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Gold nanoclusters as fluorescent sensors for selective and sensitive hydrogen sulfide detection

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ABSTRACT

As a highly toxic environmental pollutant and also an important gasotransmitter in diverse physiological processes, the selective and sensitive detection of hydrogen sulfide (H_2S) is very significant. In this work, acetylcysteine stabilized gold nanoclusters (ACC@AuNCs)-based fluorescent sensors had been successfully constructed for H_2S perception. The sensing principle was that H_2S-induced fluorescence quenching of AuNCs which attributed to both the formation of Au_2S between Au(I) in the AuNCs and H_2S and the increased particle size. The proposed sensors showed high selectivity toward H_2S over other anions, amino acids and thiols, and exhibited a stable response for H_2S from 0.002 to 120 μmol L^{-1} with a detection limit of 1.8 nmol L^{-1}. In addition, the practical application of the designed sensors was further evaluated with water and serum samples, and the tested results agreed well with those obtained by ICP-AES method. The satisfactory recoveries and good precision show that the proposed fluorescent sensors has potential application in biological and environmental fields.

1. Introduction

Hydrogen sulfide (H_2S), a flammable, highly toxic gas with the characteristic smell of rotten egg, which is produced in factory, mines, and the gas and oil industries [1–3]. If the industrial effluents including H_2S are discharged without permission or beyond pollution limits, the quality of natural water may be affected. The destruction of ecological environment and pollution of groundwater could be caused, and even human health is directly damaged. Moreover, recent studies have recognized H_2S as the third gaseous signal transmitter besides carbon monoxide and nitric oxide in many physiological and pathological processes [4,5]. H_2S is reportedly an ATP sensitive potassium channel opener and affects the cardiovascular system [6]. The physiological levels of H_2S in mammals is about 20–160 μmol/L. Its abnormal levels are associated with a series of diseases, including diabetes, hypertension, Alzheimer's disease and Down's syndrome [7–9]. Therefore, detection of H_2S in natural water and serum samples is of great importance for water quality-based pollution control and better understanding of its biological function and even an early diagnosis of diseases and cancers. Keeping those in mind, detection of H_2S has received significant attention in recent years and the design of selective and sensitive methods for its monitoring and sensing can be of interest.

Toward achieving this goal, a number of analytical techniques have been reported for the detection of H_2S at trace levels, including gas chromatography [10], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [11], electrochemistry [12,13], colorimetry [14], UV–visible absorption spectrometry (UV–Vis) [15] and fluorescence spectrometry methods [16,17]. Among these analysis methods, although gas chromatography and ICP-AES have good resolution, it is still quite costly and often requires of complicated procedures. Alternatively, electrochemical, colorimetry, and UV–Vis methods are simpler and less costly procedure in comparison to gas chromatography and ICP-AES but can suffer from interference of coexisting substances and lower sensitivity. As it is known fluorescent methods are ideal due to distinct advantages such as simple, sensitive and inexpensive, and can determine concentrations to trace levels. In this type of sensor, various fluorescent probes for the detection of H_2S have been developed based on some organic dyes or fluorophores [18–21]. However, organic molecules might suffer from small Stokes shift, short emission wavelength, short lifetime and poor photostability, which resulted in certain limitations including poor selectivity, low sensitivity, incompatible with aqueous environment, so that their practical applications were restricted [22].

Recently, luminescent metal nanoclusters (NCs) have drawn considerable attention because they could generate unique optical properties that are strongly dependent on their ultra-small size contrary to their bulk-metal counterparts. In addition, due to the extraordinary properties of luminescent metal NCs such as large Stokes shift, strong

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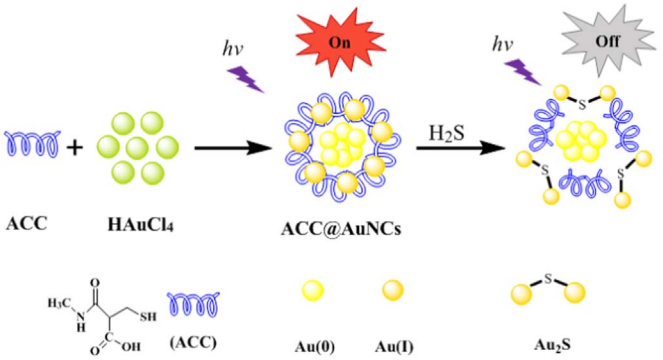
fluorescence, high photochemical stability and wide spectral line, they have been the subject of great attention in the application of sensor for H_2S or sulfide ion [23–26]. For example, a sensitive assay based on the fluorescence quenching of polystyrene sulfonate-penicillamine stabilized copper nanoclusters (PSS-PA-Cu NC) aggregates has been developed for sensing H_2S [23]. Chen et al. [24] utilized a one-pot approach to synthesize fluorescent gold/silver nanoclusters (Au/AgNCs) with DNA as template that allowed sensitive and selective detection of sulfide ion in high ionic strength media. Yang et al. [25] established a ratiometric fluorescent method for H_2S detection based on combination of bovine serum albumin templated gold nanoclusters (AuNCs) and a azamacrocyclic Cu^{2+} complex. Liang et al. [26] constructed an interesting ratiometric fluorescent platform for sulfur ion in terms of fluorescence resonance energy transfer between carbon nanoparticles and glutathione protected AuNCs. Among these studied metal nanoclusters, AuNCs have been studied most extensively since the pioneering work of Brust and coworkers in 1994 [27–29]. However, most of the reported synthesis of AuNCs involved either complicated fabrication or toxic/expensive reagents, or the as-synthesized AuNCs tended easily to aggregate owing to the weak interaction between Au and ligand. Therefore, exploring a simple and eco-friendly method that prepares AuNCs with high photostability is valuable for constructing sensor arrays.

