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Gold Nanoparticle-Based Simple Colorimetric and Ultrasensitive Dynamic Light Scattering Assay for the Selective Detection of Pb(II) from Paints, Plastics, and Water Samples

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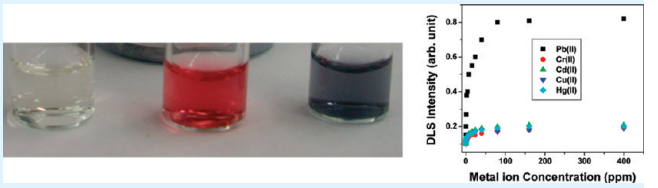
ABSTRACT: Pb (II) is a common water pollutant with high toxicity. According to the CDC, about 310 000 U.S. children of ages 1−5 have high levels of lead in their blood that it is due to the exposure to lead from plastic toys and other products. As a result, the development of ultrasensitive assays for the real-time detection of Pb(II) from plastic toys and paints is very important for water controlling, clinical toxicology and industrial processes. Driven by the need to detect trace amounts of Pb(II) from water samples, we report a label-free, highly selective and ultra sensitive glutathione modified gold nanoparticle based dynamic light scattering (DLS) probe for Pb(II) recognition in 100 ppt level from aqueous solution with excellent discrimination against other heavy metals. The sensitivity of our assay to detect Pb(II) level in water is almost 2 orders of magnitude higher than the EPA standard limit. We have also demonstrated that our DLS assay is capable of measuring the amount of Pb(II) in paint, plastic toys, and water from MS river. A possible mechanism and operating principles of our DLS assay have been discussed. Ultimately, this nanotechnology driven assay could have enormous potential applications in rapid, on-site monitoring of Pb(II) from day-to-day sample.



KEYWORDS: gold nanoparticle, dynamic light scattering, colorimetric assay, plasmon, Pb(II) detection, water sample

INTRODUCTION

Pb (II) is a common water pollutant with high toxicity. Major sources of lead contamination are mainly lead-based paints and auto emissions.[1−4] According to the Centers for Disease Control (CDC), about 310 000 U.S. children ages 1−5 have high levels of lead in their blood due to the exposure to lead from plastic toys and other products imported from countries outside of USA.[1−4] Because lead is nondegradable, accumulation of high level of lead in children can cause irreversible brain damage, retard mental and physical developments.[1−4] For adults, high levels of lead can cause irritability, poor muscle coordination, and nerve damage to the sense organs.[1−4] As a result, the development of ultrasensitive assays for the real-time detection of Pb(II) is very important for water controlling, clinical toxicology, and industrial processes.[1−4] Although current technologies such as inductively coupled plasma mass spectrometry (ICPMS) are capable of measuring Pb(II) in the U.S. water protection agency (EPA) detection limit (15 ppb), it often requires expensive sophisticated instrumentation and complicated sample preparation processes.[1−9] For the growing market needs of the 21st century, future devices must link selectivity, speed, and simplicity with cost effectiveness.[1−11] In the last 15 years, the field of biological and chemical sensors using nanomaterial has witnessed an explosion due to the unique optical properties of nanomaterials.[5−20] Different sensor concepts for analyzing Pb(II) have been reported in last 10 years, which include DNAzyme nanotechnology-based sensor.[5−12] Though DNAzyme based sensor[5,6,8] exhibits good selectivity, requirement of DNA oligomers can limit its applications for real life samples. Driven by the need, in this article, we demonstrate that glutathione (GSH) modified gold nanoparticle based colorimetric and dynamic light scattering (DLS) probe[11−14] can be used for label-free detection of Pb(II) from plastic toys, paint and water samples with excellent detection limit (100 ppt) and selectivity over other metal ions. Recently, Chai et al.[10] reported GSH functionalized gold nanoparticle based colorimetric assay for the detection of Pb^{2+} ion at 20 ppb level. Also, Ali et al.[7] have demonstrated that GSH-capped ZnCdSe and CdTe QDs based selective fluorescent probe for the detection of Pb^{2+} with the detection limit of 4 ppb. Because DLS is known to be capable of separating monomer from dimer, in this article we have reported that GSH functionalized gold nanoparticles based DLS assay can be used for the detection of Pb^{2+} at 100 ppt level. We have also shown for the first time that GSH modified gold nanoparticle-based DLS assay has a capability to detect Pb^{2+} from real plastic toys, paints and water samples from different sources.

