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Gold nanoparticle modified silicon nanowire array based sensor for low-cost, high sensitivity and selectivity detection of mercury ions

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Abstract

Heavy metals are the main factor of water pollution which seriously threaten residents and aquatic life. Here, we demonstrated a mercury ion (Hg²⁺) sensing device based on gold nanoparticles modified silicon nanowire array for highly sensitive, selective and stable detection of mercury ion. Decorated with gold nanoparticles to increase the number of the thiol groups serving as Hg²⁺ sensitive probe and improve performance, the silicon nanowire array based sensor had a large response electric signal in detecting low concentration mercury ion. Importantly, the devices exhibits excellent mercury ion sensing attributes in the range of 1 ng/l–10 μg l⁻¹ with a fairly low detection limit of 0.06 pM. With similar accuracy to ICP-MS, we detected a know sample (1 μg l⁻¹) and unknown sample in less than 1 min. Additionally, the low-cost fabricated process and label free analysis in river water sample make it a potential method in inspecting mercury in water quality.

1. Introduction

As one of the most toxic and ubiquitous heavy metal pollutants, mercury is seriously harmful to human health and environmental safety. Mercury exits in various forms such as metal oxide, metal ions and organic complexes. Among them, mercury ions (Hg²⁺) is most stable form and even Hg²⁺ in water could threaten human health, thus the rapid and sensitive detection of Hg²⁺ is of great significance to environmental protection and human health. World Health Organization (WHO) guidelines have prescribed a limit of 1 μg l⁻¹ for Hg²⁺ in drinking water [1, 2]. Therefore, it is very important to develop platforms for the detection of mercury ions. In the past few decades, a large variety of analytical techniques have been used to sensitively detect Hg²⁺, such as high-performance liquid chromatography (HPLC) [3–6], atomic fluorescence spectrometry (AFS) [7, 8], inductively coupled plasma mass spectrometry (ICP-MS) [9–12], atomic absorption spectrometry (AAS) [13–16] and so on. However, these traditional detection approaches require expensive instruments and complex sample processing procedure, resulting in high costs. Other colorimetry or fluorescence based approaches using optical methods have demonstrated their capability to detect heavy metal ions [17–19]. However, these detection approaches possess some obvious disadvantages including the insufficient sensitivity and the relative long detection time. Electrochemical and photoelectrochemical methods have also been widely used for the detection of metal ions due to their merits of low detection limit, high sensitivity and suitability for in situ applications. Ratner et al studied the electrochemical detection of Hg on GC and ITO electrodes modified with Au NPs and accomplished a remarkably lower detection limit of 1 μM l⁻¹ Hg using electrostatically adsorbed Au NPs on ITO. In addition to increasing the sensitivity, modification by Au NPs resulted in sharper and more reproducible Hg stripping peaks. Yan et al developed a ‘turn-on’ photoelectrochemical DNA sensor for the detection of Hg²⁺ which had highly sensitive, selective and robust. Under the optimized conditions, a detection limit of 0.02 nM was obtained [20–22]. However, they need relative long time scale of analysis.
Recently, nanomaterials have been widely used in the field of biochemical sensors due to their unique structure and properties [23–26], which makes them promising materials in the application of environmental monitoring. Xu et al used nanostructured magnesium silicate hollow spheres to enhance electrochemical response for heavy metal ions detection of 0.375 nM [27] with complex electrode modifications. Kim et al reported the carbon nanotubes-based FET devices for the selective detection of Hg$^{2+}$ ions from 1 nM to 1 mM [28], Sudibya et al demonstrated graphene-based sensor for detecting Hg$^{2+}$ ion of about 1 nM [29], but the limit of detection (LOD) still needs to be enhanced.

As one of the typical one-dimensional nanomaterials, silicon nanowire (SiNW) is also widely studied for its high surface to volume ratio and CMOS-compatibility. Luo et al applied bottom-up fabricated SiNWs as sensing channels in a chemical gate FET to detect Hg$^{2+}$ ions, which could measure the concentration down to 10$^{-7}$ M [30]. However, the bottom-up approach may not be a good candidate for mass production. Our team has investigated SiNW with top-down approach, comparing with the bottom-up [31, 32] approach, the top-down [33–35] approach using lithography techniques can precisely control the position of the SiNWs and provide large-scale and low-cost fabrication ability for SiNW-based devices. In our previous report [36], we detected Hg$^{2+}$ as low as 1 ppt with the MPTMS functionalized SiNW, but its stability and sensitivity still needs to be further improved for practical application.

