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A sensitive and selective sensor for the detection of chloroform using biosurfactant ethoxylated phytosterol-capped gold nanoparticles

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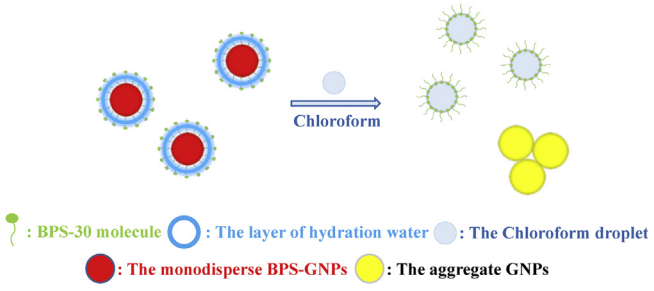
HIGHLIGHTS

- The detection of chloroform in solution was realized using gold nanoparticles.
- The detection processes could be monitored by naked eye and UV–vis spectra.
- The polar difference of sample/water was used to interpret the detection mechanism.
- The mechanism based on "double interface competitive adsorption" was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile, sensitive, and selective sensor was developed to detect chloroform using biosurfactant ethoxylated phytosterol-capped gold nanoparticles (BPS-GNPs). The BPS-GNPs were induced to aggregate rapidly with the addition of chloroform. Detection of additional chloroform of relatively small volume can be easily realized by monitoring the color fading of BPS-GNP aqueous solution by the naked eye. The presence of the chloroform with extremely small volume can be monitored by UV–vis spectra. A possible detection mechanism based on "double interface competitive adsorption" was proposed. Other common organic substances were used to further verify the selectivity of the detection.

1. Introduction

Exposure to chloroform gas can be a serious problem for human health. Many reports have focused on the detection of chloroform gas by various sensors [1–3]. Capan et al. designed a fast and reversible sensor for chloroform vapour detection using Calix [4] resorcinarene film [3]. Chloroform is produced in many industries, and even can form in nature [4]. Chloroform is a widespread contaminant in groundwater around the world. For example, the chloroform was detected in ~10% of wells in both the U.S. and Denmark [5,6]. Additionally, there have been many deaths caused by or related to chloroform [7]. However, there are few reports of methods for the detection of chloroform in aqueous solution. Hunkeler et al. detected chloroform in groundwater by compound-specific isotope analysis and determined its source as natural or anthropogenic [4]. Although trace detection of chloroform in groundwater is possible, the required apparatus and

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complications due to the presence of other contaminants in samples may limit practical application of the method.

Various noble metal nanoparticles, especially gold nanoparticles with different capping agents, have been applied to detect hydrazine, mercury ions, cadmium ions, and other hazardous substances [8–10]. Apte et al. fabricated gold nanoparticles and silver oxide nanoparticles to successfully detect dichlorvos and mercury ions, respectively [11]. We reported a facile and green approach to prepare monodisperse gold nanoparticles using the biosurfactant ethoxylated sterol (BPS-30) [12]. We found that the prepared BPS-30 capped gold nanoparticles (BPS-GNPs) showed remarkable stability even in inorganic electrolyte aqueous solutions at extremely high concentrations. BPS-GNP solution showed an obvious fade in color in the presence of additional chloroform. Detection of the chloroform in extremely small volume was achieved by analysis of UV–vis spectra. Control experiments using other common organic substances further verify the selectivity of the detection.

2. Experimental

2.1. Chemicals

The biosurfactant ethoxylated phytosterol (BPS-30, where 30 is the number of oxyethylene units, and the molecular structure is shown in Fig. S1) was a kind gift from Nikkol (Japan). Chloroform, $HAuCl_4$, methanol, tetrahydrofuran, acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, acetic acid, dichloromethane, tetrachloromethane, n-pentane, and n-hexadecane were purchased from Shanghai National Pharmaceutical Group Corporation. All other chemicals were analytical grade and used as received.

2.2. Instrumentation

The prepared gold nanostructures were characterized by transmission electron microscopy (TEM) (JEM-100CX II (JEOL)) and UV-vis spectroscopy (Hitachi U-4100).

2.3. Fabrication of BPS-30 capped gold nanoparticles (BPS-GNPs)

The BPS-GNPs were prepared according to our previous report [12]. In a typical synthesis procedure, 2.0 mL of BPS-30 (75 mM) and 0.15 mL of $HAuCl_4$ (10 mM) solutions were added into 0.85 mL of water at room temperature. The mixture was allow to sit, unstirred, for 4 h. The obtained gold nanoparticles were collected by centrifugation and washed thoroughly with deionized water. The obtained BPS-GNPs were added into 5.0 mL water to prepare the BPS-GNP aqueous solution for the detection of chloroform.