Noble metal nanostructures attract great interest because of their unique size and shape dependent properties.[15−38] Due to the presence of the surface plasmon resonances, weak scattering effects generally get significantly enhanced via strong electromagnetic fields at the surfaces of metallic nanostructures.[5−14,30−38] These unique properties, lack of toxicity and our ability to make gold nanomaterials of different sizes and shapes, make them

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potentially useful assay for daily life applications.[15−38] DLS, also known as photon correlation spectroscopy (PCS), is a well-established noninvasive technique for measuring the size of particles ranging from 0.5 nm to 6 μm.[13−16] DLS is an absolute measurement and it is a powerful tool for determining small changes in the size of particles.[13−16] Recently, we and other groups have shown that this technique coupled with noble metal nanoparticles can be used as ultrasensitive assay for chemical and bilogical detection, where nanoparticles are used as a light-scattering enhancer and DLS as a read-out system.[13−16] In this manuscript, for the first time, we have shown that GSH conjugated gold nanoparticle-based DLS assay can be used for selective detection of Pb(II) from plastic toys, paints, and water samples.

MATERIALS AND EXPERIMENTS

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$), sodium citrate, L-glutathione, and different transition metal salts were purchased from Sigma-Aldrich and used without further purification.

Gold Nanoparticle Synthesis. Gold nanoparticles of different sizes were synthesized by using $HAuCl_4$, $3H_2O$ and sodium citrate as we reported recently.[13,17,19−25] JEM-2100F transmission electron microscope (TEM) 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 we have reported recently.[13,17,19−25]

Gold Nanoparticle Surface Modification. An aqueous solution of gold nanoparticle (10 nM) and GSH (1×10^{-6} M) were mixed in the volume ratio of 8:1, respectively. The mixture was allowed to react for 2 h at room temperature in dark conditions, with continuing stirring to ensure self-assembly of the GSH onto the surface of gold nanoparticles. The pH of the resulting mixture was adjusted to 8.0 using 1 M NaOH. Upon the addition of GSH to gold nanoaprticles, no color change or aggregation of gold nanoparticle was observed. Unbound GSH molecules in solution were removed by centrifugation at 8000 rpm for 10 min. From the concentration measurement of gold nanoparticle and given GSH concentration, we have calculated that around 12 GSH molecules were bound per gold nanoparticle.

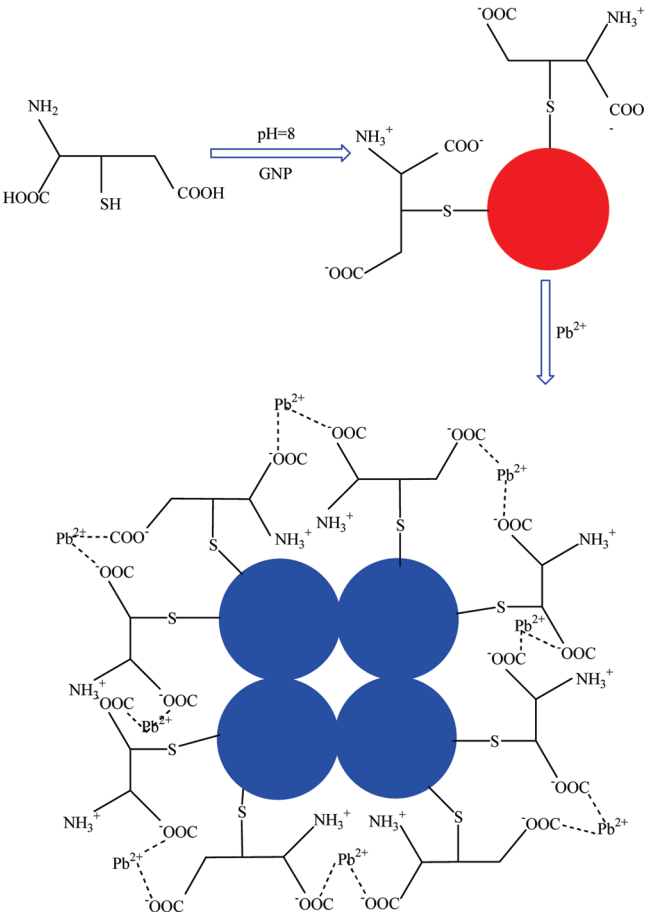
Colorimetric Detection of Pb(II). The colorimetric detection of aqueous of Pb^{2+} was performed at room temperature. A volume of 150 μL of GSH-gold nanoparticle solution was added to 100 μL of different concentrations of Pb^{2+}. The concentrations ranging from 200 ppm to 10 ppt of Pb^{2+} solution were prepared by using serial dilution of the stock solution. Samples with other transition metal ions were prepared in the same way. The color change was instant and photographs were taken using Cannon S70 digital camera.

