DOI 10.5012/bkcs.2010.31.12.3806

Alkyl Phosphate Functionalized Gold Nanoparticles-Based Colorimetric Probe for Pb^{2+} ions

Seung Kyung Kim, Sudeok Kim, Eun Ji Hong, and Min Su Han*

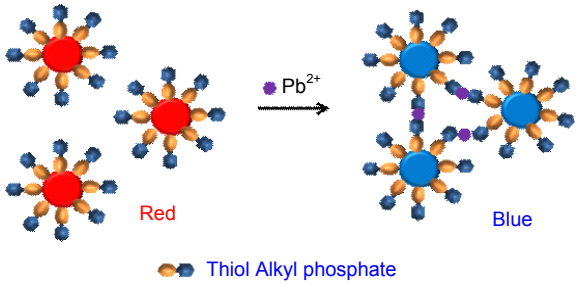
*Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea. *E-mail: mshan@cau.ac.kr*
Received September 14, 2010, Accepted October 13, 2010

Key Words: Colorimetric, Pb^{2+}, Gold nanoparticle, Probe

Lead is a common pollutant that is released routinely from a range of sources, such as lead-acid batteries, lead wire or pipes, paint, and metal recycling and foundries. Lead is extremely toxic to many organs and tissues, and interferes with a variety of vital processes.[1] In particular, the lead interferes with the development of the nervous system, which can cause learning and behavior disorders in children.[2] The detection of Pb^{2+} has attracted considerable attention in recent years and many optical probes for Pb^{2+} have been developed using organic dyes.[3] Although colorimetric probes are attractive because they can be read with the naked eye, in some cases at the point of use, most of these probes are based on a fluorescent dye to achieve high sensitivity. Therefore, it is desirable to develop a colorimetric probe for Pb^{2+} with a sensitivity as high as a fluorescent probe.

Gold nanoparticles (AuNPs) are a good chromogenic dye for the development of a colorimetric sensing system because AuNPs have extinction coefficients, 3 - 5 orders of magnitude higher than those of organic dye molecules, and have unique distance-dependent optical properties that can be programmed chemically using specific host compounds that can induce a dramatic red-to-blue color change in AuNPs.[4] Thus far, several AuNPs based-colorimetric sensing systems of Pb^{2+} have been developed using chemical functionalized AuNPs,[5] a mixture of DNA functionalized AuNPs and DNAzyme,[6] and Pb^{2+} catalyzed-leaching of AuNPs.[7] Although colorimetric sensing methods based on DNAzyme and Pb^{2+} catalyzed-leaching of AuNPs are quite sensitive and selective, these methods are quite sensitive to conditions, such as pH, temperature and composites of the reaction media, because these systems rely on catalytic reactions.[6,7] A chemical functionalized AuNPs based system is free from these problems. However, 11-mercaptoundecanoic acid-functionalized based AuNPs system showed low selectivity and sensitivity.[5a] In addition, glutathione functionalized AuNPs required additional salt to induce a color change in a AuNPs solution after adding Pb^{2+}.[5b] Therefore, these systems have particular limitations.

Alkyl phosphates are potentially good ligands for Pb^{2+} because Pb^{2+} easily forms solids with phosphates, e.g. $Pb(HPO_4)$ and $Pb_3(PO_4)_2$ have solubility products of only $10^{-11.4}$ M_2 and $10^{-44.4}$ M_5, respectively, and approximately 95% of the body burden of lead is stored in the bones as lead phosphate derivatives.[8] With this information, it is expected that alkyl phosphate-functionalized AuNPs (Phos-AuNPs) can be used as a colorimetric probe for the detection of Pb^{2+} because alkyl phosphate-functionalized AuNPs can interconnected with Pb^{2+} and induce a dramatic red-to-blue color change in the AuNPs as illustrated in Scheme 1.



