

Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Repeated appearance and disappearance of localized surface plasmon resonance in 1.2 nm gold clusters induced by adsorption and desorption of hydrogen atoms

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ryo Ishida,^a Seiji Yamazoe,^{ab} Kiichiro Koyasu,^{ab} and Tatsuya Tsukuda^{*ab}

Addition of an aqueous solution of NaBH₄ to a dispersion of small (~1.2 nm) gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) induced a localized surface plasmon resonance (LSPR) absorption for a certain period while maintaining the cluster size. The duration of the LSPR band could be lengthened by increasing the NaBH₄ concentration and be shortened by increasing the concentration of dissolved O₂, and the LSPR band could be made to appear and reappear repeatedly. The appearance of the LSPR band is explained by the electron donation to the Au core from the adsorbed H atoms that originate from NaBH₄, whereas its disappearance is ascribed to the removal of H atoms by their reaction with O₂. These results suggest that the transition between the metallic and nonmetallic electronic structures of the Au clusters can be reversibly induced by the adsorption and desorption of H atoms, which are electronically equivalent to Au.

Introduction

Gold clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) have provided us an ideal platform to study the cluster-size-dependent catalytic properties¹ and useful precursors of a variety of ligand-protected Au clusters.² This is because chemical substances can access the surface of the Au clusters exposed for catalysis and ligation. For example, it was found that Au:PVP clusters with an average diameter of ~1.2 nm show high catalytic activity for various aerobic oxidation reactions such as the oxidation of alcohols, organoboron compounds, and benzylic ketones.³ Thus, it is desirable to synthesize Au:PVP clusters with a diameter of ~1 nm for applications in catalysis.

According to the LaMer model,^{4,5} small monodisperse metal clusters can be produced by instantaneous reduction of the precursor metal ions, thereby completing nucleation and suppressing the subsequent nuclei growth. Conventionally, small Au:PVP clusters are prepared by rapid injection of an aqueous solution containing an excess amount of NaBH₄ into a mixed solution of HAuCl₄ and PVP (average molecular weight = 40 kDa).^{6,7} After stirring for 1 h, the Au:PVP clusters are collected and deionized by centrifugal ultrafiltration. TEM observation of the Au:PVP thus produced indicated that their average diameter is 1.2 nm, and MALDI mass spectrometry revealed that cluster sizes are smoothly distributed over the range of 30–70 atoms.⁸ The Au:PVP clusters were brownish

and did not have the localized surface plasmon resonance (LSPR) band,⁹ that is typically observed at around 520 nm for Au clusters larger than 2 nm.^{10,11} Interestingly, the color of the dispersion turned from yellow to red immediately after the addition of NaBH₄ and, then, to dark brown after some time. Figure 1 shows the change in the optical spectra of a Au:PVP hydrosol over time during their preparation in air by the described method. The LSPR band emerged soon after the addition of NaBH₄, and the absorbance was maintained for about 30 min, after which it rapidly disappeared. There are two possible scenarios to explain this phenomenon. One is that Au clusters larger than 2 nm were initially formed, but became smaller over time. The other is that the LSPR band appeared because of the interaction between Au:PVP (~1.2 nm) and NaBH₄.

Motivated by this phenomenon, we studied the spectral changes in the interaction of small (~1.2 nm), preformed Au:PVP clusters with NaBH₄. It was found that the duration of the LSPR band can be increased by increasing the concentration of NaBH₄ and can be shortened by increasing the concentration of O₂ dissolved in water. These phenomena were explained in terms of the reversible electronic modulation of the Au clusters, induced by the adsorption and desorption of hydrogen atoms.

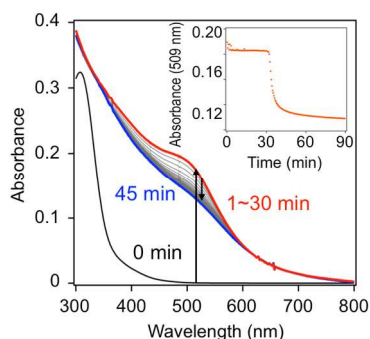


Figure 1. Changes in absorption spectra over time during the preparation of Au:PVP clusters with an average diameter of 1.2 nm. Inset shows change in absorbance at 509 nm versus time.