Dynamic Light Scattering Measurement. DLS measurement was performed using Malvern Zetasizer Nano instrument. To reduce the multiple scattering effects, noninvasive backscatter (NIBS) technology was used.[13−16] DLS detection of Pb(II) was carried out in the range of 10 ppt to 200 ppm using similar procedure as we described above for the colorimetric detection.

RESULTS AND DISCUSSION

Our detection is based on the fact that in the presence of Pb(II), GSH-conjugated gold nanoparticles undergo aggregation (as shown in Scheme 1) due to the formation of chelating complex.[10,39,40] As a result, DLS signal increases tremendously due to the increment of particle size. In our study, we have used GSH as a chelating ligand as well as the stabilizer for the gold nanoparticles. After the addition of GSH to the freshly prepared

Scheme 1. Schematic Representation of Glutathione (GSH) Conjugated Gold Nanoparticle-Based Selective Pb(II) Detection at pH 8[a]



[a] First step shows the process involving gold nanoparticle modification by GSH. Second step shows GSH modified gold nanoparticle aggregation in the presence of Pb(II) due to the formation of coordination complex through $-COO^-$ group at pH 8.

citrate-stabilized gold nanoparticles, the nanosurfaces were modified by GSH through the Au−S covalent bond (as shown in Scheme 1).

The addition of GSH does not change the color or the absorption spectra of gold nanoparticle, which indicates that there is no aggregation when 8:1 volume ratio of freshly prepared AuNPs (10 nM) and glutathione (1×10^{-6} M) were stirred. As shown in Figure 1B, TEM image of GSH modified gold nanoparticle confirmed it. GSH is a peptide, which is widely distributed in nature and plays an important role in heavy metal detoxification in cells. Pb(II) ion is known to form strong chelating complex with GSH through −SH bond, which has been used in protecting intracellular components against oxidative damage. In our current assay, GSH is linked with gold nanoparticle through −SH linkage and as a result, there is no free −SH for the formation of complex with Pb(II). Now, GSH has two free −COOH groups and one NH_2 group, which can be used for functionalization with metal ions. Metal ions like, Fe^{2+}, Zn^{2+}, and Cd^{2+} are well-known to bind to the amino group.[39,40] To avoid the interference from other metal ions, we have performed our experiment at pH 8, where $-NH_2$ group is

