with that of hydrogen cyanide or carbon monoxide [17]. In high enough concentrations, H_2S may lead to unconsciousness, permanent brain damage or even asphyxiation [18]. Considering the widespread and toxic effects of them, the development of a fast, simple and highly sensitive method for the determination of Cr(VI) and H_2S for environment monitoring is highly desirable.

Up to now, various analytical methods have been successfully developed for the determination of Cr(VI) or H_2S, including electrochemical assays, chromatography and atomic absorption spectrometry, *etc.* [19–23]. Although these methods are highly sensitive, many of them suffer disadvantages such as expensive cost, time-consuming, complicated pretreatment processes, which limit their wide application. Due to its high sensitivity, convenience and accessible instrument requirement, the fluorescent assay of Cr(VI) or H_2S is considered to be a more desirable method among these methods. Organic fluorescence dye and heavy metal-containing nanoparticles are usually used in fluorescence assays. Recently, a 1,8-naphthalimide-based fluorescent probe [24], CdS quantum dots [25] and a bodipy-based dual functional probe [26] have been reported for fluorescent assay of Cr(VI) or H_2S. However, the intrinsic toxicity and complexity of these materials have limited their practical applications in the assay of biomolecules. Meanwhile, synthesis procedures of these probes are complicated and only one analyte can be tested. Therefore, it is still crucial to develop excellent nanomaterials which are easily obtained for fabricating highly sensitive and selective biosensors to quantify both Cr(VI) and H_2S. As an inert, nontoxic, abundant and low-cost nanomaterials, SiNPs have been demonstrated to be environmentally friendly photoluminescence probes and have attracted special interest due to their outstanding properties, including high quantum yield (QY), good

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photostability, low toxicity and excellent biocompatibility [27–30]. Thus, SiNPs are being explored as an alternative for dye-based probe, toxic semiconductor quantum dots and weakly fluorescent polymers. So far as we know, the studies on SiNPs fluorescent sensor for dual detection of Cr(VI) and H_2S are rare.

Herein, we established a SiNPs-based sensing platform for effective and selective detection of Cr(VI) *via* the inner filter effect (IFE) and a fluorescence "on–off–on" strategy for the determination of H_2S based on the oxidation-reduction between Cr(VI) and H_2S. Scheme 1 illustrates the proposed mechanism for the sensing of Cr(VI) and H_2S. The fluorescence (FL) intensity of SiNPs could be quenched by Cr(VI) based on IFE (FL on–off, Scheme 1), and this sensor has lots of advantages: mild condition, fast response and high sensitivity. Addition of H_2S, Cr(VI) is reduced to lower-valent Cr species which has almost no influence on the fluorescence of SiNPs and the fluorescence of SiNPs is recovered. Therefore, the SiNPs-Cr(VI) mixture could behave as a "turn-on" fluorescent sensor (FL off–on, Scheme 1) for detection of H_2S. The proposed biosensor developed a simple, sensitive method for monitoring of both Cr(VI) and H_2S.

2. Experimental

2.1. Reagents and chemicals

(3-Aminopropyl)trimethoxysilane (APTMS) (97%) was purchased from Aladdin. Trisodium citrate dihydrate (≥99.0%), potassium dichromate, sodium hydrosulfide and the other metal salts were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade and used as received without further purification. Hydrogen sulfide (NaHS was used as the hydrogen sulfide source in all experiments) stock solution (2.5 mM) was freshly prepared before experiments. Phosphate buffer solution (PBS) (pH 6.0, 20 mM) and Milli-Q ultrapure water (Millipore, ≥18 MΩ cm) were used throughout the experiments.

2.2. Apparatus

UV–vis absorption spectra were recorded on a UV2450 spectrophotometer (Shimadzu, Japan) and fluorescence spectra were performed using an F-7000 spectrophotometer (Hitachi, Japan). The quantum yield (QY) of SiNPs was estimated using quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield: 58%) as a reference standard, which was freshly prepared to reduce the measurement error. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet Nexus 670 FTIR spectrometer (Nicolet Instrument Co., U.S.A.). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL-1230 transmission electron microscope equipped with energy dispersive X-ray (EDX) spectroscopy.

