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Short communication

Photoelectrochemical determination of inorganic mercury ions based on energy transfer between CdS quantum dots and Au nanoparticles

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ABSTRACT

A novel photoelectrochemical (PEC) sensor for mercury ions (Hg^{2+}) was fabricated based on the energy transfer (ET) between CdS quantum dots (QDs) and Au nanoparticles (NPs) with the formation of T–Hg^{2+}–T pairs. In the presence of Hg^{2+} ions, a T-rich single-strand (ss) DNA labeled with Au NPs could hybridize with another T-rich ssDNA anchored on the CdS QDs modified electrode, through T–Hg^{2+}–T interactions, rendering the Au NPs in close proximity with the CdS QDs and hence the photocurrent decrease due to the ET between the CdS QDs and the Au NPs. Under the optimal condition, the photocurrent decrease was proportional to the Hg^{2+} concentration, ranging from 3.0×10^{-9} to 1.0×10^{-7} M, with the detection limit of 6.0×10^{-10} M.

1. Introduction

Due to its high toxicity at low concentrations and the bioaccumulative effect in the human body, mercury (Hg^{2+}) contamination has been recognized as a severe worldwide problem [1,2]. It is therefore of topical interest to develop rapid, sensitive, selective and cost effective methods to detect Hg^{2+} in the presence of other background ions. The Environmental Protection Agency (EPA) standard for the maximum allowable level of Hg^{2+} in drinking water is 2×10^{-6} g L^{-1} [3]. Addressing this issue, various Hg^{2+} sensors based on metal nanoparticles [4,5], biomaterials [6], and proteins [7,8] have been developed to date. Recently, the coordinative interaction between Hg^{2+} and thymine bases has prompted many new platforms for Hg^{2+} sensors with good performance [9–11]. Specifically, thymine–thymine (T–T) mismatches in DNA duplexes would attract Hg^{2+} in aqueous solution to form stable DNA duplexes with T–Hg^{2+}–T pairing, which ensures excellent selectivity [12].

Photoelectrochemical (PEC) analysis is a newly appeared yet rapidly developing technique for sensing application with low background and good analytical performance [13,14]. Numerous researches have focused on the PEC approach that involves the use of various nanometer materials, such as semiconductor quantum dots (QDs) and Au nanoparticle (NP) [15,16]. Interesting, Au NP has been found as a unique quencher for QDs through energy transfer when the two particles are in close proximity [17,18], our group has previously reported its first application in the PEC DNA detection [19]. On the other hand, ion detection is of significant importance in the field of bioanalysis, and to date some works have explored the application of PEC method in ion detection [20]. However, to our best knowledge, there's no work have been done with the energy transfer-based strategy in such field [21–23].

In this communication, a sensitive and selective PEC sensor for Hg^{2+} was fabricated based on energy transfer between CdS QDs and Au NPs with the formation of T–Hg^{2+}–T pairs. As shown in Scheme 1, with the presence of Hg^{2+} ions, two T-rich DNA oligonucleotides could form T–Hg^{2+}–T hybrid structure and the CdS QDs and Au NPs would be in close distance, which will result in the inter-particle energy transfer and thus the decline of the photocurrent [19]. The experimental results demonstrated that the proposed platform could achieve the selective sensing of Hg^{2+}.

2. Experiment

2.1. Reagent

The oligonucleotides (Probe DNA: 5′-NH_2-$(CH_2)_6$-TTT-TTT-TTT-TTT-3′, Target DNA: 5′-SH-$(CH_2)_6$-TTT-TTT-TTT-TTT-3′) were obtain from Sangon Biotech (Shanghai, China) Co., Ltd. Thioglycolic acid (TGA), ascorbic acid (AA), N-(3-Dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC), poly(dially-ldimethylammonium chloride) (PDDA; 20%, w/w in water, MW = 200,000–350,000), and sodium borohydride were purchased from Aladdin (Shanghai, China). N-hydroxysuccinimide (NHS), Monoethanol Amine (MEA) and $AuCl_3 \cdot HCl \cdot 4H_2O$ were purchased from Sinopharm Chemical

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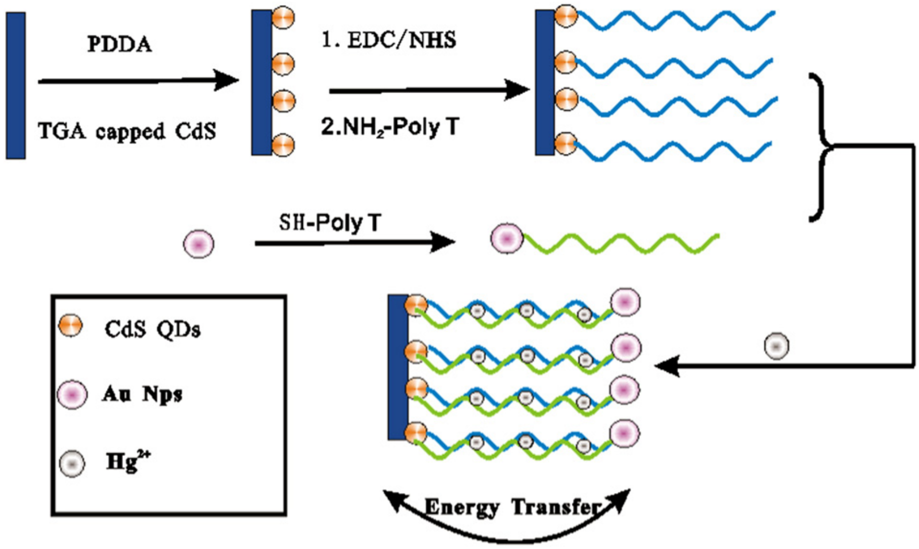

Scheme 1. The development process of the developed PEC sensor.

