Notes

Molecular Sensing Efficiency of Gold-Silver Alloy Nanowires

Weon-Sik Chae,* **Hee-Ok Lee, Eun-Mee Kim, and Hyunung Yu[†]**

*Gangneung Center, Korea Basic Science Institute (KBSI), Gangneung 210-702, Korea. *E-mail: wschae@kbsi.re.kr*
[†]Korea Research Institute of Standards and Science (KRISS), Daejeon 305-340, Korea

Noble metal nanomaterials with a controlled dimension and shape have attracted much attention for their unique physical and chemical properties such as tunable surface plasmonics, surface enhanced Raman scattering (SERS), high-efficiency electrochemical sensing, enhanced fluorescence, and quantum conductance for the last decade.[1] Surface plasmon resonance characteristics are highly affected by size, shape, and morphology of noble metal nanomaterials.[2] In the case of silver (Ag) nanomaterials, plasmonic resonance absorption is typically observed in the wide spectral range from ultraviolet (for nanoparticles) to near-infrared (for high aspect ratio nanowires).[3] Gold (Au) nanomaterials also have tailorable plasmonic characteristics, and there are facile accessible routes to synthesize well-featured nanomaterials.[4] Recently, porous gold (p-Au) materials have been developed in different morphology and pore size in order to use them as good SERS substrates because nanopores act as SERS 'hot spot'.[5] Porous gold materials are rationally synthesized through electrochemical gold-silver alloying and silver dealloying route. If the alloying-dealloying route processes in a cylindrical nanopore (e.g., in anodic aluminum oxide membrane), p-Au has a one-dimensional (1D) morphology (i.e., nanowire).[6]

Meanwhile, the composite form of gold-silver (AuAg) alloy has also been synthesized in the different morphologies of particle, wire, and cage in nanometer size.[7] An alloy nanoparticle supported in a mesoporous matrix has been used as a catalyst for carbon monoxide oxidation.[8] Unusual electron dynamics is observed in alloy nanoparticles due to a nonequilibrium electron distribution.[9] A recent notable report is that AuAg alloy nanocage shows bright three-photon luminescence which enables ultrasensitive and high contrast imaging for biological samples (e.g., cells, tissues, etc.).[10] Even though AuAg alloy nanomaterials have unique characteristics, there is still a limited study on molecular sensing application using them.[11]

In this study, we prepared AuAg alloy nanowires (NWs) through templating route using anodic aluminum oxide (AAO) templates, and used them as SERS platforms. AuAg alloy was electrochemically deposited in nanocylindrical nanopores, and then the AAO hard template was completely removed by a HF aqueous solution. The resulting alloy

nanowires are dispersed in a cresyl violet acetate (CV) solution (1×10^{-6} M) under sonication. Raman spectrum was
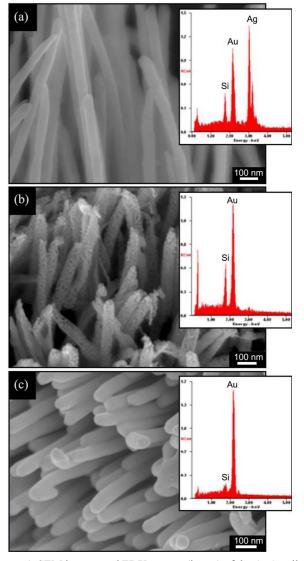

Figure 1. SEM images and EDX spectra (insets) of the AuAg alloy (a), p-Au (b), and s-Au (c) nanowires. The samples are dispersed on silicon wafers for the measurements.
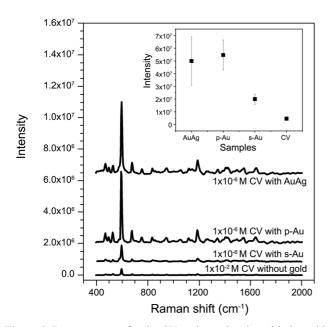
Notes

Bull. Korean Chem. Soc. **2011**, Vol. 32, No. 4   1347

Figure 2. Raman spectra for the CV probe molecules with the gold nanomaterials; AuAg alloy, p-Au, and s-Au NWs. Inset is the SERS intensity measured at 592 cm^{-1} with an error range for a better comparison.

