



Aggregation induced photoacoustic detection of mercury (II) ions using quaternary ammonium group-capped gold nanorods

Yan Huang^{a,1}, Fan Li^{a,1}, Gongcheng Ma^a, Wuwei Yang^a, Xiaofen Zhang^b, Jing Lin^a, Yongxiang Luo^{a,*}, Peng Huang^{a,*}

^a Guangdong Key Laboratory for Biomedical Measurements and Ultrasound Imaging, Laboratory of Evolutionary Theranostics, School of Biomedical Engineering, Health Science Center, Shenzhen University, Shenzhen 518060, China

^b School of Public Health, Xiamen University, Xiang'an South Rd, Xiamen 361102, China

ARTICLE INFO

Keywords:

Photoacoustic detection
Gold nanorods
Sulfhydryl group
Mercury ions
Aggregation

ABSTRACT

Photoacoustic imaging is an emerging detection tool of metal ions. Mercury is a typical heavy metal pollutant that can cause severe water and soil pollution. Therefore, it is particularly meaningful to develop a photoacoustic probe with excellent selectivity and sensitivity for the detection of mercury ions. In this study, gold nanorods modified with (11-mercapto-undecyl)-trimethylammonium (MTA) molecules containing sulfhydryl groups were designed and synthesized for the photoacoustic detection of mercury ions (Hg^{2+}). In the presence of Hg^{2+} , MTA molecules would be displaced quickly from the surface of gold nanorods due to the high affinity of Hg^{2+} toward sulfhydryl group. Then gold nanorods were aggregated due to the loss of ligand protection on their surface, resulting in the enhancement of photoacoustic signals. In addition, this work showed a good linear relationship between the change of photoacoustic signal at 780 nm and the concentrations of Hg^{2+} (0–10 μM). More importantly, the devised photoacoustic detection system performs good stability and anti-interference compared to the traditional colorimetric detection system, making it possible to apply to the actual Hg^{2+} -contaminated water samples.

1. Introduction

Non-biodegradable mercury is considered to be one of most toxic metal pollutants. It could cause serious harm to human beings and environment even at low concentrations. Ionic mercury (Hg^{2+}) is one of main forms of mercury in nature [1,2]. The traditional methods for mercury detection are including inductively coupled plasma-mass spectrometry (ICP-MS) [3], mass spectroscopy (MS) [4], gas chromatography (GC) [5] and so on. These methods offer sufficient sensitivity to detect Hg^{2+} in most settings, but the time-consuming pretreatment procedures, complex instrumentation, and skilled personnel limit their wide applications. Therefore, there is a high demand on a simple method for Hg^{2+} detection.

So far, a lot of nanomaterials such as gold nanoparticles (GNPs) [6–8], silver nanoparticles [9], carbon nanomaterials [10], quantum dots [11] and silica nanoparticles [12], have been widely developed as biosensors for Hg^{2+} detection. These nanomaterials-based biosensors are mainly based on two strategies including colorimetric and fluorescence detections [13–16]. Thanks to the relatively low-cost, fast and

instrument-free features, colorimetric strategy of Hg^{2+} detection has drawn much attention [17]. For instance, He *et al.* reported a colorimetric nanoprobe consisted of GNPs and thiolated thymine oligonucleotides. When treated with Hg^{2+} , adjacent thymine (T) at the surface of each GNP formed the T- Hg^{2+} -T complex. It caused the aggregation of GNPs and eye-sensitive red-to-blue color change, so that the colorimetric detection of Hg^{2+} realized [18]. Nevertheless, the colorimetric assay system almost has the above discussed advantages, the biggest obstacle to the application of colorimetric detection in real Hg^{2+} -polluted samples is its poor color anti-interference ability. But what bothers us is actual samples of Hg^{2+} -pollution are usually colored and turbid. In fact, most of the optical-related tests, such as UV–vis spectroscopy and fluorescence spectroscopy, have such drawbacks as they are easily affected by autofluorescence, ambient light, light scattering and so on, which will be very detrimental to their use for actual sample testing.

Actually, nanomaterials-based biosensors were not only used for colorimetric detection, but also for photoacoustic imaging (PAI) [19]. In brief, photoacoustic signal are actually ultrasonic waves generated

* Corresponding authors.

E-mail addresses: luoyongxiang@szu.edu.cn (Y. Luo), peng.huang@szu.edu.cn (P. Huang).

¹ Y. H. and F. L. contributed equally to this work.

by the thermal expansion which was induced by endogenous or exogenous contrast agents absorbed-laser energy [20]. In addition, in contrast to the optical-related tests, photoacoustic technique is insensitive to light scattering signals but reveals optical absorption [21,22]. The interference of endogenous signals (hemoglobin, lipids, water, melanin and so on) in the analyte can be overcome by using ideal exogenous contrast agents [23]. Another advantage of photoacoustic technology is that the sample can be directly measured for photoacoustic signals without preconditioning. Owing to the above-mentioned features, PAI shows huge potential for ion detection in real samples. At present, some studies have successfully applied photoacoustic imaging technology for metal ion detection [24–28]. For example, Lee and co-workers designed a NIR dye molecules-based nanosensor for ion-selective potassium detection, which aimed at *in vivo* photoacoustic chemical imaging of the extracellular environment [26]. Recently, we developed a ratiometric photoacoustic probe composed of cyanine dye and liposome for the real-time detection of methylmercury (MeHg^+) in living subjects [27].