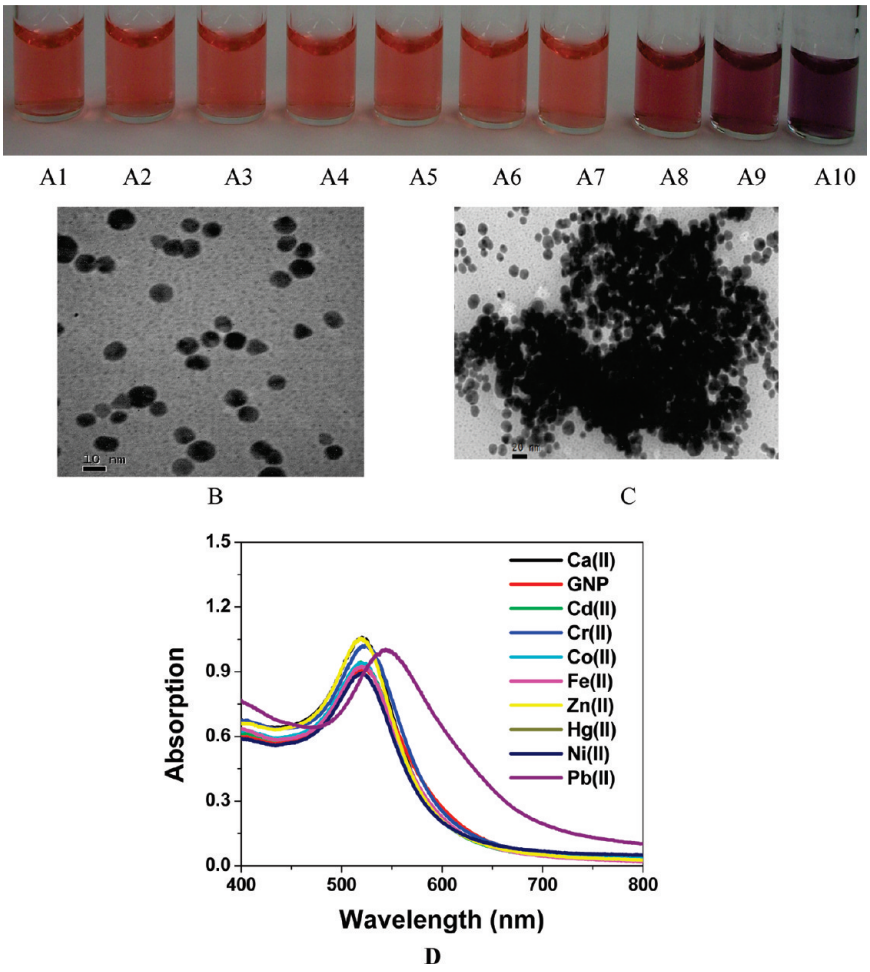


Figure 1. (A) Photographs showing colorimetric images of GSH conjugated gold nanoparticle in the presence of different concentrations of Pb(II) ions, (A1) 0 ppt, (A2) 10 ppt, (A3) 100 ppt, (A5) 1 ppb, (A6) 100 ppb, (A7) 800 ppb, (A8) 1 ppm, (A9) 2 ppm, (A10) 3 ppm. (B) TEM image of GSH modified gold nanoparticle in the absence of Pb(II) and (C) TEM image of GSH modified gold nanoparticle in the presence of 10 ppm Pb(II). (D) Absorption spectra of GSH modified gold nanoparticle in the presence of different metal ions. The absorption spectra shifted to longer wavelength in the presence of 1 ppm Pb(II). On the other hand, absorption spectra remained same in the presence of other metal ions even at the concentration of 10 ppm.

protonated to $-NH_3^+$. As a result, $-COO^-$ is the only binding site, which is known to bind strongly with Pb(II). As shown in Figure 1, at pH 8, when we added Pb(II) ion to glutathione modified gold nanoparticle, gold nanoparticles undergo aggregation due the formation of strong chelating complex via carboxylate ions. Aggregation of gold nanoparticles in the presence of Pb(II) ions yields both a substantial shift in the plasmon band energy to longer wavelength and a red-to-bluish color change (as shown in Figure 1D and 1A). This red shift might be due to two factors. One is the change in the local refractive index on the nanoparticle surface caused by the specific binding of the glutathione-conjugated gold nanoparticles with Pb(II). The other is the interparticle interaction resulting from the assembly of nanoparticles.