An aqueous solution of NaBH_4 was added to the hydrosol of the preformed Au:PVP (1.2 nm) clusters in air. The changes in the absorption spectra were measured over time and showed that the LSPR emerged soon after the addition of NaBH_4 , remained constant for ~ 70 min, and then disappeared rapidly (Figure S1). The sizes of the Au:PVP clusters before and after the reaction with NaBH_4 were compared by transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, and X-ray absorption fine structure (XAFS) spectroscopy. Figure 2 compares the TEM images and size distributions of the Au:PVP clusters before and after the reaction with NaBH_4 . The average diameter of the Au:PVP clusters did not change appreciably after the reaction. This conclusion is supported by both XRD and XAFS analyses (Figures S2 and S3). These findings indicate that the appearance of the LSPR band at the initial stage of the reaction was not associated with the growth of Au clusters, but was caused by the interaction between the preformed Au:PVP clusters and NaBH_4 . In the framework of this mechanism, the duration of the LSPR is related to the concentration of NaBH_4 in water. To test this assumption, the duration of the LSPR was measured as a function of the concentration of added NaBH_4 ($[\text{NaBH}_4]$). An aqueous solution of NaBH_4 with concentrations of 0.1, 0.2, or 0.3 M was added to the hydrosol of Au:PVP (1.2 nm) in air. The changes in absorbance at 509 nm over time at different $[\text{NaBH}_4]$ (Figure S4) show that the LSPR duration lengthened monotonically with increasing $[\text{NaBH}_4]$ (Figure 3a), as anticipated. The repeatability of this phenomenon was studied by adding a fresh solution of NaBH_4 to the deionized dispersion of Au:PVP clusters. Figure 4 shows the change in the absorbance at 509 nm over time after repeated addition of NaBH_4 to the Au:PVP (1.2 nm) hydrosol. These results indicate that the electronic structure of the Au:PVP clusters can be modulated repeatedly by reaction with NaBH_4 .

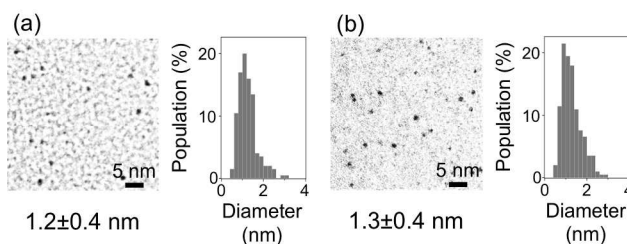


Figure 2. TEM images and size distributions of Au:PVP clusters before (a) and after (b) reaction with NaBH_4 .

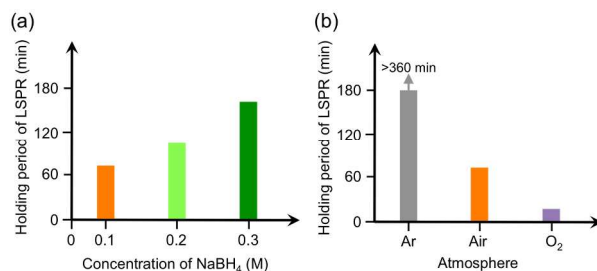


Figure 3. Dependence of the duration of the LSPR on (a) the concentration of NaBH_4 in air and (b) the presence of different gases in the measurement cell ($[\text{NaBH}_4] = 0.1$ M)

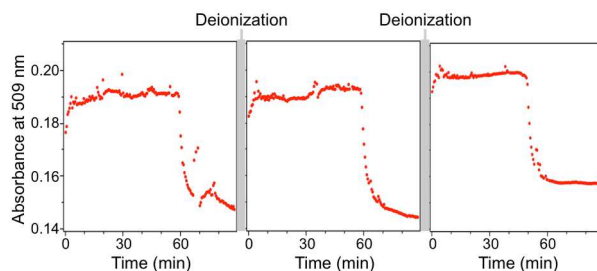


Figure 4. Three measurements of the change in absorbance at 509 nm versus time after addition of aqueous solutions of NaBH_4 .

What kind of species were produced during the reaction, and what determined the duration of the LSPR band? It is known that Au nanoparticles catalyze the hydrolysis of BH_4^- (Refs. 12,13) and the reduction of 4-nitrophenol by NaBH_4 .¹⁴ It has been proposed that the catalytic reduction proceed via the Langmuir-Hinshelwood mechanism, in which substrates and reductants adsorbed on the nanoparticle surface are involved in the reaction.¹⁴ According to computational studies, hydrides or borohydrides can be bound strongly to the Au nanoparticles¹⁵ and donate negative charge to the Au core.¹⁶⁻¹⁸ In order to gain insights into the chemical nature of the reaction products, the duration of the LSPR was measured as a function of O_2 concentration (Figure S4). The LSPR duration was greater when air was replaced by Ar in a closed vessel, whereas it was shortened when air was replaced with pure O_2 (Figure 3b). This result suggests that the appearances and disappearances of the LSPR band are associated with the adsorption of hydrogen atoms

to the Au clusters (1.2 nm) and removal of the hydrogen atoms by the reaction of O₂ dissolved in water, respectively.^{19,20}

