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Tetrahedron Letters
Tetrahedron Letters 46 (2005) 8827–8829

Colorimetric detection of fluoride ion in an aqueous solution using a thioglucose-capped gold nanoparticle

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Received 2 September 2005; revised 15 October 2005; accepted 20 October 2005
Available online 2 November 2005

Abstract—The thioglucose-capped gold nanoparticles have been prepared by the chemical reduction of $HAuCl_4$ using thioglucose as the reducing and capping agent, which displays selective colorimetric detection of fluoride ion in 10 mM HEPES buffer at physiological pH.

Gold nanoparticles have attracted much attention as a unique and advantageous platform for highly sensitive chemical sensors.[1] In particular, they have an intense plasmon band in the visible region,[2] which is exquisitely sensitive to their aggregation states.[3] Recently the colorimetric nanoprobes have been developed for sensitive and selective detection of alkali metal ions,[4] heavy metal ions,[5] lectine,[6] and DNA.[7] However, there is still a need for colorimetric nanoprobes sensing a wide variety of analytes, in particular biologically important anions.[8,9] A common problem on nanoprobe development is that the limited gold nanoparticles are available as platforms. Gold nanoparticles widely used at present, prepared by citrate, were dispersed in an aqueous solution through the ionic repulsion of the surface-adsorbed ions. In the presence of electrolytes, the ionically stabilized gold nanoparticles undergo uncontrolled aggregation because of the charge shielding. In order to stabilize the dispersion, the gold nanoparticles protected with nonionic hydrophilic polymers,[10] such as poly(ethylene glycol), were prepared but the thick protecting layer preventing the core metals to be close together has disadvantages in the color change. Further development requires uncharged gold nanoparticles protected with a monolayer of hydrophilic molecules. Here we report the simple, easy, and quantitative preparation of the novel uncharged gold nanoparticles modified with thioglucose. We also found through UV–vis titration study that the thioglucose-capped gold nanoparticle (TG Au-NP) caused the F^--selective aggregation associated with a dramatic color change in aqueous solution. There are various colorimetric F^- probes based on calx[4]-pyrroles,[11] dipyrrolyquinoxalies,[12,13] diaminoanthraquinones,[14,15] azophenols,[16] and others.[17–19] However, these molecular-based probes are useful only in nonaqueous solution. The TG Au-NP is a potential candidate to construct the reliable colorimetric sensing systems, which enabled the naked eye detection of fluoride ion.

Thioglucose-capped gold nanoparticles (1-TG Au-NP) have been prepared by the chemical reduction of $HAuCl_4$ using 1-thio-β-D-glucose (1-TG) as the reducing and capping agent (Fig. 1). An aqueous thioglucose solution (5.0 ml, 2–20 mM) was added to a boiling solution of $HAuCl_4$ (50 ml, 0.5 mM) under vigorous stirring. On addition of 1-TG, the solution changed color from pale yellow to ruby red within 10 s, and then the reaction mixture was further heated for 10 min under reflux. The extinction spectrum of the suspension showed the maximum at 523 nm attributed to the surface plasmon band of gold. The reaction mixture was cooled, dialyzed

Keywords: Gold nanoparticle; Glucose; Fluoride ion; Colorimetric detection.
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doi:10.1016/j.tetlet.2005.10.097

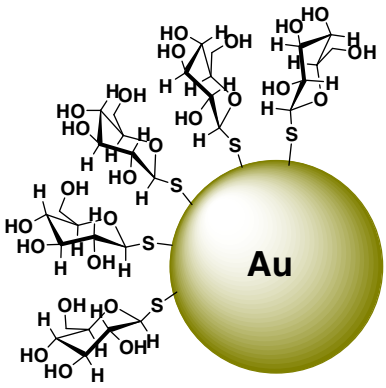

Figure 1. A schematic speculation about the structure of the 1-TG Au-NP.

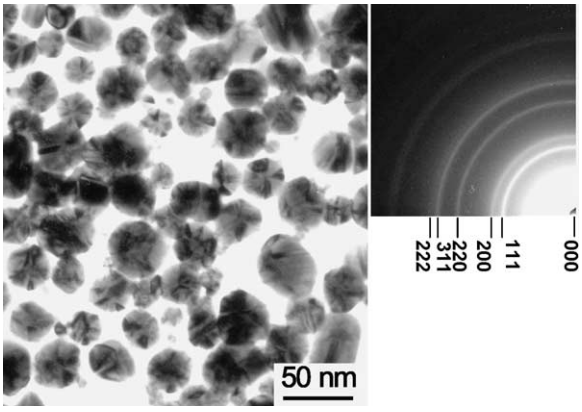

Figure 2. TEM image and electron diffraction pattern of the 1-TG Au-NP. The accelerating voltage is 100 kV.