To evaluate the sensitivity of our GSH attached gold nanoparticle-based colorimetric assay, different concentrations of Pb(II) from one stock solution were evaluated. As shown in Figure 1A, our colorimetric assay is highly sensitive to the concentration of Pb(II). Our experimental results (as shown in Figure 1A) clearly demonstrate that the sensitivity of our colorimetric assay is as low as 1 ppm of Pb(II) . Because the EPA limit for the detection of Pb(II) in drinking water is much lower (15 ppb) than our colorimetric assay, we have employed GSH attached gold nanoparticle-based DLS technique. DLS is a powerful method to determine the small change in the size of the particles.[13−16] As shown in Figure 2C1−C5 and 2D1−D3, when different concentrations of Pb(II) were added to GSH modified gold nanoparticle, at a lower concentration of Pb(II), only smaller aggregates formed. As a result, colorimetric change was not observed at low concentrations. Because DLS has the capability to separate dimer from the monomer,[11−15] GSH conjugated gold nanoparticle based DLS assay should be able to show the response at a very low concentration of Pb(II), when only dimers, trimers and slightly bigger aggregates were formed. Figure 2A clearly shows that DLS technique is highly sensitive to the concentration of Pb(II), even at very low concentration. Our experimental results demonstrate (as shown in Figure 2B) that the sensitivity of our DLS assay for Pb(II) detection is as low as 100 ppt, which is almost 2 orders of magnitude higher than the EPA standard limit.

For real life applications, in water sample, there can be several impurities due to the heavy metal ions. To understand whether our assay is selective to Pb(II), we have also performed experiments on our assay response to the addition of other heavy metal

