Gold nanomaterial-based miniaturized NSET Probe for rapid and ultra-sensitive detection of toxic metals from environment

Paresh Chandra Ray, Gopala Krishna Darbha, Anandhi Ray

Department of Chemistry, Jackson State University, Jackson, MS, USA, paresh.c.ray@jsums.edu

ABSTRACT

Contamination of the environment with heavy metal ions has been an important concern throughout the world for decades. Here we discuss our recent effort on the development of a miniaturized and battery operated ultra-sensitive gold nanoparticle based nanomaterial surface energy transfer (NSET) probe for screening toxic metal levels in contaminated soil, water and fish which has excellent sensitivity and selectivity. Further we describe the quenching efficiency and mechanism as a function of size and shape of gold nanoparticles.

Keywords: Gold Nanoparticle, NSET, Mercury, Arsenic, Sensor.

1 INTRODUCTION

Environmental pollution has been a major concern of today's society. The environmental issues are complex due to the variety in contamination sources, the chemical composition of the contaminants, the environmental transport pathways, the effects on the natural environment and human health, the diversity of diseases, and the genomic responses to the polluted environmnet. Industry and automobiles now are considered to be one of the largest sources of heavy metals. Most heavy metals are *extremely toxic* because, as ions or in certain compounds, they may be taken into the body, where they tend to combine with and inhibit the functioning of particular enzymes. Frequently, concentrations of toxic metals from contamination are small, and the number of different possible toxic metals is large. As a result, it is not easy to test for toxic metals in every water sample collected. Development of sensors for real-time detection of toxic metals in water supplies is a high priority with applications in domestic preparedness and for ensuring the safety of municipal and recreational water supplies. To meet these needs, the sensors must be sensitive, rapid, and robust with long operational lifetime. The benefits of nanotechnology [1-13] make it ideal for sensor development, for environmental and biological monitoring. Their extremely small size enables them to access a variety of biological environments; their size also endows them with valuable size dependent properties that can be exploited in applications. Driven by the need, here we report gold nanomaterial based, nanomaterial surface energy transfer NSET probe for ultrasensitive detection of toxic metals selectively.

2 EXPERIMENTAL DETAILS

Gold nanoparticles of 15 nm or above diameters were synthesized using reported method[5-9]. Gold nanoparticles of different sizes and shapes were synthesized by controlling the ratio of $HAuCl_4$, $3H_2O$ and sodium citrate concentration as we reported recently[5-9]. . For smaller gold nanoparticles, we have used sodium borohydride method as reported before. Transmission Electron Microscope (TEM) (as shown in Figure 1) and UV-visible absorption spectrum were used to characterize the nanoparticles. The particle concentration was measured by UV-visible spectroscopy using the molar extinction coefficients at the wavelength of the maximum absorption of each gold colloid as reported recently[5-9]. Gold nanorods were synthesized using a seed-mediated, surfactant-assisted growth method in a two-step procedure. Colloidal gold seeds (~1.5 nm diameter) were first prepared by mixing aqueous solutions of hexadecylcetyltrimethylammonium bromide (CTAB, 0.1 M, 4.75 mL) and hydrogen tetrachloroaurate(III) hydrate (0.01 M,0.2 mL). Nanorods were purified by several cycles of suspension in ultrapure water, followed by centrifugation. Nanorods were isolated in the precipitate, and excess CTAB was removed in the supernatant. Nanorods were characterized by TEM (as shown in Figure 1) and absorption spectroscopy.

