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Sensitive iodate sensor based on fluorescence quenching of gold nanocluster

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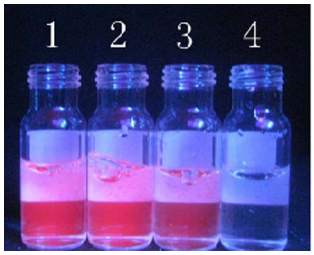
HIGHLIGHTS

- BSA-stabilized gold nanoclusters were synthesized.
- Iodate etched the gold core of nanocluster and resulted in fluorescence quenching.
- Excessive iodide enhanced the etching and related quenching.
- A highly sensitive iodate sensor was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this report we described a highly selective and sensitive iodate sensor. Due to its interaction with fluorescent gold nanoclusters, iodate was capable of oxidizing and etching gold core of the nanoclusters, resulting in fluorescence quenching. Furthermore, it was found that extra iodide ion could enhance this etching process, and even a small amount of iodate could lead to significant quenching. Under an optimized condition, linear relationship between the iodate concentration and the fluorescence quenching was obtained in the range 10 nM–1 μM. The developed iodate sensor was found selective and capable of detecting iodate as low as 2.8 nM. The sensor was then applied for the analysis of iodate in real sample and satisfactory recoveries were obtained.

1. Introduction

Iodine, an essential trace element for life, is required for the normal function of thyroid as a constituent of related hormones, thyroxine and triiodothyronine. Deficiency of iodine may result in serious health problems, such as cretinism and endemic goiter, from which a large population of the world is still suffering [1]. One of the most effective means against iodine-deficiency is adding iodine-containing nutrient into table salt (iodised salt). Due to its stability, iodate (as potassium iodate) is usually adopted as the iodine source. However, excess intake of iodine may also lead to thyrotoxicosis, a disease relating to excessive amount of thyroid hormones. Therefore, it is of significant importance to detect the amount of iodate in salt and other samples. In order to achieve this goal, various methods, such as fluorescence spectroscopy [2], ion chromatography [3], electrochemistry [4–8], photometry [9], resonance scattering spectroscopy [10] have been developed. General deficiencies of these methods are the limited sensitivity, complex procedure and requirement of complicated instrumentation. Therefore, simple and effective methods will be favorable for iodate analysis.

Recently fluorescent noble metal nanoclusters (NCs), such as gold and silver ones, are intensively reported as materials for sensor assemblies [11]. These ultra-small size particles

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(with diameter <2.5 nm) consist of only several to tens of metal atoms and are stable under suitable stabilizers [11,12]. Specific interactions with either the metallic core or the protecting stabilizer might significantly alter the fluorescence property of the NCs, which are frequently adopted for related sensing schemes. Sensors toward various targets, such as metal ions [12–14], anions [15,16], small molecules and even large biomolecules [17–24] have been developed with this strategy. In our work here, the interaction between gold nanoclusters and iodate was investigated, and it was found that under suitable conditions, even small amount of iodate could result in significant fluorescence quenching. This scheme was then applied for the development of a sensitive iodate sensor.

2. Experimental

2.1. Reagents and materials

Chloroauric acid ($HAuCl_4 \cdot 4H_2O$), sodium borohydride ($NaBH_4$) and salts containing different anions were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Bovine serum albumin (BSA) was purchased from Yacoo Chemical Reagent Co. (Suzhou, China). All other chemicals were of analytical grade and used as received. Double-distilled water was used throughout the experiments.

2.2. Synthesis of the gold nanoclusters

Bovine serum albumin protected gold nanoclusters (BSA-AuNC) were synthesized as previously reported [14,24]. An aliquot of 5 mL aqueous $HAuCl_4$ (0.01 M) was mixed with 5 mL BSA solution (50 mg mL^{-1}) under vigorous stirring. After 2 min, 0.5 mL 1 M NaOH solution was introduced and the mixture was left to incubate at 37 °C (with continuous stirring) for 24 h. The obtained gold nanocluster was stored at 4 °C in dark before use.

