



Gold nanorod-based mercury sensor using functionalized glass substrates

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ABSTRACT

We report on the development of a gold nanorod-based mercury sensor, immobilizing these anisotropic metal nanoparticles on glass substrates. This novel approach is expected to find applications in the measurement of mercury traces in stream-flow. We present first a “modified” wet chemistry procedure to functionalize glass surfaces with gold nanorods, which confer control on the density of particles on the glass substrate. Then, we demonstrate that this mercury sensor, using immobilized gold nanorods on glass substrates, retains the outstanding selectivity of our previously reported mercury sensor using suspended gold nanorods, presents an extraordinary sensitivity and, does not require any sample separation and/or sample pre-concentration. The analytical figures of merit demonstrate precise and accurate analysis at the parts-per-billion level, figures with great potential for monitoring low levels of mercury in flowing water. The entire procedure in solution takes less than 60 s.

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1. Introduction

Mercury (Hg) is considered a highly toxic heavy metal that is widely dispersed in the environment and can be found in water, air and soil [1]. This pollutant, mainly released to the atmosphere from power plants, burning fossil fuels, and solid waste incineration [2], is a recognized hazardous contaminant that accumulates in living organisms [3,4]. Upon the extended exposure to low levels of Hg, mostly from natural waters [5–7], humans can be severely harmed and suffer from brain, heart, kidney, lung, and immune system damage [8–10]. The dangerous consequences on public health mentioned above, represent a global problem demanding solutions. Therefore, the development of selective and sensitive methods to monitor traces of this metal and to understand its distribution, contamination potential, and bioaccumulation, have been the aim of study of many scientists of our community during the last two decades [11].

Among the most established techniques, used to detect Hg at the parts-per-billion level, there is Gas Chromatography–Inductively Coupled Plasma–Mass Spectrometry (GC–ICP–MS) [12], Atomic Fluorescence Spectrometry (AFS) [13,14], Atomic Absorption Spectroscopy (AAS) [15,16], Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) [17], and reversed-phase High

Performance Liquid Chromatography (HPLC) [18]. Although these techniques have been proven to offer excellent performance, they require elaborate and time-consuming sample preparation and pre-concentration procedures, as well as costly and bulky equipment that limit their practical application in the field. This last point is a desired feature for real-time Hg determination and speciation on-site.

In order to surmount these barriers, novel approaches using optical test strips [19], polymers [20], remote electrochemical sensors [21], molecular probes [22,23], ion-selective electrodes [24], optical fibers [25], oligonucleotides [26–28] and proteins [29], fluorescence-based sensor membranes [30], piezoelectric quartz crystals [31], carbon nanotubes [32], quantum dots [33], metal nanoparticles [26,28,34–38], and gold (Au) based gravimetric [39,40], resistivity [41] and reflectivity [42] sensors, have promoted the growth of this field in recent years.

Although most of these approaches provide low detection limits and fast response times, they lack procedural simplicity for on-site analysis and/or are susceptible to interferences from other heavy metal ions and the formation of Hg²⁺ complexes. In addition, their applicability is typically limited to solutions.

In an attempt to find an approach that could overcome the existent limitations in mercury sensing, few years ago we reported the development of an original mercury sensor based on the spectral shift of the longitudinal surface Plasmon resonance (SPR) band of Au nanorods (Au-NRs) in the presence of Hg(0) in solution [43]. The strong affinity and specificity between Au and Hg conferred our sensor a high selectivity in front of other metal ions and Hg²⁺ complexes. In addition, it offered the desired procedural simplicity

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for field applications and a sensitivity range in the low part-per-trillions. However, the determination of Hg was still restricted to solutions. In order to extend the application of our Hg sensor to stream-flow, we have recently explored the possibility of using immobilized Au-NRs on glass substrates.

In this article we report on a “modified” wet chemistry procedure to functionalize glass substrates with Au-NRs, controlling the density of particles on the glass surfaces to avoid the surface Plasmon coupling between neighbor nanoparticles, an effect that could decrease the sensitivity of the sensor. We demonstrate that this new Hg sensor retains the outstanding selectivity of the original sensor and presents a high sensitivity in the low parts-per-billions. In addition, it does not require any sample separation and/or sample pre-concentration. The limit of detection (1.0 $\mu\text{g/L}$) shows excellent potential for monitoring traces of mercury in flowing water.

2. Experimental

2.1. Chemicals and materials

Analytical-reagent grade chemicals were used in all experiments. Hexadecyltrimethylammonium bromide (CTAB) ($\text{C}_{19}\text{H}_{42}\text{BrN}$), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$), silver nitrate (AgNO_3), sodium borohydride (NaBH_4) and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) were purchased from Sigma–Aldrich. Mercury(II) chloride (HgCl_2), potassium fluoride (KF), lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$), barium chloride (BaCl_2), copper nitrate ($\text{Cu}(\text{NO}_3)_2$), arsenic trioxide (As_2O_3), chromic nitrate ($\text{Cr}(\text{NO}_3)_3$), sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were purchased from Fisher chemicals. All deionized (DI) water used was obtained from a Milli-Q Millipore integral water purification system. All glassware was cleaned with aqua regia and rinsed with DI water prior to the preparation of solutions. Silane coated glass slides with APTMS (3-aminopropyltrimethoxysilane) were obtained from Lab Scientific Inc.