2.3. Fluorescent assays

SiNPs were synthesized by a hydrothermal method [31] (the detailed synthesis process was presented in Supporting material). 20 μL of the as-prepared solution of SiNPs was mixed with PBS (20 mM, pH 6.0) followed by the addition of diluted solutions of Cr(VI). The final volume of the solution was 1.0 mL, and the absorbance of SiNPs at 350 nm was equal to 0.008. After mixing for 2 min at room temperature, the fluorescence spectra of the solutions were recorded under excitation at 350 nm.

In the determination of H_2S, 200 μM Cr(VI) was mixed with PBS (20 mM, pH 6.0) followed by the addition of different concentrations of H_2S. After incubation for 30 min at room temperature, 20 μL SiNPs was added into the mixture and the final volume of the solution was 1.0 mL. The fluorescence spectra of the solutions were recorded under excitation at 350 nm.

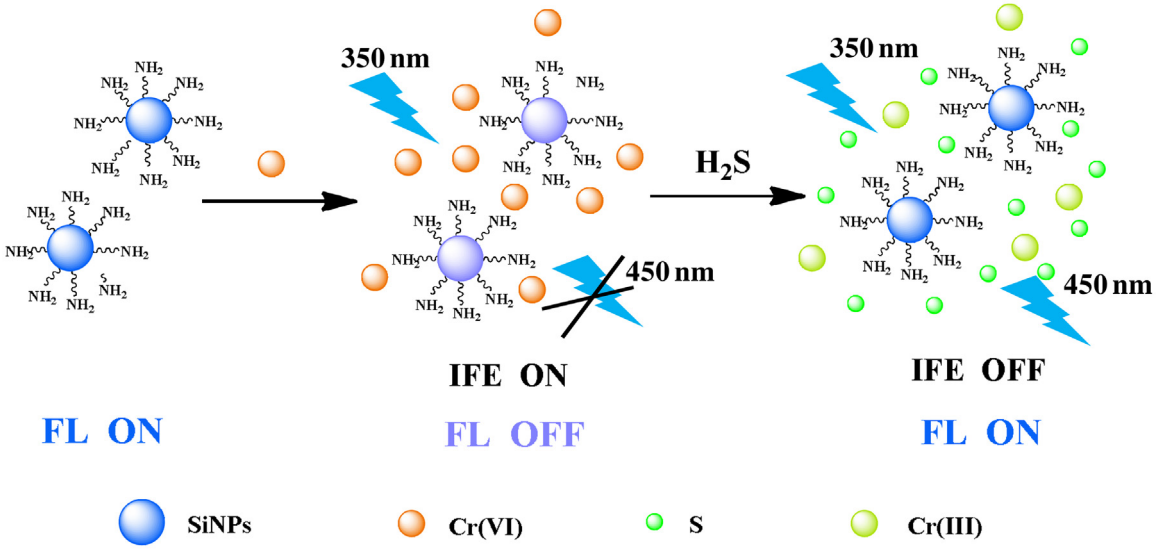
2.4. Water samples analysis

The standard addition method was used to test the practical application of the proposed sensor in the water samples (tap water and river water). The water samples were simply filtered before the measurement and then were spiked with standard solutions containing different concentrations of Cr(VI) or H_2S. The resulting samples were further analyzed by fluorescent nanosensor. The fluorescence spectra of the solutions were recorded under excitation at 350 nm.

3. Results and discussion

3.1. Mechanism of the fluorescent sensor

The IFE refers to the absorption of the excitation and/or emission light of the fluorophores by absorbers in the detection system [32–34]. Moreover, it has been reported that a good spectral over-



Scheme 1. Schematic illustration of fluorescence "on–off" assay for Cr(VI) and "on–off–on" assay for H_2S.