Scheme 1. Schematic representation of the Pb^{2+} chemosensor

To evaluate the sensitivity of Phos-AuNPs for Pb^{2+}, Figure 1a shows the absorbance changes in Phos-AuNPs in the presence of various concentrations of Pb^{2+}. The addition of Pb^{2+} induced a decrease in absorbance at 520 nm, and as shown in Figure 1b, the observed absorbance intensity was almost proportional to the Pb^{2+} concentration. The absorbance changes are a well-known phenomenon that is used to confirm the formation of nanoparticle aggregates[5] and the aggregation of Phos-AuNPs was identified by transmission electron microscopy (Figure 1c). Therefore, Phos-AuNPs were aggregated by Pb^{2+}, which caused a dramatic red-to-blue color change as illustrated in Scheme 1. The detection limit of Phos-AuNPs for Pb^{2+} was estimated to be 1.637 μM from the titration results and was as low as fluorescent probes. Also, we studied the effect of the pH value of the medium on Pb^{2+} sensing of Phos-AuNPs in the pH range of 4 - 9 because phosphate derivatives are generally sensitive to pH. The Phos-AuNPs aggregated immediately in pH 4 and was not sensitive to Pb^{2+} in pH 5 and 9. However, Phos-AuNPs are stable in the pH range of 6 - 8 and Pb^{2+} can lead to a strong response in the pH range (see supporting information). In addition, this method was more sensitive than the alkyl carboxylic acid modified AuNPs-based method,[5a] and did not require an additional salt to induce dramatic color changes in the AuNP solution, unlike the cysteine modified AuNPs-based method.[5b]

Another important property of this method is its selectivity for Pb^{2+} over other metal ions. The selectivity of Phos-AuNPs for various metal ions was evaluated and the absorbance changes in the Phos-AuNPs in the presence of other metal ions were measured. Figure 2 shows the absorbance spectra of the solutions of Phos-AuNPs recorded after adding each metal ion. As shown in Figure 2, Zn^{2+} also induced a slight color change in Phos-AuNPs but no significant changes in the absorbance were observed upon the addition of other metal ions. This selectivity