Reagent Co., Ltd. Other chemicals were of analytical grade. The washing buffer solution was PBS (0.01 M, pH 7.4). The blocking buffer was 0.01 M MEA. 0.1 M PBS containing 0.1 M AA was used as the electrolyte solution for photocurrent measurements. All aqueous solutions were prepared using ultrapure water (MilliQ, Millipore).

2.2. Apparatus

A 500 W Xe lamp was used as irradiation source with the light intensity of about 400 μW cm^{-2}. Photocurrent was measured on a CHI 850c with a three-electrode system: a 0.25 cm^2 modified ITO as the working electrode, a Pt wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. All the photocurrent measurements were performed at a constant potential of 0 V (versus Ag/AgCl). Atomic force microscopy (AFM) was carried out with a MicroNano AFM-III to characterize the surface morphology of the electrodes.

2.3. Synthesis of Au NPs and Au NPs labeled target DNA

All glassware and mechanical stirrers were thoroughly cleaned in aqua regia before the synthesis of Au NPs, then, carefully washed by ultrapure water, then, oven-dried prior to use. The colloidal solution of Au NPs was synthesized according to our reported literature [24]. Briefly, an amount of 0.6 mL of 0.1 M sodium borohydride solution prepared by ice water was gradually added to the constantly stirring 20 mL of 2.5×10^{-4} M $HAuCl_4$ in the round-bottomed flask. The solution was stirred for 10 min in ice water, the color changed from light yellow to wine red. Then being stirred for 3 h at room temperature. After the reaction, the solution was kept in 4 °C refrigerator for future use. According to literature with slight modification [25,26], 10 μL 50 μM target DNA was added to 490 μL colloidal Au NPs solution (contain 0.1 M NaCl), then gently swung 12 h at the room temperature. To remove unreacted target DNA, the Au-DNA was purified two times by centrifugation at 15 000 rpm for 30 min. The final product was re-dispersed into 100 μL of 0.01 M PBS buffer (0.1 M, pH 7.4). Then, the solution stored at 4 C for future use. The size of Au NPs is about 5 ± 1 nm by TEM measurement.

2.4. PEC sensing for Hg^{2+} detection

The synthesis of TGA-stabilized CdS QDs was according to the previous report [27]. Then the probe NH_2-DNA was immobilized onto the surface of CdS QDs modified ITO electrode via the classic EDC coupling reactions [28]. In detail, the CdS QDs modified ITO electrode was activated by dipping into 1.0 mL of ultrapure water containing 20 mg of EDC and 10 mg NHS for 50 min at room temperature, followed by thoroughly rinsing with washing buffer (0.01 M PBS, pH 7.4). Next, 10 μL of 2 μM Probe NH_2-DNA was dropped onto the surface of CdS QDs modified electrode for incubation overnight at 4 °C, then washed with washing buffer. Subsequently, the electrodes were blocked with 1 mM monoethanol amine solution for 2 h at 4 °C and then washed thoroughly. After that, 10 μL of target DNA labeled with Au NPs prepared above and 10 μL of various concentration of Hg^{2+} were spread

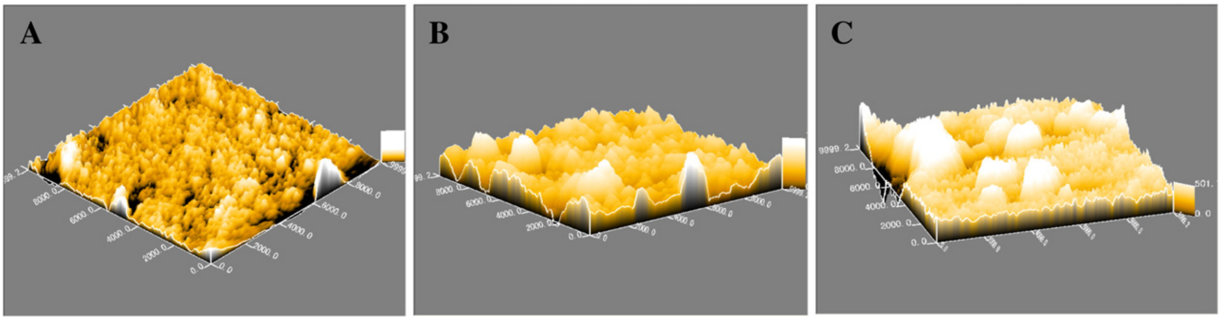

Fig. 1. AFM image of (A) CdS modified ITO electrode; (B) fabricated with probe NH_2-DNA, then blocked with 1 mM MEA; (C) after hybridization with the target DNA labeled with Au NPs and 30 nM Hg^{2+} ion.