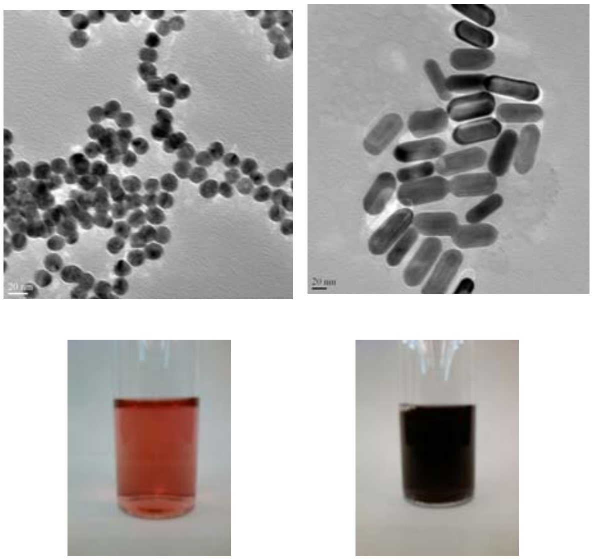
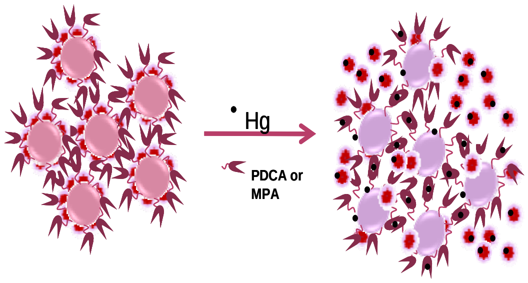
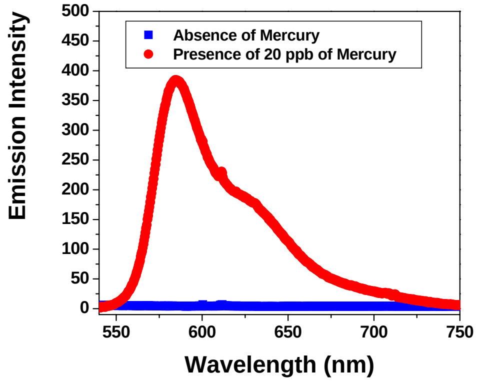


Figure 1: TEM and photographic images of gold nanoparticle and gold nanorod

3 RESULTS AND DISCUSSIONS

Our mercury detection approach [5,7,9] is based on the use of gold nanoparticle based NSET which provides high sensitivity for the detection of metal ions because of their unique super quenching property for chromophores through both energy-transfer and electron-transfer processes. To detect Hg(II) ion selectively, we modified the gold nanoparticle surface with mercaptopropionic acid and homocystine and we added a chelating ligand 2,6-pyridinedicarboxylic acid (PDCA), to the solution. Our results indicate that modifying the gold nanoparticles with both MPA and PDCA, selectivity increases 40-60 times towards mercury ions than that of Cd, Pb and Zn ions. Rhodamine B (RhB) molecules which are highly fluorescence in aqueous solution were self-adsorbed on the surface of gold nanoparticles (as shown in Figure 2). Fluorophore is completely quenched by efficient nonradiative energy transfer to the gold particle and the strong quenching abilities of colloidal gold are related to its large molar extinction coefficients (~ 10^{10} cm^{-1} M^{-1} for 20-30 nm particles) and its nanomolar binding affinities for organic dyes. In the presence Hg(II) ions, Rhodamine B molecules are released from the gold nanoparticle surface and thus we observed a very distinct, fluorescence signal change (as shown in Figure 2). Fluorescence signal enhancement was observed within few seconds by a factor of 400 after the addition of 2 ppb of mercury (as shown in Figure 2). Figure 2 also shows the colorimetric response in the presence of various environmentally relevant metal ions. Our result shows excellent selectivity over alkali, alkaline earth (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) and transition heavy metal ions (Pb^{2+}, Pb^+, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}).





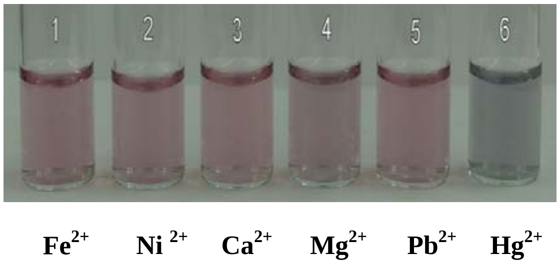


Figure 2: i) Schematic representation of Hg(II) detection process. ii) Fluorescence response of RhB adsorbed onto 5 nM gold nanoparticle solution upon addition of 2 ppb of Hg(II) ions. iii) Photographic images of color of MPA-PDCA modified gold nanoparticles in presence of 40 ppm of different metal ions.

To evaluate whether our NSET probe can detect Hg (II) ions from environmental samples, we have measured mercury content in water and fish collected from Mississippi river. Fish collected from river were dissolved in HNO_3 and the resulting solutions were brought to pH 7. Mercury content was measured using our nanoparticle based NSET probe (as shown in Table 1) and also verified using ICPMS. Hg(II) measured in soil sample by our method was in very good agreement (90-95%) with ICPMS values (as shown in Table 1)

Table 1: Mercury amounts in different sources measured by NSET and ICP-MS methods

Source	Hg by NSET	Hg by ICPMS
Tape Water	1.8 ppb	1.84 ppb
MS River Water	6 ppb	5.4 ppb
Mackerel	1.6 ppm	1.52 ppm
Swordfish	2.8 ppm	2.6 ppm
Crab	520 ppb	534 ppb
Catfish	250 ppb	241 ppb
Crawfish	450 ppb	490 ppb
Salmon	150 ppb	140 ppb