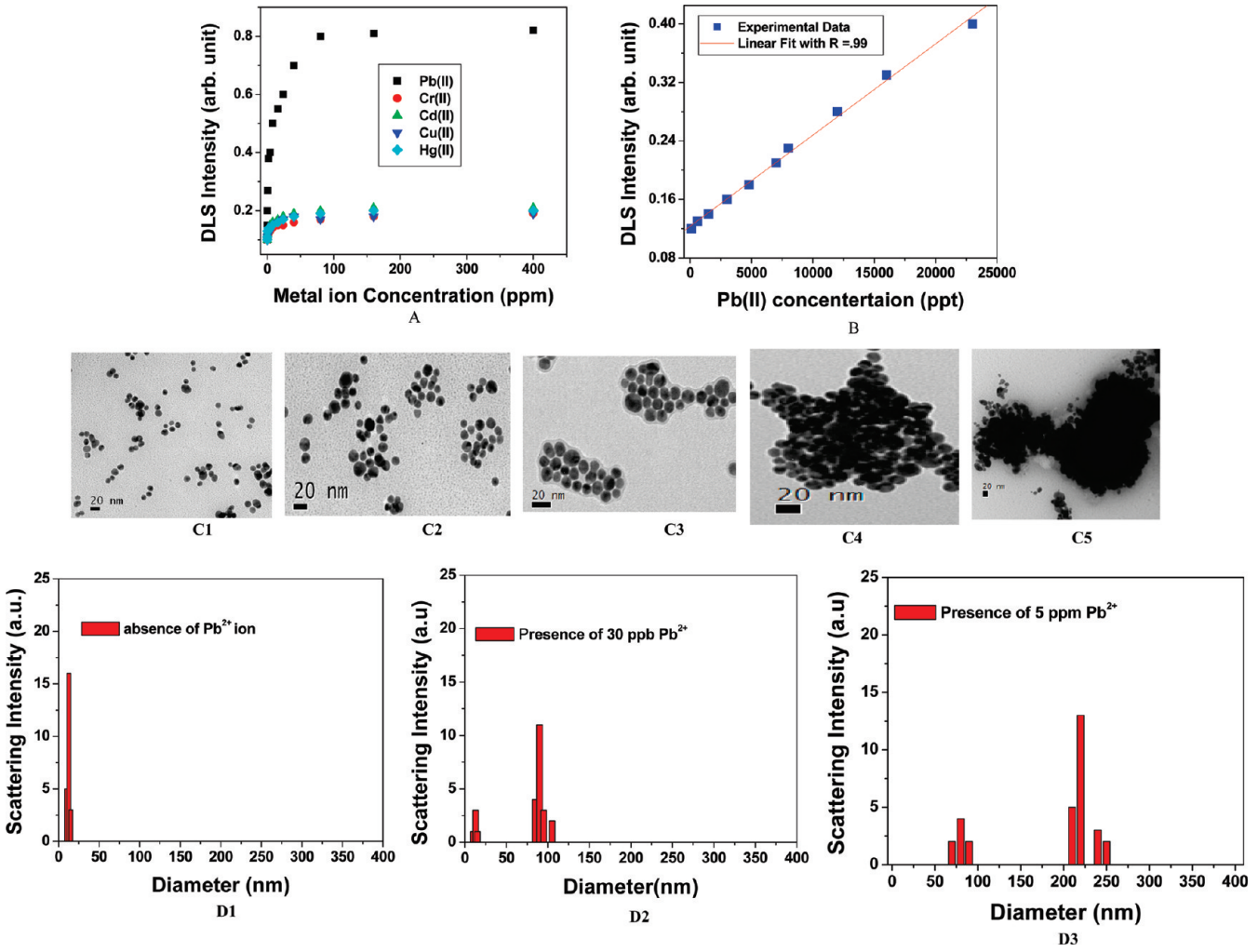


Figure 2. (A) Demonstrating how DLS intensity varies in response to the addition of different concentrations, from 0.1 to 400 ppm of different metal ions. Our results clearly show that our GSH-modified gold nanoparticle based DLS assay is highly selective toward Pb(II). DLS intensity remains unchanged in the presence of other metal ions. 2B: Demonstrating how DLS intensity varies in response to different concentrations of Pb(II) from 50 to 25000 ppt concentration ranges. Our result shows that DLS intensity varies linearly with the concentration of Pb(II) in the above range. (C) TEM images showing how GSH attached gold nanoparticle aggregate sizes vary in response to the addition of different concentrations of Pb(II): (C1) in the presence of 100 ppt Pb(II), (C2) in the presence of 500 ppt Pb(II), (C3) in the presence of 50 ppb Pb(II), (C4) in the presence of 3 ppm Pb(II), (C5) in the presence of 30 ppm Pb(II). D) Size distribution of GSH attached gold nanoparticles measured by DLS. (D1) in the absence of Pb(II), (D2) in the presence of 30 ppb Pb(II), and (D3) in the presence of 5 ppm Pb(II).

ions. Panels A and B in Figure 3 show the colorimetric and DLS response of our GSH modified gold nanoparticle based probe in the presence of various alkaline and transition heavy metal ions (Mg^{2+}, Ca^{2+}, Hg^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}). Figure 1D demonstrates the absorption spectral response in the presence of various alkaline and transition heavy metal ions. Our colorimetric data, DLS assay data and absorption spectra measurement clearly show that our GSH modified nano probe is highly selective for the detection of Pb(II) ion. This high selectivity toward Pb(II) ion is mainly due to several factors and these are as follows. (1) Pb(II) ion binds with glutathione carboxylate ions much stronger than other heavy metal ions as reported by other groups[39,40] through NMR studies. (2) Because −SH group is linked to gold nanoparticle, Hg^{2+} and As^{3+} binding probability is much lower for GSH modified gold nanoparticle. (3) At pH 8, NH_2 group is protonated as NH^{3+} and as a result, binding ability of Fe^{2+}, Zn^{2+}, and Cd^{2+} ions remains low. (4) Lead ion has the ability to coordinate up to eight oxygen atoms or four acetate molecules and as a result, it will be able to form bigger aggregates.[39] As we discussed before, to avoid the interference from other metal ions, we have performed our experiment at pH 8, where $-NH_2$ group is protonated to $-NH_3^+$ and as a result, $-COO^-$ is the only binding site which is known to bind strongly to Pb(II).[40] To understand how pH affects the selectivity of our assay, we have also performed the same experiment at pH 6 and pH 9. Images C and D in Figure 3 clearly show that at pH 6 and 9, GSH modified gold nanoparticle is highly stable, but interference from other metal ions are very high.

To understand whether the aggregation process is reversible, we have added ethylene diamine tetraacetic acid (EDTA) after the aggregation in the presence of Pb^{2+} ion. Since EDTA is a strong metal ion chelator than GSH for Pb^{2+} ion, the presence of 800 μM EDTA, the color change is completely reversed (as shown in Figure 3E). Similar observation has also been reported before by Kim et al.[9] So our experimental results show that the