2.3. Detection

The so-prepared nanocluster was diluted 300-fold for the fluorescence measurement unless stated otherwise. Aliquots (1 mL) of 20 mM citrate–phosphate buffer solutions containing the BSA-AuNCs and the target anion were mixed. After reaction the fluorescence signal was measured on an FL-2500 fluorescence spectrophotometer (Hitachi, Japan) with excitation at 365 nm. The slit width was set at 5 nm and 10 nm for excitation and emission, respectively. Microscopic images of the NCs were obtained under a Tecnai G2F20 transmission electronic microscope (TEM) (FEI, USA). Fluorescence images of the samples were recorded with a Cannon SD1100 digital camera (Cannon Inc., Japan) under a 365 nm UV lamp (Cnlight Co., China).

2.4. Dialysis of the nanoclusters and measurement of gold

The gold nanocluster samples were firstly mixed with different iodate solutions. After 1 h incubation, the mixtures and an AuNC sample without iodate were transferred into dialysis tubings (Solarbio Inc., Beijing, China, with molecular weight cut off (MWCO) at 14 kD) and dialyzed against double-distilled water. Every 2–3 h, the dialysis solution was replaced with fresh water, 4 times in total. The amount of gold inside the tubing was analyzed with a Varian 710-ES atomic emission spectrophotometer (Agilent Inc.).

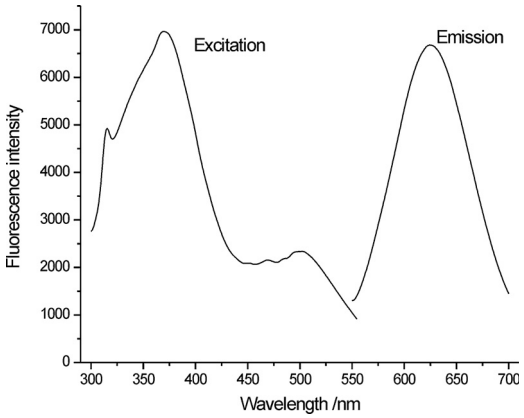

Fig. 1. Fluorescence excitation and emission spectra of the BSA-AuNC. The BSA-AuNC stock solution was diluted 5-fold with water. The fluorescence excitation spectrum was obtained with emission at 625 nm and the emission spectrum was measured with excitation at 370 nm.

2.5. Analysis of real samples

A table salt solution was prepared by dissolving 1.00 g sample with water into a final volume of 100 mL. Tap water and pond water samples were collected and filtered with 0.22 μm membranes to remove possible large particulates. Then 100 μL of these samples were directly mixed with nanocluster probe, respectively, and diluted with the buffer to final volume of 1.00 mL for analysis.

3. Results and discussions

3.1. Direct fluorescence quenching from iodate

The gold nanoclusters were synthesized with BSA acting as both the reducing agent and the stabilizer (BSA-AuNC) under basic condition [24]. This protein was adopted since its wide availability and stability. The TEM image showed most the clusters were of diameter <2.5 nm (Supplemental data Fig. S1). As compared with BSA, the thus obtained Au_{25} NC had a much stronger absorption in the

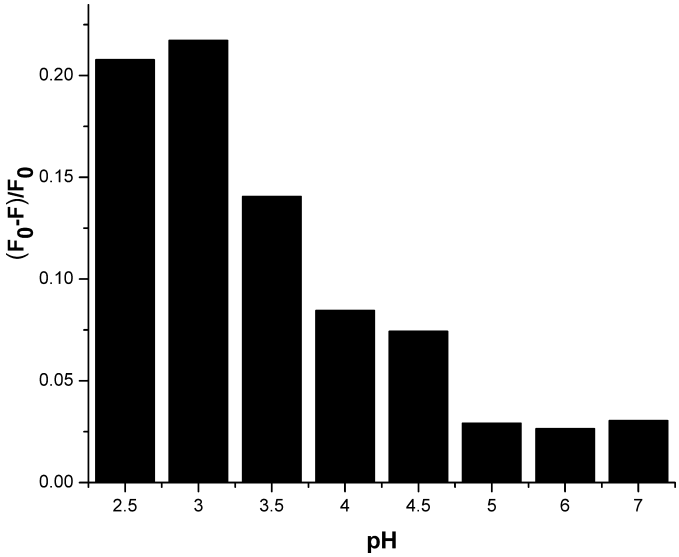

Fig. 2. Iodate related fluorescence quenching under different pH values. The gold nanocluster was diluted 100-fold and the fluorescence intensities of AuNC were measured after 1 h incubation with 15 μM iodate. The measurement was performed under 20 mM citrate–phosphate buffers.