GOLD NANOPARTICLE-BASED MICROFLUIDIC SENSOR FOR MERCURY DETECTION

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ABSTRACT

The contamination of natural resources by human activity can have severe socio-economical impacts. Conventional methods of environmental analysis can be significantly improved by the development of portable microscale technologies for remote/field sensing. A gold nanoparticle-based lab-on-a-chip device was developed for the rapid, in-field detection and quantification of mercury in aquatic environments. Rhodamine 6G functionalized gold nanoparticles allowed the on-chip fluorescence detection of mercury in aqueous samples with a limit of detection of 7 nM.

KEYWORDS: Mercury Detection, Gold Nanoparticles, Environmental Analysis, Fluorescence

INTRODUCTION

Exposure to heavy metals, such as mercury (Hg), can have devastating toxicological effects on the cognitive and physiological systems, especially in children [1]. Exposure to Hg is a particular concern in population where fish is a dietary staple. It is therefore of the utmost importance to develop reliable, rapid and portable devices for the analysis of this trace contaminant. The use of lab-on-a-chip (LOC) systems in environmental analysis has increased considerably in recent years. However, for practical reasons (no native fluorescence, low sensitivity and selectivity) fluorescence and absorbance have not been widely used for the detection of environmental contaminants on LOCs [2]. Although several nanoparticle (NP)-based methods have been developed for toxic metals [3], [4] the synergistic combination of gold nanoparticle (AuNP)-based detection with LOC devices remains widely unexplored to this day. He et al [5] designed a gold nanoprobe for rapid Hg detection on a simple microfluidic device, but with a detection limit of 5 µM, 500 times higher than the 10 nM maximum contaminant level (MCL) established by the US EPA [6], its usefulness for the detection of Hg in real samples is very limited. Wang et al [7] used Rhodamine B functionalized AuNPs to detect Hg on a microfluidic device by surface-enhanced Raman spectroscopy (SERS), but with a linear detection range (0.5 to 10 nM) entirely below the MCL established by the US EPA, the usefulness of the method for the analysis of real samples is compromised.

THEORY

In conventional environmental analytical procedures, samples are collected from a relatively small number of pre-defined locations, and brought back to the laboratory for analysis using state of the art sample preparation techniques (preconcentration, derivatization, etc) and instruments (such as ICP-MS[1] and CV-AAS[2]). However, these methods are time-consuming, expensive and, in the delay between sampling and analysis, the sample is very susceptible to losses (through evaporation, adsorption, chemical instability…) and contamination. The development of economically viable microscale technologies which are rapid, reliable and require minimal sample handling for the detection of trace metals is highly desirable. LOC devices, in which all sample preparation and analysis steps are performed on a single, small microfluidic-based portable device, can be used to perform analyses directly in the field, minimizing these potential errors. NPs are attractive for the development of a new generation of environmental monitoring devices because of their size-dependent colorimetric and fluorescent properties. Due to their stability, AuNPs can easily be stored on LOC devices for field sampling or long-term monitoring, and their optical properties allows on-site analysis using simple detection equipment.

EXPERIMENTAL

In this study, 15 nm AuNPs were prepared by the Frens-Turkevitch method [8]. All glassware was thoroughly washed with aqua regia. In a round bottom flask equipped with a condenser, sodium citrate (1.5 mL, 38.8 mM) was added to a boiling solution of chloroauric acid (50 mL, 0.25 mM) under vigorous stirring. The mixture was refluxed until an intense red/orange color was observed (~10 minutes). The Rhodamine 6G (R6G) functionalized AuNP probes were prepared by spiking the AuNP solution (0.5 nM in 5 mM sodium tetraborate buffer, pH 9.14) with Rhodamine 6G (20 µL, 0.2 mM) and allowing to equilibrate at room temperature for 2 hours. Aliquots (1 mL) of the AuNP probes were subsequently spiked with a Hg(II) standard solution and allowed to equilibrate for 15 minutes.

The microfluidic device (Figure 2) was made by conventional micromilling of polymethylmethacrylate (PMMA). The microfluidic network allows the mixing of three components (Hg, water and R6G AuNPs) as well as the introduction of an optional immiscible fluid to enhance mixing via a two-phase flow. The components are mixed in a long, circular-shaped, meandering channel (300 µm wide) at the center of which a deep detection chamber (1.5 mm deep, 250 µm diameter) allows

[1] Inductively Coupled Plasma Mass Spectrometry
[2] Cold Vapor Atomic Absorption Spectrometry

fluorescent measurements. The presence of a deep detection cell at the center of the microfluidic chip provides enhanced sensitivity at low fluorescence levels. Fluorescence measurements were recorded on an Olympus IX71 inverted microscope (λ_{ex} = 510-550 nm, λ_{em} = 590-800 nm) equipped with a Canon 550D digital camera.