How do the hydrogen atoms affect the electronic structure of the Au cluster? Given that the LSPR band is specific to Au clusters larger than 2 nm, the above results can be understood if the adsorption of hydrogen atoms has similar effect as Au cluster size increases. This assumption is plausible because the electronic properties of gold and hydrogen are similar; they have similar electronic configurations with a single valence electron in an *ns* orbital; moreover, they have comparable electronegativities as a result of the strong relativistic effects in gold.^{21,22} It has also been reported that the chemical properties of gold are very similar to those of hydrogen.²³⁻²⁷ Buckart et al. proposed, based on the almost identical photoelectron spectra of Au_{*n*}⁻ and Au_{*n-1*}H⁻ (*n* = 3–8), that hydrogen atoms mimic gold atoms.²⁸ Based on these reports, we concluded that the adsorption of hydrogen atoms on the surface of the gold clusters increased both the number of confined *s*-electron and the electron density, thus, inducing LSPR.²⁹

In order to test whether NaBH₄ substantially increased the electron density in the Au cluster, the spectral changes were studied after adding NaBH₄ to larger (1.8 ± 0.5 nm) Au:PVP clusters that showed the LSPR band. According to the Drude model,³⁰ the plasmon wavelength is blue shifted as the electron density in the metal nanoparticles increases. The LSPR peak of Au:PVP (1.8 nm) was blue shifted after the addition of NaBH₄ (Figure S5), and there was a small increase in absorbance. This result confirms that reaction with NaBH₄ increases the electron density of the Au:PVP clusters due to electron transfer from hydrogen to the Au core.

We have recently demonstrated that an LSPR band appears on going from Au₁₄₄(SC12)₆₀ to Au₁₈₇(SC12)₆₈, where SC12 represents dodecanethiolates.¹¹ The theoretically predicted Au cores were Au₁₁₄ and Au₁₄₈ with 84 and 121 valence electrons, respectively.³¹ Roughly speaking, the confinement of ~100 electrons in the Au₁₃₀ core is critical for the appearance of an LSPR band. The sizes of the Au:PVP clusters were distributed in the range of 30–70 atoms, as found by MALDI mass spectrometry.⁸ If we assume that all the surface atoms of the Au cluster are capped by a single H atom and that each H provides one electron to the Au cluster, the total number of *s*-electrons confined in the Au core is estimated to be 120 at most, even for the largest Au₇₀ cluster. This rough estimate suggests that the critical size for the appearance of the LSPR band for a H-capped Au cluster is comparable or smaller than that of a Au_{*n*}(SR)_{*m*} cluster. This difference is probably due to the difference in the atomic sizes of Au (144 pm) and H (0.53 pm).^{32,33} Adsorption of hydrogen atoms can increase the electron density of Au clusters without any increase in the total cluster volume.

In summary, small (~1.2 nm) Au clusters stabilized by PVP exhibited LSPR on reaction with NaBH₄. We explain this observation as being a consequence of the adsorption of H atoms, derived from NaBH₄, on the cluster surfaces. Hydrogen atoms adsorbed on the Au cluster electronically mimic Au atoms and do not significantly increase the volume of the cluster and,

therefore, the volume of electron confinement because of their significantly smaller size than Au atoms. This unique feature of hydrogen atoms allows us to modulate the electronic structures of small, non-metallic Au clusters reversibly and repeatedly; that is, adsorption makes the electronic structure metallic, and desorption returns the clusters to a nonmetallic state.

Acknowledgements

This research was financially supported by the Elements Strategy Initiative for Catalysis & Batteries (ESICB) and by a Grant-in-Aid for Scientific Research (no. 26248003) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

Notes and references

^a Department of Chemistry, School of Science, The University of Tokyo, 7–3–1 Hongo, Bunkyo-ku, Tokyo 113–0033.

^b Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615–8520.