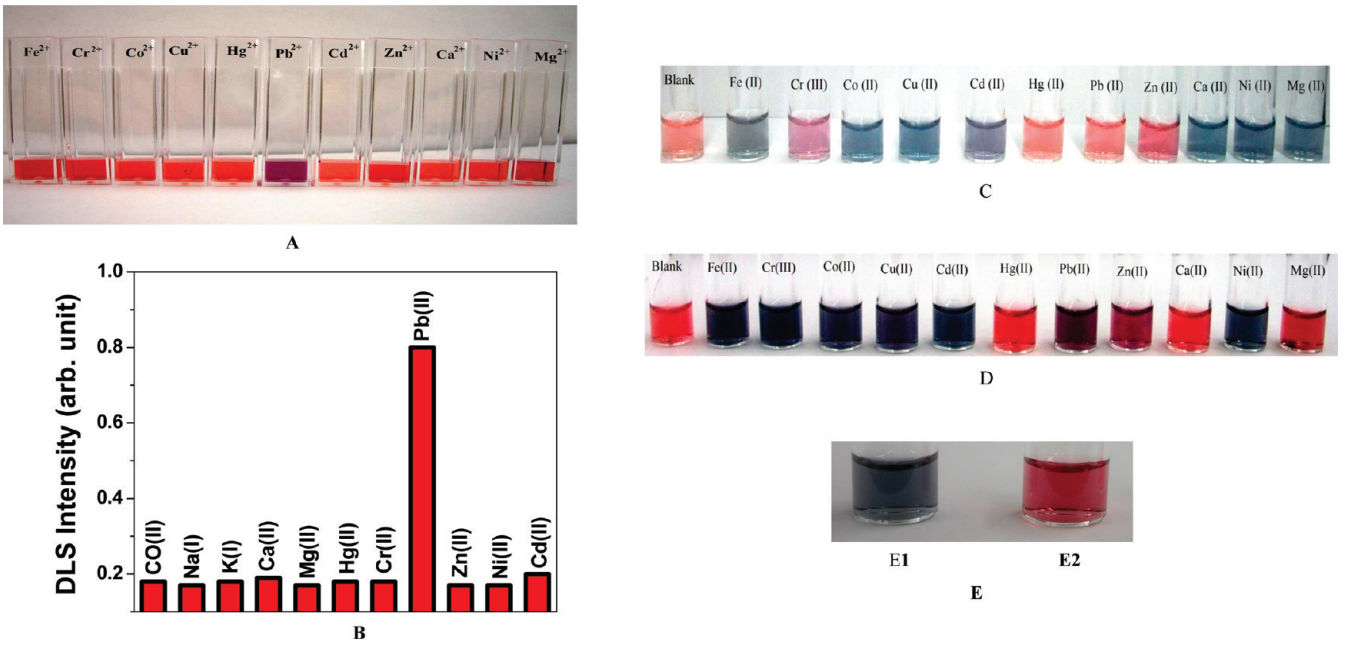


Figure 3. (A) Colorimetric assay demonstrating selectivity of our GSH attached gold nanoparticle based assay for Pb(II) ions over other heavy metal ions. Pb(II) ions have been added at 1 ppm level, whereas other metal ions have been added at 10 ppm concentration level. (B) Demonstrating selectivity of our DLS assay for Pb(II) ions over other heavy metal ions at 10 ppm concentration level. Our both assays clearly demonstrate that GSH attached gold nanoparticle based assay is highly selective for Pb(II). (C) Demonstrating how other metal ions interfere with our GSH attached gold nanoparticle based colorimetric assay at pH 6. (D) Demonstrating how other metal ions interfere with our GSH attached gold nanoparticle based colorimetric assay at pH 9, E) Demonstrating how EDTA addition reverses the aggregation process when 20 ppm Pb^{2+} forms chelating complex with GSH attached gold nanoparticle, E1) in the absence of EDTA, (E2) in the presence of 800 μM EDTA.