In this paper, we design a novel stable and high-performance sensor based on gold nanoparticles (GNPs) modified SiNW array for mercury ion (Hg$^{2+}$) detection (as shown in figure 1). The GNPs are self-assembled on the nanowire surface by the help of 3-Aminopropyltriethoxysilane (APTES) and two thiol groups chemical molecule dithiothreitol were subsequently functionalized on the GNPs surface, remaining one thiol group to recognize the Mercury ions. The new GNPs functionalization strategy improves the electrical properties of the SiNW array by increasing the surface area and the number of probes so as to adjust the gate voltage and promote the channel carrier transfer of nanowires. Compared with simple chemical modification, the new functionalization method amplified the response signal. The GNPs modified SiNW array based sensor possessed high sensitivity and selectivity for stable mercury detection and even real-time environmental monitoring.

2. Materials and methods

2.1. Materials

(3-Mercaptopropyl)trimethoxysilane (MPTMS), 3-Aminopropyltriethoxysilane (APTES), Ethanolamine were purchased from Sigma-Aldrich (USA). GNPs was purchased from BBI. Solutions (Shanghai China), the
concentration of 5 nm/15 nm gold particles is 83 nM/2.33 nM, and both are considered to be citrate coated. Dithiothreitol and Water Sample Mercury Ion (Hg$^{2+}$) Concentration Assay Kit were purchased from Beijing Solarbio Science & Technology Co., Mercury and other heavy metal standard solutions were purchased from Ltd, Guobiao (Beijing) Testing & Certification Co., Ltd (GBTC) and were diluted by deionized water. River water samples were collected in industrial area river.

2.2. Fabrication of SiNW array based sensor

The fabrication for the SiNW array based sensor was firstly covered with a 100-nm-thick silicon nitride (Si$_3$N$_4$) layer. Then, the top layer of silicon on the SOI wafer was etched reaching the oxide layer by deep reaction ion etching to form two adjacent rectangular etched cavities. Based on the anisotropic wet-etching mechanism, a silicon wall with self-stop etching (1 1 1) planes was formed between the adjacent etched cavities with a controllable size-reduction process. After the self-limiting oxidation, the SiNW with an inverted-triangle shaped cross-section was generated on the top center of the wall. Importantly, a top-grid electrode was simultaneously fabricated on the suspended silicon nitride film, which could protect the whole SiNW from breakage when the silica wall was removed. After removing the wall, the single SiNW was finally fabricated [37, 38].

In our fabrication method, there were a special protective structure to keep the silicon nitride film on the surface of the silicon wafer, we designed and manufactured a gate on the suspended silicon nitride film. This gate structure could not only adjust the conductivity of SiNW channel, but also comprehensively protect the SiNW from fracture for various reasons. This structure greatly improves the yield of the device. At present, the yield of SiNW devices in this paper is more than 90%. The SiNWs were attached to silicon nitride. Because silicon nitride and silicon oxide had good corrosion selectivity ratio in hydrofluoric acid corrosion, silicon nitride could play a good role in protecting SiNWs when removing the oxide layer.

2.3. Modification with $-\text{NH}_2$ or $-\text{SH}$

In order to functionalize our sensor, the SiNW array was firstly treated with oxygen plasma for 300 s. Then SiNW array was immersing in APTES solution (2% ethanol) overnight with the amino groups terminal on the surface of nanowire. The SiNW array based sensor was then washed with absolute ethanol to remove unreacted APTES. Followed by heating the device at 120 °C for 5 min, a stable self-assembled monolayer with a terminal amino group modified sensor was prepared.

Replacing the APTES with MPTMS(2% ethanol) and repeating the process, and we prepared a self-assembled monolayer with a terminal thiol group modified sensor.