overnight against ultra pure water to remove unreacted TG, using a dialysis tube (Spectra/Por, Cellulose Ester, MWCO = 5000, Spectrum Laboratories Inc., USA). The SH group is required to prepare well-dispersed gold nanoparticles because, under the same conditions, the gold nanoparticle prepared by using glucose as the reducing agent immediately precipitated. The position of the SH group is also an important parameter for the particle synthesis. 5-Thio-D-glucose (5-TG) was somewhat less active, and the prepared 5-TG Au-NP partially aggregated and then precipitated in a few days. The particle size and size distribution of gold nanoparticles were measured using dynamic light scattering with a He–Ne laser as excitation source (DLS-6000, Otsuka Electronics, Japan). The average particle diameter can be tuned over a size range of 20–50 nm by varying the molar ratio of TG/Au from 0.45 to 0.51. The 1-TG Au-NP prepared at the 1-TG/Au ratio of 0.5 had a particle diameter of 32 nm with a polydispersity index of 0.15. The morphology of the 1-TG Au-NP was observed by using a transmission electron microscope (JEM-100CX, JEOL Ltd., Japan). Figure 2 shows a typical TEM image of the 1-TG Au-NP. The shape of the 1-TG Au-NP was slightly irregular irrespective of the 1-TG/Au ratio. The diffraction rings in the figure are clearly due to a face centered cubic gold unit cell structure. The oxidation state of gold in the 1-TG Au-NP was determined by X-ray photoelectron spectroscopy (ESCA-3300, Shimazu Corp., Japan). The Au $4f_{7/2}$ and $4f_{5/2}$ peaks were observed at 84.4 and 88.1 eV, respectively, which are characteristic of Au^0. The FT-IR spectrum of the TG Au-NP measured by using a JASCO FT/IR-460 plus spectrometer was essentially featureless. The ξ potential measurements were carried out with an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics, Japan). The ξ potential of the 1-TG Au-NP was close to zero (−2.0 mV) at the physiological pH, indicating TG molecules coordinate with the exterior to shield the surface charge.

The 1-TG Au-NP is well dispersed in the buffer solution at physiological pH compared with the citrate-capped gold nanoparticles highly sensitive to pH and ionic strength. The colorimetric detection of halide anions (F^-, Cl^-, Br^-, I^-) and oxoanions ($H_2PO_4^-$, $CH_3CO_2^-$, NO_3^-) was investigated using UV–vis spectroscopy in an aqueous solution of 10 mM HEPES buffer (pH 7.4) at 20 °C. As shown in Figure 3, addition of F^- to a solu-

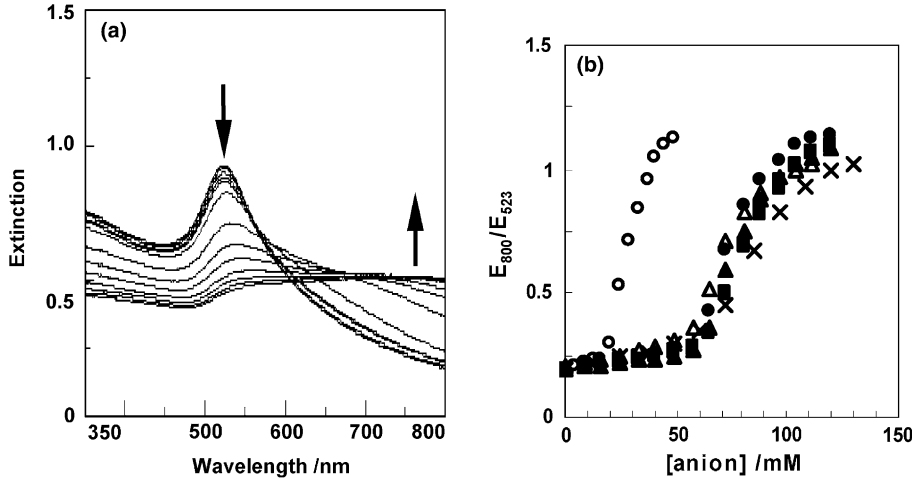

Figure 3. (a) Change in the UV–vis extinction spectrum of the 1-TG Au-NP upon addition of 0–50 mM of F^- in 10 mM HEPES buffer (pH 7.4). (b) Titration curves of the TG Au-NP with anions: F^- (○), Cl^- (△), Br^- (□), I^- (×), $H_2PO_4^-$ (●), $CH_3CO_2^-$ (▲), NO_3^- (■).

Figure 4. Color changes of the 1-TG Au-NP in 10 mM HEPES buffer (pH 7.4); [anion] = 30 mM.

tion of the 1-TG Au-NP causes a red shift in the surface plasmon band. Extinction at wavelengths above 600 nm corresponds to the collective plasmon resonance of closely spaced gold nanoparticles, indicating the anion-induced nanoparticle aggregation. DLS measurements also indicate the size distribution of the 1-TG Au-NP change from 30 to 100 nm upon the addition of anions.