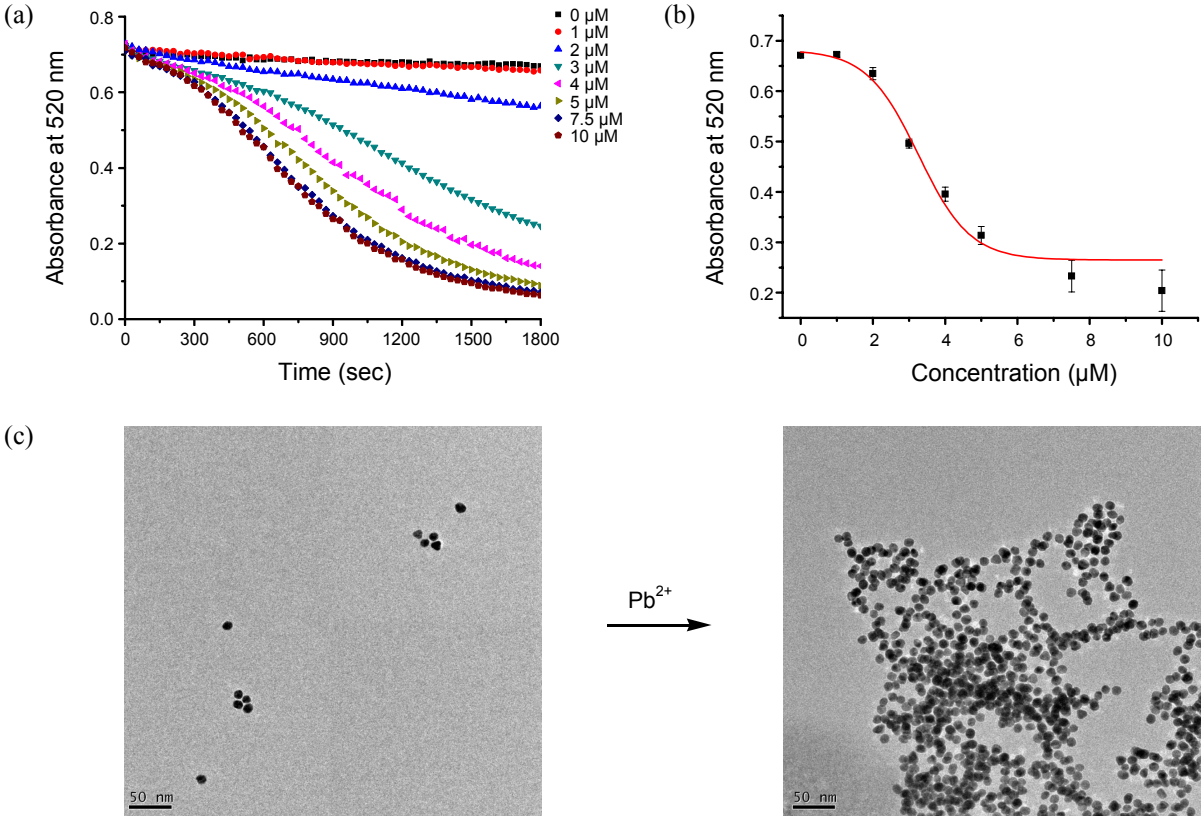


Figure 1. (a) Absorbance changes in pH 7.0 buffer solutions (10 mM HEPES) containing Phos-AuNPs (3 nM) in the presence of various concentrations of Pb^{2+}. (b) Plot of the assay solution absorbance intensities at 520 nm *versus* Pb^{2+} concentration. (c) TEM images of Phos-AuNPs in the absence of Pb^{2+} and presence of Pb^{2+} at pH 7. Scale bar represents 50 nm.

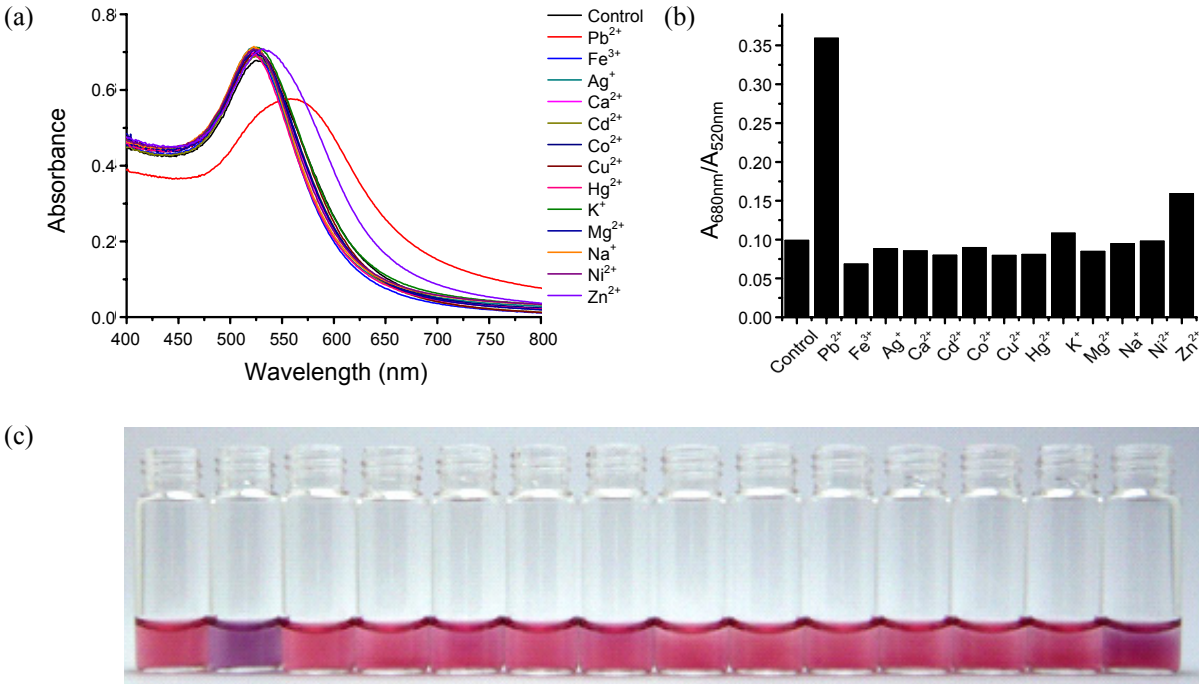


Figure 2. (a) UV-vis spectra obtained by adding various metal ions (3 μM) in pH 7.0 buffer solution (10 mM HEPES) containing Phos-AuNPs (3 nM). (b) Plot of the absorbance ratios of the assay solutions *versus* various metal ions. (c) The color of the solution in the presence of various metal ions (3 μM): from left to right; control, Pb^{2+}, Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Na^{+}, Ni^{2+}, Zn^{2+}.