Electronic Supplementary Information (ESI) available:

- 1 S. Yamazoe, K. Koyasu and T. Tsukuda, *Acc. Chem. Res.* 2014, **47**, 816.
- 2 T. Tsukuda, *Bull. Chem. Soc. Jpn.* 2012, **85**, 151.
- 3 T. Tsukuda, H. Tsunoyama and H. Sakurai, *Chem. Asian. J.* 2011, **6**, 736.
- 4 V. K. La Mer and R. H. Dinegar, *J. Am. Chem. Soc.* 1950, **72**, 4847.
- 5 T. Sugimoto, *Adv. Colloid Interface Sci.* 1987, **28**, 65.
- 6 H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Neighs and T. Tsukuda, *Langmuir* 2004, **20**, 11293.
- 7 H. Tsunoyama, N. Ichikuni and T. Tsukuda, *Langmuir* 2008, **24**, 11327.
- 8 H. Tsunoyama and T. Tsukuda, *J. Am. Chem. Soc.* 2009, **131**, 18216.
- 9 H. Tsunoyama, H. Sakurai and T. Tsukuda, *Chem. Phys. Lett.* 2006, **429**, 528.
- 10 H. Qian, M. Zhu, M. Z. Wu and R. Jin, *Acc. Chem. Res.* 2012, **45**, 1470.
- 11 Y. Negishi, T. Nakazaki, S. Malola, S. Takano, Y. Niihori, W. Kurashige, S. Yamazoe, T. Tsukuda and H. Häkkinen, *J. Am. Chem. Soc.* 2015, **137**, 1206.
- 12 H. C. Brown and C. Brown, *J. Am. Chem. Soc.* 1962, **84**, 1493.
- 13 M. J. Hossain, H. Tsunoyama, M. Yamauchi, N. Ichikuni and T. Tsukuda, *Catal. Today* 2012, **183**, 101.
- 14 T. Aditya, A. Pal and T. Pal, *Chem. Commun.* 2015, **51**, 9410.
- 15 S. M. Ansar, F. S. Ameer, W. Hu, S. Zou, C. U. Pittman Jr. and D. Zhang, *Nano Lett.* 2013, **13**, 1226.
- 16 R. Ciganda, N. Li, C. Deraedt, S. Gatard, P. Zhao, L. Salmon, R. Hernandez, J. Ruiz and D. Astruc, *Chem. Commun.* 2014, **50**, 10126.
- 17 M. M. Giangregorio, M. Losurdo, G. V. Bianco, A. Operamolla, E. Dilonardo, A. Sacchetti, P. Capezzuto, F. Babudri and G. Bruno, *J. Phys. Chem. C* 2011, **115**, 19520.

- 18 D. Sil, K. D. Gilroy, A. Boulesbaa, S. Neretina and E. Borguet, *ACS Nano* 2014, **8**, 7755.
- 19 K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.* 2004, **126**, 10657.
- 20 Y. H. Ng, S. Ikeda, Y. Morita, T. Harada, K. Ikeue and M. Matsumura, *J. Phys. Chem. C* 2009, **113**, 12799.
- 21 Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276.
- 22 Desclaux, J. P.; Pyykkö, P. *Chem. Phys. Lett.* **1976**, *39*, 300.
- 23 B. Kiran, X. Li, H.-J. Zhai, L.-F. Cui and L.-S. Wang, *Angew. Chem., Int. Ed.* 2004, **43**, 2125.
- 24 X. Li, B. Kiran and L.-S. Wang, *J. Phys. Chem. A* 2005, **109**, 4366.
- 25 B. Kiran, X. Li, H.-J. Zhai and L.-S. Wang, *J. Chem. Phys.* 2006, **125**, 133204.
- 26 H.-J. Zhai, L.-S. Wang, D. Y. Zubarev and A. I. Boldyrev, *J. Phys. Chem. A* 2006, **110**, 1689.
- 27 T. K. Ghanty, *J. Chem. Phys.* 2005, **123**, 241101.
- 28 S. Buckart, G. Ganteför, Y. D. Kim and P. Jena, *J. Am. Chem. Soc.* 2003, **125**, 14205.
- 29 S. Malola, M. J. Hartmann and H. Häkkinen, *J. Phys. Chem. Lett.* 2015, **6**, 515.
- 30 N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunders College, 1976.
- 31 M. Walter, J. Akola, O. Lopez-Acevedo, P. D. Jadzinsky, G. Calero, C. J. Ackerson, R. L. Whetten, H. Grönbeck and H. Häkkinen, *Proc. Natl. Acad. Sci. U. S. A.* 2008, **105**, 9157.
- 32 E. Clementi, D. L. Raimondi and W. P. Reinhardt, *J. Chem. Phys.* 1967, **47**, 1300.
- 33 A. M. James and M. P. Lord, *Macmillan's Chemical and Physical Data*. MacMillan, 1992.