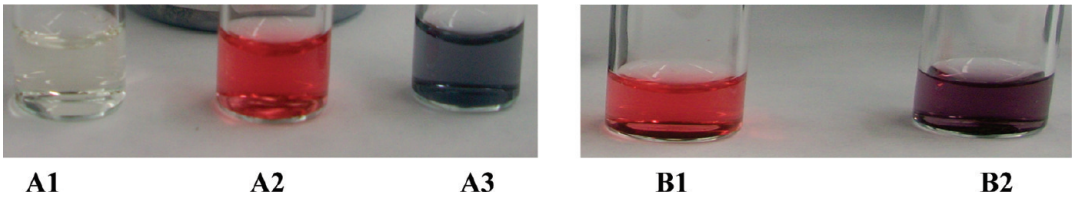


Figure 4. Demonstrating our colorimetric assay response to the addition of paint, plastic toys and river water sample. (A1) dissolved paint solution at pH 8, (A2) GSH modified gold nanoparticle without paint solution, (A3) GSH modified gold nanoparticle in the presence of paint solution. Clear color change can be seen after the addition of paint solution. B1) color remains unchanged after the addition of Mississippi river water, (B2) color change after the addition of plastic toy solution. Our results clearly show that our colorimetric assay can detect Pb^{2+} from plastic toys and paint sample.

color change due to the addition of Pb^{2+} ion is mainly due to the formation of chelating complex between Pb^{2+} ion and GSH modified gold nananoparticle, which helps gold nanoparticles to aggregate.

To demonstrate the potential practical applications of our assay to measure the Pb(II) content in samples that are used everyday, we have tested Pb(II) content in plastic toys and paint bought from Walmart, Jackson, MS, USA. We have also tested water sample from Mississippi river at Jackson, MS. Before performing experiments with river water sample, we have also tested how the presence of salt can affect our assay response. Our experimental results indicate that the presence of up to 20 mM salt does not affect the assay selectivity and sensitivity. It only makes the aggregation process faster and as a result, we observed a very fast color change in the presence of Pb^{2+} ions. But it does not change the selectivity at all. For the measurement of the amount of Pb^{2+} ions in plastic toys and paints, we have dissolved them separately first in nitric acid solution and then adjusted the pH of the solution to 8 by adding sodium hydroxide. As shown in Figure 4, our colorimetric assay clearly shows that the amount of Pb(II) in plastic toys is around 3 ppm and the amount of Pb(II) in paint is more than 10 ppm. Our colorimetric data (as shown in Figure 4B1) indicate that Pb(II) content in tap water from Jackson, MS and Mississippi river water is lower than 1 ppm. As a result, we did not observe any visible color change. To measure the Pb(II) amount quantitatively from paint, plastic toys and river water sample, we used our DLS assay. For the comparison

Table 1. Pb(II) Amounts in Different Water Sources, Plastic Toys and Paint Measured by DLS and ICP-MS methods

source	amount of Pb(II) measured by DLS (ppb)	amount of Pb(II) measured by ICPMS (ppb)
tap water	250 ± 12	255 ± 10
river water	625 ± 25	639 ± 20
plastic toys	5000 ± 255	5080 ± 340
paint	48000 ± 940	47600 ± 860

of our data to other well-established techniques, we also measured the Pb(II) content using ICP-MS technique. As shown in Table 1, ICP-MS data are highly comparable to our DLS assay data.

CONCLUSION

In conclusion, in this article, we have reported for the first time GSH conjugated gold nanoparticle based highly selective and ultra sensitive DLS probe for Pb(II) recognition from different day-to-day sample. Our experimental results show that Pb(II) can be detected quickly and accurately without any tagging in 100 ppt level with excellent discrimination against other heavy metals. This DLS assay is rapid and takes less than 20 min from Pb(II) binding to detection and analysis. Our experimental results demonstrate that the sensitivity of our DLS assay to detect Pb(II) level in water is almost 2 orders of magnitude higher than the environmental protection agency (EPA) standard limit. We have also demonstrated that our DLS assay is capable of measuring amount of Pb(II) in water samples from different sources, as well as from extensively used samples like plastic toys and paints. Our experimental results reported here open up a new possibility for rapid, easy, and reliable diagnosis of Pb(II) from water sample by measuring the DLS intensity. Given the simplicity, speed, and sensitivity of this approach, the described methodology could easily be extended to a high throughput format and it can become a new method of choice in all applications that require an assay for toxic metal ion detection. It is probably possible to improve our DLS assay sensitivity by several orders of magnitudes by choosing proper materials. As a result, we still need a much greater understanding on how to control surface architecture in order to stabilize and maximize the DLS response.

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