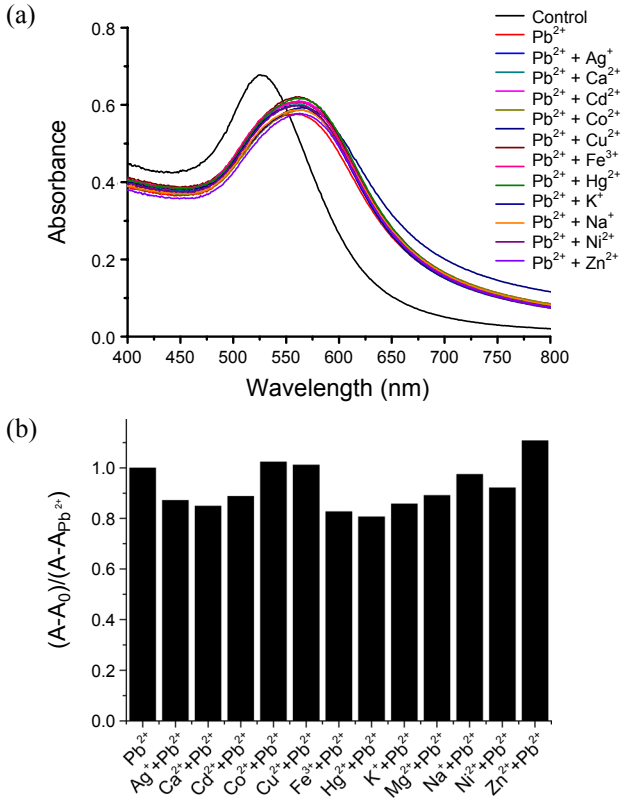


Figure 3. (a) UV-vis spectra obtained by the addition of Pb^{2+} (3 μM) with other metal ions (3 μM) to the buffer solution containing sAuNPs (3 nM). (b) Plot of the absorbance intensity of the assay solution *versus* Pb^{2+} (3 μM) and other metal ions (3 μM) at 520 nm.

might be due to the fact that the ionic radius of Pb^{2+} is larger than that of other metal ions because the large ionic radius of Pb^{2+} may provide multivalent sites for phosphate ligands on AuNPs.[9] In addition, sensors that can detect analytes by the naked eye are attractive because of their convenience. The use of this method for such a purpose is demonstrated in Figure 2C. Although the red to blue color change occurred when Zn^{2+} were added to an aqueous solution of Phos-AuNPs, Pb^{2+} caused a more dramatic color change than Zn^{2+}.

The presence of background metal ions can interfere with the selectivity of the developed probe. To eliminate the possibility, the Pb^{2+}-induced absorbance changes in the Phos-AuNPs were measured in the presence of these metal ions. The UV-vis spectra of the Phos-AuNPs solutions were recorded 15 min after adding Pb^{2+} (3 μM) and a possible interfering metal ion (3 μM). As shown in Figure 3, no other metal ions affected the selectivity of the Phos-AuNPs for Pb^{2+}.

In conclusion, Phos-AuNPs is an effective colorimetric probe for Pb^{2+}. The proposed Probe can detect Pb^{2+}, both spectrophotometrically and visually, in aqueous solutions at physiological pH with high selectivity toward Pb^{2+} over a variety of metal ions. Moreover, the selectivity is retained even in the presence of other metal ions. In addition, this AuNP-based method has a low detection limit as low as fluorescent chemosensor.

Experimental Section

Chemicals. All chemicals used were of analytical grade or of the highest purity available. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), citric acid and metal salts were purchased from Sigma Aldrich (USA). All glassware was cleaned thoroughly with freshly prepared aqua regia (3:1 (v/v) HCl/HNO_3) and rinsed thoroughly with Milli-Q water prior to use. Milli-Q water was used to prepare all the solutions in this study.