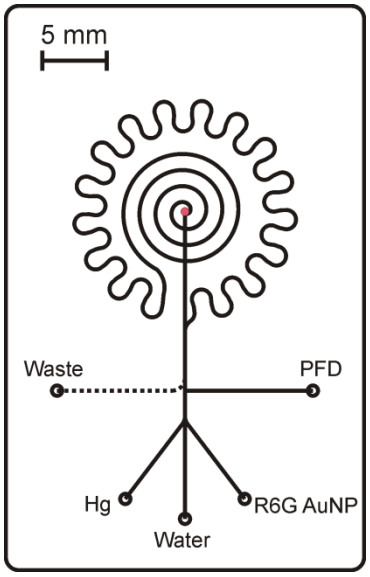

Figure 1: Schematic illustration of the polymeric microfluidic device. The microfluidic network allows the mixing of three components as well as the introduction of an optional immiscible fluid (perfluorodecalin - PFD) to enhance mixing via a two-phase flow. The deep fluorescence cell is emphasized in red. The waste channel (dotted line) is located on the backside of the chip.

RESULTS AND DISCUSSION

Characterization of the prepared AuNPs by Transmission Electron Microscopy (TEM) indicated the size of the particles to be 15 nm. The AuNPs were characterized by an absorption maximum at 517 nm and their concentration was estimated at 2 nM using $\varepsilon_{(450\ nm)} = 2.18 \times 10^{08}\ M^{-1}cm^{-2}$ [9] for 15 nm particles.

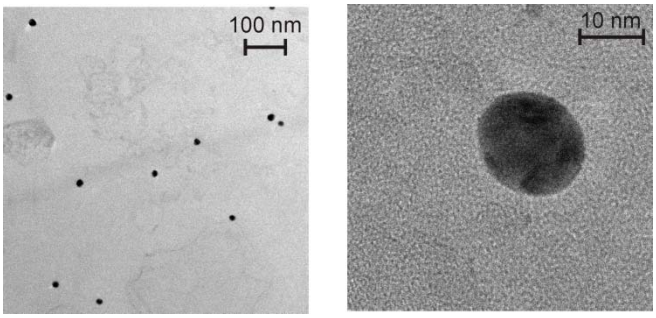

Figure 2: TEM images of the prepared gold nanoparticles.

As shown in Figure 3(a), the R6G-AuNPs exhibit very weak fluorescence. However, as Hg(II) is added to the R6G-AuNP probe, R6G molecules are released from the surface of the AuNPs and their fluorescence is restored (Figure 3(b-d)). As shown in Figure 3(e), the fluorescence enhancement was proportional to Hg(II) concentration over the concentration range studied (0 - 534 nM). The detection limit, calculated as 3 σ_{blank}, was 7 nM. These results show that this device could be used to detect Hg at levels below the MCL recommended by the US EPA for drinking water. In the analysis of samples with a more complex matrix, potential interferences by other heavy metals, such as lead (Pb) and cadmium (Cd) could be reduced by the addition of metal chelators, such as pyridinedicarboxylic acid [10].

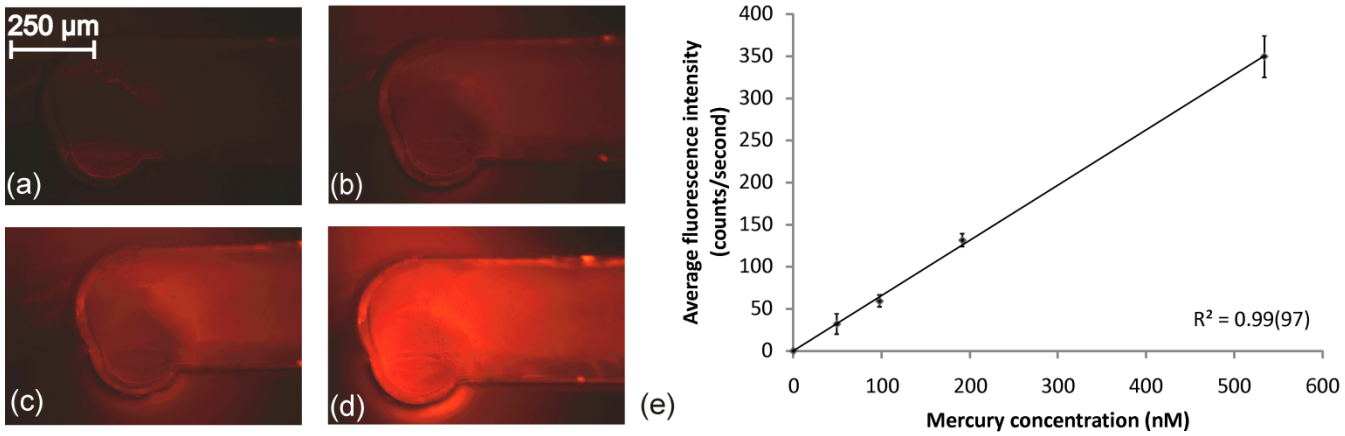

Figure 3. (a-d) Fluorescence microscope images of the on-chip detection cell filled with the R6G AuNP probe upon the addition of (a) 0 nM Hg, (b) 98 nM Hg, (c) 192 nM Hg and (d) 534 nM Hg. (e) Corresponding calibration curve.

CONCLUSION

These results show the great potential of this AuNP based microfluidic sensor for environmental monitoring of Hg. Simple detection equipment could be used to obtain results directly in the field, minimizing risks of sample losses and contaminations brought by the necessity to bring samples back to the laboratory for analysis by conventional methods.

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