2.2. Synthesis of Au-NRs and functionalization of glass substrates

2.2.1. Gold nanorods

Gold nanorods (GNRs) were synthesized via a modified seed-mediated growth method based on the procedure reported by El-Sayed and co-workers [44].

2.2.2. Seed solution

A 10 mL aqueous solution containing 5.0 mL of 0.2 M CTAB and 5 mL of 0.5 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was prepared. Then, 740 μL of an ice cold aqueous 0.01 M freshly prepared NaBH_4 solution was added to the previous solution, all at once while stirring. Using 740 μL of NaBH_4 solution instead of the 600 μL recommended in the literature [44], the solution turned brownish yellow immediately, indicating the formation of nanoparticles. The seed solution was kept at 25 °C and used within 2–5 h after preparation.

2.2.3. Growth solution

5.0 mL of a 0.2 M CTAB solution was mixed with 65 μL of 4.0 mM AgNO_3 at 25 °C. Then, 5.0 mL of a 1.0 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was added followed by gently adding 240 μL of a 0.0788 M freshly prepared ascorbic acid solution. The orange color of the gold salt dissolved in the CTAB solution disappeared when ascorbic acid was added, indicating the occurrence of a mild reduction of gold.

2.2.4. Synthesis of Au-NRs

12 μL of the seed solution, at a temperature between 27 and 30 °C, was added to the growth solution without stirring. The

solution color gradually changed to dark blue within 10–20 min, indicating the formation of the Au-NRs (longitudinal SPR band was centered at 625 nm). By using slightly greater quantities of AgNO_3 and Ascorbic acid (on the growth solution) than those reported in the literature [44], we were able to synthesize, in a reproducible manner, Au-NRs of aspect ratio (AR) between ~ 1.6 and 1.9.

2.2.5. Cleaning Au-NRs

In order to remove CTAB from Au-NRs, the growth solution was centrifuged for 2 h at 7100 rpm and then re-suspended. The supernatant was withdrawn by decantation. This procedure was repeated twice. The precipitate was then collected and re-dispersed in DI water to obtain a clean Au-NRs solution necessary for the functionalization of glass substrate (longitudinal SPR band was centered at 615 nm).

2.2.6. Preparation of glass substrate

Silane coated glass slides were cleaned in piranha solution at 70 °C for 1 h. This procedure removes any residual oxide layer on the surface of the glass slides before their functionalization. After cleaning, the glass slides were rinsed with DI water and stored fully submerged in DI water to prevent oxidation by air.

2.2.7. Functionalization of glass substrates with Au-NRs

As shown in Scheme 1, cleaned Silane coated glass slides were placed in a beaker containing 5 mL of Au-NRs solution (left side of the diagram), for 24 h at 25 °C (center of the diagram). The functionalized glass slides were then rinsed with DI water and dried in the oven at 70 °C for 15 min (right side of the diagram). By controlling the initial amount of Au-NRs in solution, an optimal density of particles on the glass substrate of approximately 55 Au-NRs/ μm^2 can be obtained. The density of particles was determined by counting manually the number of GNRs per area on TEM pictures of different substrates. After the Au-NRs were attached to the glass substrate, their longitudinal SPR band was centered at 570 nm.

2.2.8. Mercury detection using Au-NRs/glass substrates

Au-NRs/glass slides were placed in a beaker containing 50 mL of 0.01 M NaBH_4 . The solution was continuously stirred to assure homogeneous contact of the functionalized substrate with the reducing agent (longitudinal SPR band was centered at 565 nm). Twenty-five different aliquots of 40 μL of 0.15 mM HgCl_2 (6.0×10^{-9} mol) were injected into the beaker, as exemplified in Scheme 2. The Au-NRs/glass slides were left fully submerged in the mercury containing solution for ca. 5 min after each injection. Then, the substrates were removed from the solution, rinsed with DI water and air-dried before measuring the UV–vis spectrum through them. This procedure was repeated after each aliquot was added. Scheme 2 illustrates the change in the GNRs length after the addition of consecutive aliquots of Hg(II) to the sodium NaBH_4 solution. In this diagram one can understand how GNRs of initial AR = 1.8 transform, progressively, into gold nanospheres of diameter equal to the initial width of the GNRs (30 nm). The change in the GNRs AR is represented by the change in color of the functionalized substrate. Because GNRs are very stable in aqueous solution, the lifetime of the sensor only depends on the exposure time of these nanoparticles to liquid mercury, i.e. the necessary time to make enough Hg(0) transform the original GNRs into nanospheres.

2.2.9. Interferences

In order to measure the effect of interference from several inorganic ions as potential contaminants found in drinking water, according to the EPA, eight Au-NRs functionalized glass slides,

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