Quantitative analysis of anions was performed using a ratiometric method that is unaffected by variations in sample conditions. The ratio of extinction at 523 and 800 nm was used, which represent the relative amount of free and aggregated gold nanoparticles, respectively. A plot of this extinction ratio as a function of anion concentration shows a sigmoidal titration curve (Fig. 3b). At a certain threshold concentration of anions, the difference in the anion concentration can be seen by the naked eye as the color change from red to blue. The degree of the threshold concentration for the 1-TG Au-NP was determined to be $F^- < CH_3CO_2^- \approx Cl^- \approx H_2PO_4^- \approx NO_3^- \approx Br^- \approx I^-$. The 1-TG Au-NP is capable of selectively detecting F^- in the range of 20–40 mM. The preference for F^- over other anions may be explained by the strong basicity and the spherical shape of F^-. According to the basicity of anions, F^- and AcO^- give strong complexes with the TG molecules on the particle surface. In particular, the multidentate F^- ion readily induces the particle aggregation compared to the bidentate AcO^- ion. Figure 4 displays the colorimetric detection of F^-. Each vial contains a solution of the 1-TG Au-NP in 10 mM HEPES buffer. The addition of 30 mM of F^- induces the appearance of a blue color while the addition of 30 mM of the other anions induces no color change.

In conclusion, we report herein a simple way for the direct synthesis of the TG Au-NP by using the reducing and stabilizing abilities of TG. Halide anions and oxoanions induce the aggregation of the 1-TG Au-NP in aqueous solution. The striking color change associated with the F^--induced aggregation has been successfully employed for the naked eye detection of F^-. Further development of colorimetric nanoprobes with improved selectivity and sensitivity are ongoing in our group.

Acknowledgments

This work is supported by a Grant-in-Aid for Scientific Research (B) No. 15350083 from the Japan Society for the Promotion of Science (JSPS), by a Special Research Grant for Green Science from Kochi University, and by a Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Corporation (JST).

References and notes

1. (a) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346; (b) Shi, J.; Zhu, Y.; Zhang, X.; Baeyens, W. R. G.; Garcia-Campana, A. M. *Trends Anal. Chem.* **2004**, *23*, 351–360; (c) Nath, N.; Chilkoti, A. *J. Fluorescence* **2004**, *14*, 377–389.
2. (a) Maye, M. M.; Han, L.; Kariuki, N. N.; Ly, N. K.; Chan, W.-B.; Luo, J.; Zhong, C.-J. *Anal. Chim. Acta* **2003**, *496*, 17–27; (b) Hussain, I.; Brust, M.; Papworth, A. J.; Cooper, A. I. *Langmuir* **2003**, *19*, 4831–4835; (c) Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 12674–12675.
3. (a) Zhao, L.; Kelly, K. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 7343–7350; (b) Lazarides, A. A.; Kelly, K. L.; Jensen, T. R.; Schatz, G. C. *Theochem* **2000**, *529*, 59–63; (c) Storhoff, J. J.; Lazarides, A. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L.; Schatz, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4640–4650.
4. (a) Obare, S. O.; Hollowell, R. E.; Murphy, C. J. *Langmuir* **2002**, *18*, 10407–10410; (b) Lin, S.-Y.; Liu, S.-W.; Lin, C.-M.; Chen, C.-h. *Anal. Chem.* **2002**, *74*, 330–335.
5. Liu, J.; Lu, Y. *J. Fluorescence* **2004**, *14*, 343–354.
6. Otsuka, H.; Akiyama, Y.; Nagasaki, Y.; Kataoka, K. *J. Am. Chem. Soc.* **2001**, *123*, 8226–8230.
7. Thaxton, C. S.; Mirkin, C. A. In *Nanobiotechnology*; Niemeyer, C. M., Mirkin, C. A., Eds.; Wiley-VCH: Weinheim, 2004; pp 288–307, and references cited therein.
8. Kubo, Y.; Uchida, S.; Kemmochi, Y.; Okubo, T. *Tetrahedron Lett.* **2005**, *46*, 4369–4372.
9. Watanabe, S.; Sonobe, M.; Arai, M.; Tazume, Y.; Matsuo, T.; Nakamura, T.; Yoshida, K. *Chem. Commun.* **2002**, 2866–2867.
10. Ishii, T.; Otsuka, H.; Kataoka, K.; Nagasaki, Y. *Langmuir* **2004**, *20*, 561–564.
11. (a) Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jursikova, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268–10272; (b) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777–1780; (c) Gale, P. A.; Twyman, L. J.; Handlin, C. I.; Sessler, J. L. *Chem. Commun.* **1999**, 1851–1852.
12. Ghosh, T.; Maiya, B. G. *J. Chem. Sci.* **2004**, *116*, 17–20.
13. (a) Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134–1135; (b) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438–10439.
14. Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448.
15. Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154–157.
16. (a) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5–8; (b) Lee, K. H.; Lee, H.-Y.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 5447–5449.
17. Zhou, L. L.; Zhang, X. H.; Wu, S. K. *Sens. Actuators, B* **2005**, *106*, 343–346.
18. Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372–11375.
19. Ward, C. J.; Patel, P.; James, T. D. *Chem. Lett.* **2001**, 406–407.