Acetylcysteine (ACC) is a commercially available medication used to treat paracetamol overdose and to loosen thick mucus such as in cystic fibrosis or chronic obstructive pulmonary disease. ACC contains multiple functional groups such as thiol, secondary amine and carboxylic acid. It is known that the thiol group of ACC has high binding affinity with the surface of gold nanoparticles/nanoclusters, and the carboxylic acid and secondary amine groups of ACC can endow the AuNPs/AuNCs good water solubility [30]. In this work, ACC was chosen as a stabilized agent to simply prepare thiolate-protected AuNCs in one pot route, in which only the reactants of ACC and $HAuCl_4$ were used and the reactions were green and eco-friendly. Because of the strong gold-S interactions, the introduction of H_2S could lead to the generation of Au_2S and the increased size of AuNCs, which resulted in quenching fluorescence of ACC@AuNCs. The sensors based on fluorescent AuNCs showed good selectivity and sensitivity and was applied to the determination of H_2S in water and serum samples with satisfactory recoveries.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4{\cdot}3H_2O$) was purchased from Aldrich (Milwaukee, WI, USA). Acetylcysteine (ACC) was obtained from International Laboratory (San Bruno, CA, USA). Glacial acetic acid (CH_3COOH) and absolute methyl alcohol (CH_3OH) were provided by Tianjin Chemical Reagent Company (Tianjin, China). Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) was obtained from Chengdu Cracia Chemical Technology Co., Ltd. (Chengdu, China). Inorganic salts of anions (NO_3^-, HCO_3^-, Ac^-, $C_2O_4^{2-}$, CO_3^{2-}, ClO_3^-, PO_4^{3-}, NO_2^-, $Cr_2O_7^{2-}$, $Citric^{3-}$, Br^-, I^-, $S_2O_4^{2-}$, $S_2O_3^{2-}$, SCN^-, SO_4^{2-}, SO_3^{2-}) were purchased from Beijing Chemical Reagent Co., Ltd. (Beijing, China). Cysteine (Cys, > 99%), histamine (His, ≥99.5%), prolene (Pro, ≥99%), homocysteine (Hcy, ≥99%), DL-Valine (Val, ≥99%), tyrosine (Tyr, ≥99%), glycine (Gly, ≥99%) and glutathione (GSH, > 98%) were provided by Sigma-Aldrich (St Louis, USA). All of these reagents were of analytical grade or above and used as received. 10 mmol L^{-1} phosphate buffer solutions (PBS) with different pH values were prepared by mixing appropriate volumes of standard solutions of 10 mmol L^{-1} Na_2HPO_4 and 10 mmol L^{-1} NaH_2PO_4. Cellulose ester membrane tube (500 Da cut-off) was purchased from Spectrum Laboratories (Rancho Dominguez, CA, USA). The water used throughout the experiments was ultrapure water purified by a Milli-Q water system (resistivity 18.2 MΩ, Millipore, USA).



Scheme 1. Schematic illustration of fluorescent sensors based on ACC@AuNCs for H_2S detection.

2.2. Apparatus

UV–vis absorption spectrum was recorded on a Shimadzu UV-2450 absorption spectrophotometer (Tokyo, Japan). Fluorescence intensities and lifetimes were measured using an Edinburgh Instrument FLS-920 time-resolved/steady state fluorescence spectrometer (Livingston, UK). pH measurements were taken on a FE20 pH-meter (Mettler Toledo Instrument Inc, Shanghai, China). Transmission electron microscopic (TEM) images were obtained on a JEOL JEM-2100 (Tokyo, Japan) at an accelerating voltage of 200 kV. The dynamic light scattering (DLS) and zeta potential analysis were performed with a Malvern Instruments Nano-ZS90 Zetasizer (Malvern, UK). X-ray photoelectron spectrum (XPS) was acquired on a Leybold Heraeus SKL-12 X-ray photoelectron spectrometer (Shenyang, China). Fourier transform infrared (FTIR) spectra were captured on a PerkinElmer Paragon 1000 FTIR spectrometer (Waltham, MA, USA). ICP-AES measurement was carried out on a Thermo iCAP 6300 atomic emission spectrometer (Waltham, MA, USA).

2.3. Synthesis of ACC@AuNCs

Freshly prepared solutions of $HAuCl_4$ (0.10 mol L^{-1}, 0.4 mL) and ACC (0.10 mol L^{-1}, 0.6 mL) were mixed with a 1.6 mL MeOH/glacial acetic acid (6:1, v/v) solution under magnetic stirring at 25 °C for 30 min, which turned from bright yellow to orange with some white suspensions. 8.7 mL Milli-Q water was then added to the mixture. Subsequently, the solution was heated to 70 °C with reflux under magnetic stirring for 24 h. An aqueous solution of strongly orange emitting gold nanoclusters (ACC@AuNCs) was formed. Finally, the solution was dialyzed against pure water using a cellulose ester dialysis membrane (molecular weight cut-off 500 Da) for three days. And the ACC@AuNCs products were obtained. The final solution was stored at 4 °C before use.

2.4. Quantum yield of ACC@AuNCs

The quantum yield of the ACC@AuNCs was calculated using the following equation:

$$\Phi_x = \Phi_s \times (A_s/A_x) \times (I_x/I_s) \times (n_x/n_s)^2$$

where the subscripts s and x refer to luminescence standard and ACC@AuNCs, respectively. Φ is the quantum yield, A is the absorbance, I is the integrated luminescence intensity, and n is the refractive index of solvent. Quinine sulfate in 0.10 mol L^{-1} H_2SO_4 with a quantum yield of 0.54 was used as the luminescence standard. The excitation wavelength of the standard and ACC@AuNCs was 340 nm.

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