2.4. Modification with small GNPs and DTT

For the preparation of GNPs modified sensor, we firstly functionalized the sensor with APTES as the former process to produce the terminal amino group, then the size of 5 nm GNPs were dropped on the surface of SiNW array for 2 h at room temperature to form GNPs monolayer, then washed twice with the deionized water. Finally, the two thiol group chemical molecular dithiothreitol(30.85 g l$^{-1}$) was added to the surface of GNPs for 2 h and washing by the deionized water, then the amplified thiol group 3D layer were prepared.

2.5. Electrical measurements

The devices operate as FET. When the polar molecules like different heavy metal ions are adsorbed on the surface of the decorated silicon nanowire array, the grid voltage changes, resulting in the change of source drain current measured in a semiconductor parameter analyzer (Keithley 4200-SCS).
3. Results and discussion

3.1. Fabrication of SiNW array based sensor

A top-down fabrication technology was used to develop SiNW array sensor on commercial SOI (111) wafer, by conventional microfabrication process. After the fabrication processes, the wafer was cut and each part was glued and gold-wire-bonded on a printed circuit board (PCB), forming a sensor chip (figure 2(a)). For each chip, there were hundreds of high-quality SiNWs with the same dimensions. As shown in figure 2(b), the 160 well-ordered SiNWs were arranged on a chip as the core sensing part. The high-quality SiNW array chip could effectively reduce noise of background compared with single SiNW based sensor chip. Because the diameter of each SiNW in the SiNWs array were excellent uniformity, the current signals of SiNW in the array could be overlapped with each other, which made the total current signal stronger and more stable. At present, most of the current signals of single SiNW reported in the literature were at the nA level, which required expensive and precise testing equipment to complete the detection. However, the signal generated by our SiNW array based sensor in this paper was at the μA level, and the signal had been greatly improved. For each SiNW, it can be observed after removing the oxide, to give lateral dimensions of about 90 nm. The scanning electron microscopy (SEM) image of a wire SiNW was shown in figure 2(c) which serve as one sensing unit.

Figure 3. (a) Schematic diagram of GNPs-decorated SiNW sensor for mercury ion (Hg$^{2+}$) detection. (b) Schematic illustration of SiNW surface modification process. (c) the GNPs of 15 nm were self-assembled on the surface of single SiNW. (d) The I-V curves of the sensor before and after modification. (e) shows the I-V curves of the sensor before and after modification.
3.2. Characterization of GNPs modified sensor

After the depletion p-type SiNW array based sensor was prepared. The thin silicon oxide layer facilitates surface modification of SiNW array, since sensitive groups can hardly attach to hydrogen terminated surfaces of SiNW array after hydrogen fluoride acid etching. Figure 3(a) illustrates the whole modification process and the complexation process between Hg$^{2+}$ and thiol groups. In the complexation process, the H$^+$ was released after reaction, leading to conductance of SiNW changing. In the modification process, GNPs were added after APTES modification. Figures 3(b), (c) shows the GNPs of 15 nm are self-assembled on the surface of single SiNW. Electronic energy spectrum of gold particles modified nanowire is shown in figure 3(d), compared with spectrum of nanowire before modification, there are energy spectrum peaks of gold, which proves the gold particles are modified successfully. The modification of GNPs is the key process in the modification which influencing the performance of sensors by increasing the surface area and the number of probes.
As for the whole modification process, figure 3(e) shows the I–V curves of the sensor before and after modification. The linear I–V characteristics indicate that ohmic contact is formed between SiNW and the electrodes. Furthermore, the modification makes the conductance of the SiNW array increase.