2.4. Detection of chloroform in aqueous solution

The detection of chloroform in aqueous solutions was performed at room temperature. For an additional volume of chloroform larger than 5 μL (for an additional chloroform/solution volume ratio (R) larger than 1:1000), the chloroform was directly added to 5.0 mL of BPS-GNP aqueous solution by microsyringe. If the necessary chloroform volume was too small (<5 μL), the chloroform was first diluted into alcohol before addition into 5.0 mL of BPS-GNP aqueous solution. After addition, the mixture was shaken vigorously for 5 s.

In control experiments, chloroform was replaced with other organic substances.

3. Results and discussion

In the previous report, we explained the superior stability of BPS-30 capped gold nanoparticles (BPS-GNPs) using Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [12]. The layer of hydration water, caused by the long oxyethylene chains of BPS-30, promotes the resistance of BPS-GNPs to high concentrations of inorganic electrolyte aqueous solutions. As shown in Fig. 1a, the adsorption peak at ~530 nm was attributed to the surface plasmon resonance (SPR) of spherical gold nanoparticles (Fig. 1a) [13]. Interestingly, addition of chloroform results in dramatic changes in the UV–vis spectra of the BPS-GNP aqueous solutions (Fig. 1b-f, and the enlarged optical image is presented in Fig. S2). Upon addition of chloroform/BPS-GNP aqueous solution at a volume ratio (R) of 2:1000, the SPR peak decreased greatly in intensity with no evident shift. At the same time, the BPS-GNP solution obviously faded in color immediately. For a value of R in the range of 4:1000–8:1000, the BPS-GNP solutions became opaque and turbid. The spectra show a broad adsorption bond without any peak (Fig. 1c-e). When more chloroform is added (R = 10:1000), the BPS-GNP solution seems to be colorless and turbid, and all the adsorption bonds disappear in the UV–vis spectrum (Fig. 1f). The corresponding TEM images of the monodisperse and aggregate BPS-GNPs are shown in Fig. 2. These images are in accordance with the results of UV–vis spectra. It is worth noting that the precipitates in the samples were distinctly increased in mass with additional chloroform. Thus, chloroform detection in BPS-GNP solution can be easily realized by naked eye by monitoring color fading or the appearance of precipitate.

Many groups have examined the detection of heavy metal ions (Hg^{2+}, Cr^{3+}, Pb^{2+}, and Mn^{2+}) or organic material (hydrazine, dichlorvos, and dopamine) using various gold nanostructures [8–11,14–19]. The strong coordination between the capping agent and the determinant leads to the aggregation of gold nanostructures. The color of gold nanoparticle solutions can change from red or pink to blue grey or violet, and the solutions remain clear and transparent in the detection process. However, there are few reports of the detection of chloroform by gold nanostructures. This may be because it is difficult for the simpler structure of the chloroform molecule to effectively interact with capping agents. In our system, the discolored BPS-GNP solution became turbid with the addition of chloroform (Fig. S2). Our results allow the proposal

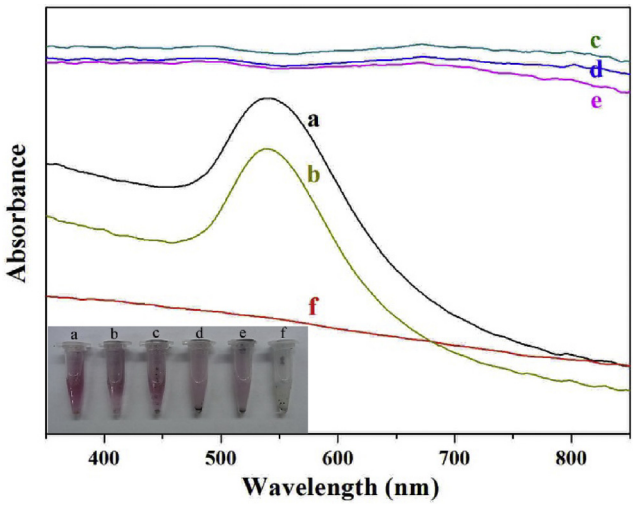

Fig. 1. UV–vis spectra of (a) the as-prepared BPS-GNP solution and (b-f) after the addition of different volumes of chloroform: R = 2:1000 (b); 4:1000 (c); 6:1000 (d); 8:1000 (e); 10:1000 (f). The inset image is the corresponding optical image of the samples.