Our arsenic detection [13] approach is based on gold nanorod based NSET which provides high sensitivity for the detection of As^{3+} because of their unique super quenching property for chromophores through both energy-transfer and electron-transfer processes. The nanorods prepared by cetyltrimethylammonium bromide (CTAB) methods were capped with a bilayer of CTAB, which is positively charged. Since As^{3+} will have repulsion to positively charged CTAB, the positively charged surface of the nanorods was changed to a negatively charged surface by exposing the nanoparticles to poly(styrenesulfonate) (PSS) polyelectrolyte solution. The PSS-capped nanorods were then mixed with diluted solution of methylene blue and allowed to react for 20 min. Methylene blue is probably bound to the PSS-coated nanorods by a mechanism similar to that used for binding organic dyes to nanospheres, i.e., by electrostatic physisorption interaction. Methylene blue molecules, which are highly fluorescent in aqueous solution, were self-adsorbed on the surface of gold nanoparticles. Our experimental data showed a quenching efficiency of nearly 100% when the fluorophore was statically adsorbed on the particle (static quenching). Fluorophore is completely quenched by efficient nonradiative energy transfer to the gold nanorod and the strong quenching abilities of colloidal gold are related to its large molar extinction coefficients (~ 10^9 cm^{-1} M^{-1} for gold nanorod of aspect ratio 3.4) and its nanomolar binding affinities for organic dyes. In the presence As(III) ions, methylene blue molecules are released from the gold nanorod surface and thus we observed a very distinct, fluorescence signal change (as shown in Figure 3). Fluorescence signal enhancement was observed within few seconds by a factor of 600 after the addition of 7 ppm of Arsenic (as shown in Figure 3).

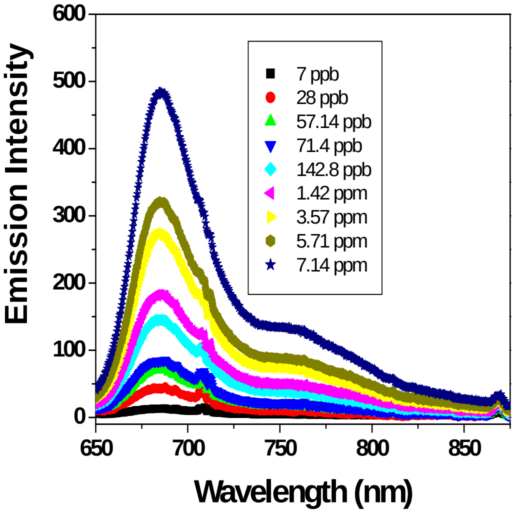


Figure 3: Fluorescence response of methylene blue adsorbed onto 40 nM gold nanorod solution upon addition of different concentrations of As(III) ions.

4 PORTABLE NSET SENSOR DEVELOPMENT

The photograph of the minimized system components for the NSET sensor configuration [5,7,9] to detect biological and chemical toxin is shown in the Figure 4. For fluorescence excitation, we have used a continuous wavelength (CW) Melles-Griot green laser pointer (18 Lab 181) operating at 532 nm, as an excitation light source. The laser pointer can maintain 10~13 hours with two AAA size batteries, and its maximum output power is ~5mW.

Figure 4: Photograph of the minimized NSET probe box, connected with laptop computer for data acquisition.

This light source has a capability that can minimize whole sensor configuration. The total size of the sensor configuration was 5” x 8” x 5” including the laser pointer, optical fiber and OOI spectrometer in the aluminum box. This probe consists of total seven optical fibers, each having 200 µm core diameters with one launching fiber and six surrounding collecting fibers. Excitation light source was first attenuated using appropriate neutral density (ND) filter and coupled to the excitation arm of the Y-shaped reflection probe through a plano-convex lens (*f*:~4.5mm). A typical laser energy at the sample was adjusted to ~1.3mW with 0.3 ND filter. The diverging output beam from the fiber provided nearly uniform illumination onto the sample.

In conclusion, we have discussed our recent efforts on development of a miniaturized, inexpensive and battery operated ultra-sensitive gold nanoparticle based NSET probe for screening Hg(II) and As(III) in ppt level from environmental samples with excellent sensitivity and selectivity for Hg^{2+} over competing analytes. The sensitivity of our probe to detect mercury level in soil, water and fish is about 2-3 orders of magnitude higher than the EPA standard limit. Looking into the future, we expect these compact sensor developments will have important implications in the development of better assay for application to toxic metal ion detection from environmental samples.

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