3.3. High performance of GNPs modified sensor

Different recognition layer has a great influence on the nanodevices, the electrical performance even varies with the density and uniformity of the recognition layer. In order to eliminate the influence of amino group and compare with previous functionalization approaches [35], three different functionalization approaches of SiNW were carried out in our research: (a) 3-Aminopropyltriethoxysilane (APTES) (figures 4(a)), (b) 3-Mercaptopropyltrimethoxysilane (MPTMS) (figures 4(b)), (c) Amination followed by covalent attachment of small size GNPs through the interaction of amino groups with gold and thiolation with DTT (figure 4(c)). A relative current change representing the sensitivity of the SiNW device induced by the binding of the targets can be defined as: sensitivity = ΔI/I₀ (ΔI = I – I₀). Compared with the other two functionalization approaches, the current change ΔI/I₀ (ΔI = I – I₀) increased by more than 150%, the modified gold particles had little effect on the response time, but the response signal to the same concentration increased. It is also obvious that the response range tends to widen after gold particles were modified (figure 4(e)).
| Detection method                              | Detection limit | Cost       | References          |
|----------------------------------------------|-----------------|------------|---------------------|
| Mercury ion (Hg^{2+}) assay kit              | 1 ng l^{-1}     | 75 dollar  | Tested              |
| BiNPs@Gr-CNTs modified carbon electrode      | 500 nM          | 1.5 dollar | Commercial          |
| ssDNA aptamer GFET array                     | 0.2 nM          | ~1 dollar  | [40]                |
| SiNW based FET                               | 40 pM           | /          | [41]                |
| GNP decorated nanowire array                 | 0.1 μM          | /          | [30]                |
| GNPs decorated nanowire array                | 12 pg l^{-1} (0.06 pM) | ~0.4 dollar | This work           |

3.4. Highly sensitive and selective detection of GNPs decorated nanowire sensor

For the high sensitive analysis, we gradient diluted the $10^6 \mu g l^{-1} Hg^{2+}$ with deionized water and performed the detection process on a semiconductor parameter analyzer (Keithley 4200-SCS). Because of the amplification effect of GNPs, the nanowire array based sensor had a highly sensitivity in low concentration Hg^{2+}. In figure 5(a), the real-time response to mercury ions ranging from 1 ng/L to 10 μg l^{-1} was showed. Linear relationship between the logarithmic concentration of metal ions and the current change was observed in figure 5(b), the linear equation was $Y = 178.287 + 31.236lgc(Hg^{2+})$ and the correlation coefficient was 0.995, the detection limit was about 0.06 pM after calculating by $3\sigma$ method [39]. And when the concentration of 1 ng/L mercury ions was flowed through the sensor surface, a rapid increase of the electrical current was observed in figure 5(c), the sensor showed excellent electrical properties and highly sensitive for recognizing mercury ion solutions with significant signal to noise ratio. In order to identify the selectivity of the sensor, Mercury and other heavy metal solutions of the same concentration were flowed through the sensor surface, In figure 5(d) and figure 5(e), the real-time response and bar plots to various metal ions with the concentration of 10 μg l^{-1} are shown. The sensor shows better selectivity to Hg^{2+} compared with others because of the specific combination of thiol group and mercury. Sulphydryl group is a typical soft basic coordination group, which can form a stable complex with soft acid ions. However, the larger radius of mercury ion, the less positive charge and the higher polarizability will make the compound more stable. The standard deviation for Hg^{2+} measured by different devices is represented by the error bar in the graph. In figure 5(e), the standard deviation for Hg^{2+} is 0.064. Compared with other similar detection methods and sensors (table 1), the constructed sensor presented low-cost, high sensitivity detection of mercury ions.

3.5. River water sample analysis

We applied the GNPs modified SiNW array based sensor for detecting mercury ions in unknown river samples and the concentration of 1 μg l^{-1} known samples. The result was shown in the figure 5(f), the red histogram indicated the results analyzed by inductively coupled plasma mass spectrometer (ICP-MS). The green histogram were the results tested by our sensor and the blue one was tested by mercury ion (Hg^{2+}) assay kit respectively. As shown in the figure, the detection result of GNPs-decorated nanowire array sensor is closer to the calibration value. This shows the advantages of our device in low concentration detection.

4. Conclusion

In summary, we demonstrated the fabrication and operation of a mercury ion sensor with high performance. The SiNWs array was the core sensing part, it was depended on top-down preparation technology and low-cost fabricated methods with a conventional microfabrication process, many high-quality SiNWs with the uniformity dimension leaded to the accuracy of each SiNWs based sensor, because the decreased random noise made the total current signal stronger and more stable. The GNPs were used to provide large surface areas for terminal thiol groups, thus both enhancing the sensitivity to mercury ion with firstly reported LOD of 0.06 pM. The developed device exhibits great selectivity for Hg^{2+} over other heavy metal ions. Remarkably, the present sensor was applied for detecting mercury ion in river water and shown great potential to be used in environmentally toxic mercury detection. Overall, the low-cost fabrication procedure and the excellent sensing performance of the sensor made it promising for contaminant detection of Hg^{2+} in water environment.

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