As far as we know, previous studies are almost focused on organic dye molecules-based photoacoustic probes for metal ions detection. Actually, inorganic nanomaterials, especially GNPs have been proved to be the excellent photoacoustic contrast agents as their better photostability than organic dyes [29]. Herein, we firstly developed gold nanorods (GNRs)-based photoacoustic probes for Hg^{2+} detection (Scheme 1). The (11-mercapto-undecyl)-trimethylammonium (MTA) [30,31], containing a sulfhydryl group, was modified on the surface of GNRs through Au-S binds to form MTA-GNRs. It was reported that the Hg^{2+} had a strong binding ability to sulfhydryl groups over other metal ions, and the binding constant between Hg^{2+} and sulfhydryl group was higher than that of gold-sulfhydryl group [32]. Therefore, among the various representative metallic ions, only Hg^{2+} was able to detach the MTA from the surface of GNRs, which ensured the high specificity of Hg^{2+} . The MTA-GNRs could be stably dispersed in acidic aqueous solution. When Hg^{2+} was added, sulfhydryl groups could quickly bind to Hg^{2+} , which leading to the destruction of Au-S bonds between MTA and GNRs [33]. Due to the loss of MTA protection, GNRs were aggregated with the enhancement of photoacoustic signals at 780 nm. Under the optimal conditions, a good linear relationship was exhibited between the change of photoacoustic signal at 780 nm and the concentrations of Hg^{2+} (2–10 μM). Moreover, this strategy overcame poor environmental interference as well as showed good stability in high salt or really

complicated environments.

2. Materials and methods

2.1. Materials and instrumentation

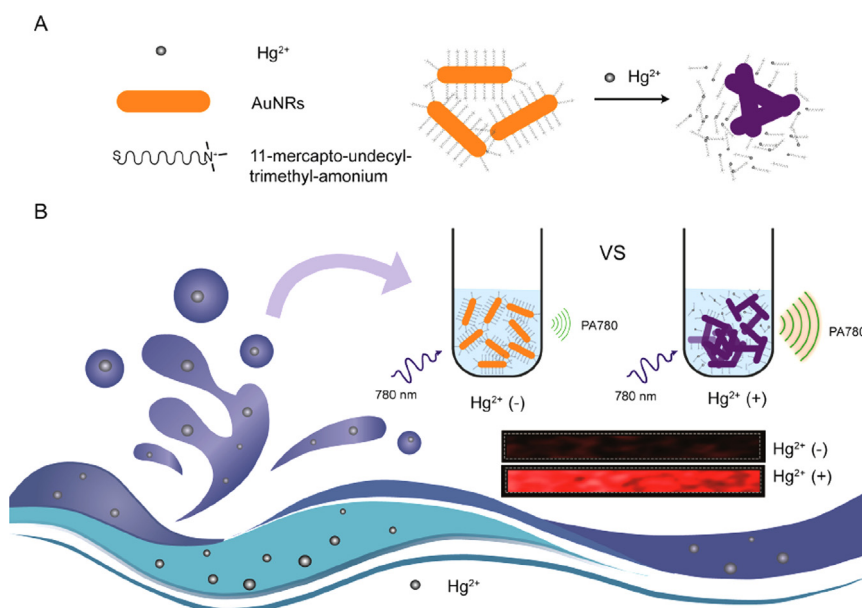
11-mercapto-undecyl-trimethyl-ammonium was purchased from Prochimia (Sopot, Poland). Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and cetyltrimethylammonium bromide (CTAB) were purchased from Strem Chemicals, Inc. (Boston, USA), silver nitrate (AgNO_3), ascorbic acid and sodium borohydride (NaBH_4) were purchased from J&K Chemicals Ltd. (Shanghai, China). Metallic salts such as HgCl_2 , CaCl_2 , CdCl_2 , FeCl_3 , MgSO_4 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Pb}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Four types of real water samples were collected from bottled pure water (Wahaha brand, Hangzhou Wahaha Group Co., Ltd., China), bottled mineral water (King Hundred Mountain brand, Jing Tian Industrial Group Co., Ltd., China), tap water and Wenshan Lake (Shenzhen University campus, Shenzhen, Guangdong, P.R.China), respectively.

The size and morphology of the probe were characterized by transmission electron microscopy (TEM) on JEM-1230 microscope (Shenzhen, China) with accelerating voltage 200 kV. Ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were obtained by an Agilent Cary 60 UV-vis-NIR spectrophotometer (Shenzhen, China). The pH of the probe solution was detected by a Thermo Scientific Orion Star A111 pH meter (Shenzhen, China). Zeta potential and hydrodynamic diameter distribution were detected by Zeta Sizer Nano ZS90 (Shenzhen, China). The photoacoustic imaging was carried out by a VisualSonic Vevo 2100 LAZR system equipped with a 40 MHz, 256-element linear array transducer (Shenzhen, China).

2.2. Methods

2.2.1. Synthesis of GNRs

The one-pot seedless method was used to synthesize GNRs [34]. First of all, 5 mL of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (1.0 mM) was added to 5 mL of CTAB aqueous solution (0.2 M) under gently shaking at 25 °C, followed by adding 250 μL of AgNO_3 (4.0 mM). Afterwards 12.0 μL of HCl (37%) was rapidly added to the solution to obtain a pH of 1–1.15. Then 75 μL of ascorbic acid (85.8 mM) was added to the mixed solution under



Scheme 1. Mechanism of photoacoustic detection of Hg^{2+} based on GNRs.

Download English Version:

<https://daneshyari.com/en/article/7675608>

Download Persian Version:

<https://daneshyari.com/article/7675608>

[Daneshyari.com](https://daneshyari.com)