Preparation of Phos-AuNPs. All glassware was washed with freshly prepared aqua regia (3:1 = HCl:HNO_3) followed by extensive rinsing with doubly distilled H_2O. Citric acid stabilized Au particles with a diameter of 13 nm were prepared by adding 50 mL of a citrate solution (38.8 mM) to 500 mL of boiling 1.0 mM $HAuCl_4 \cdot 3H_2O$ with vigorous stirring. After the appearance of a deep red color, boiling and stirring were continued for 15 min. The solution was then allowed to cool to room temperature with continued stirring. 1% TWEEN 20 solution (1.5 mL) was added to the 30 mL of the citric acid stabilized AuNPs (11.5 nM) and 12 mL of 11-mercaptoundecyl phospholic acid (10 mM) in THF was added to the solution 5 times in 36 hours at the same intervals. The solution was adjusted with a 1 mM HEPES buffer (pH 7.0) using 30 mM HEPES buffer and incubated for 12 hours. After incubation, the un-reacted 11-mercaptoundecyl phospholic acid and TWEEN 20 were eliminated by centrifuging 2 times and the Phos-AuNPs were kept in distilled water.

Colorimetric assay for Pb^{2+}. Solutions of Phos-AuNPs (3 nM) in HEPES buffer were mixed with various concentrations of Pb^{2+} and the UV/Vis spectra of the solutions were recorded after incubation for 15 minutes.

Acknowledgments. This research was supported by the Chung-Ang University Research Grants in 2010.

References

1. Rifai, N.; Cohen, G.; Wolf, M.; Cohen, L.; Faser, C.; Savory, J.; DePalma, L. *Ther. Drug Monit.* **1993**, *15*, 71.
2. Winder, C.; Carmichael, N. G.; Lewis, P. D. *Trends Neurosci.* **1982**, *5*, 207.
3. (a) Chen, C.-T.; Huang, W.-P. *J. Am. Chem. Soc.* **2002**, *124*, 6246. (b) Buie, N. M.; Talanov, V. S.; Butcher, R. J.; Talanova, G. G. *Inorg. Chem.* **2008**, *47*, 3549. (c) He, Q.; Miller, E. W.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 9316. (d) Kwon, J. Y.; Jang, Y. J.; Lee, Y. J.; Kim, K. M.; Seo, M. S.; Nam, W.; Yoon, J. *J. Am. Chem. Soc.* **2005**, *127*, 10107. (e) Zapata, F.; Caballero, A.; Espinosa, A.; Tárraga, A.; Molina, P. *J. Org. Chem.* **2009**, *74*, 4787. (f) Kim, J. S.; Kim, H. J.; Kim, H. M.; Kim, S. H.; Lee, J. W.; Kim, S. K.; Cho, B. R. *J. Org. Chem.* **2006**, *71*, 8016. (g) Chang, K.-C.; Su, I.-H.; Senthilvelan, A.; Chung, W.-S. *Org. Lett.* **2007**, *9*, 3363. (h) Wu, J.-S.; Hwang, I.-C.; Kim, K. S.; Kim, J. S. *Org. Lett.* **2007**, *9*, 907.
4. (a) Rosi, N. L.; Mirkin, C. A. *Chem. Rev.* **2005**, *105*, 1547. (b) Lu, Y.; Liu, J. *Acc. Chem. Res.* **2007**, *40*, 315. (c) Stewart, M. E.; Anderton, C. R.; Thompson, L. B.; Maria, J.; Gray, S. K.; Rogers, J. A.; Nuzzo, R. G. *Chem. Rev.* **2008**, *108*, 494. (d) Ghosh, S. K.; Pal, T. *Chem. Rev.* **2007**, *107*, 4797. (e) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
5. (a) Kim, Y.; Johnson, R. C.; Hupp, J. T. *Nano Lett.* **2001**, *1*, 165. (b) Chai, F.; Wang, C.; Wang, T.; Li, L.; Su, Z. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1466.
6. Liu, J.; Lu, Y. *J. Am. Chem. Soc.* **2004**, *126*, 12298.
7. Chen, Y.-Y.; Chang, H.-T.; Shiang, Y.-C.; Hung, Y.-L.; Chiang, C.-K.; Huang, C.-C. *Anal. Chem.* **2009**, *81*, 9433.
8. Da Costa, C. P.; Sigel, H. *J. Biol. Inorg. Chem.* **1999**, *4*, 508.
9. Saxena, S.; D'Souza, S. F. *Environ. Int.* **2006**, *32*, 199.