Table 1. EF values of the gold nanowires examined for SERS experiments

Samples	EF value	EF_{sample}/EF_{s-Au}
AuAg alloy NW	$\sim 1.1 \times 10^6$	~ 8.5
p-Au NW	$\sim 1.2 \times 10^6$	~ 9.2
s-Au NW	$\sim 1.3 \times 10^5$	–

measured on a home-built micro-Raman microscope using a He-Ne laser ($\lambda_{ex} = 633$ nm).

The resulting template-free alloy, p-Au, and solid Au without pores (s-Au) have 1D wire morphology with an average diameter of ~55 nm (Fig. 1) which is well correlated with the inner pore size of the AAO templates. The p-Au NWs show a porous network having a pore size of ~10 nm (Fig. 1(b)). Energy-dispersive X-ray (EDX) spectra reveal that the AuAg alloy NWs have an average atomic composition of $Au_{24}Ag_{76}$, while the p-Au and the s-Au NWs consist of pure gold atoms.

Figure 2 shows the representative Raman spectra of CV probe solution including the gold nanomaterials. The observed Raman signal intensity is dramatically enhanced for the CV with the gold nanomaterials compared with that of the bulk CV solution without gold. Enhancement factor (EF), which is an intensity ratio (I_{SERS}/I_{RS}) of an observed SERS for molecules with a metal to a normal Raman scattering without a metal, is estimated by comparing the peak at 592 cm^{-1}. This peak corresponds to the characteristic C-N-C and C-C-C in-plane skeletal deformation modes of the CV probe molecule. The estimated EF values are summarized in Table 1. For all the gold nanomaterials examined, the EF values are above ~10^5. Furthermore, it is notable to mention that I_{SERS} for the CV probe is stronger with the AuAg alloy and the p-Au NWs than with the s-Au NWs. The AuAg alloy NWs show a comparable SERS activity to the p-Au NWs. It is previously reported that the strong SERS activity with the p-Au NWs is attributed to nanopores, which work as 'hot spot', as well as enlarged surface area.[6c]

Previously, plasmonic nanomaterials with characteristic features, such as nanopore, roughened surface, and bimetallic composition, typically showed intense SERS signals.[6c,12,13]

Here, the AuAg alloy NWs does not have any distinct features of nanopore and roughened surface compared to the s-Au NWs (Fig. 1). Meanwhile, it was previously reported that uneven elemental distribution could be formed in bimetallic nanomaterials, for examples, solid solution, core-shell, and multilayer structure.[12,13] Notable SERS activity was observed in such the bimetallic nanomaterials, which could be explained by local electromagnetic fields caused by plasmon coupling between constituent phases.[13]

In this study, the fabricated AuAg alloy NW is a solid solution consisting of gold and silver elements. According to a previous report,[14] electroplated bulk AuAg alloy has homogeneous mixture of component elements. However, it may not be real in the electrochemically grown alloy NWs inside AAO nanocylinders since the hydrophilic alumina surface seems to be more attractive to one of the constituent elements. To prove plausible spatial disproportionation of elements, supplementary SERS experiment is performed using pyridine in this study, as a standard probe molecule,[11] and it is clearly proved that Ag atom is rich at the surface of the alloy NWs (data not shown), which means that Ag atom has higher affinity to the alumina template during electroplating. Hence, it is considered that the uneven distribution of Au and Ag (surface rich) elements seems to be a reason for the observed intense SERS signal when using the AuAg alloy NW platform through plausible plasmon coupling, in addition to minor chemical effects between the alloy and the probe molecules.

In summary, we estimated SERS efficiency for the AuAg alloy NWs which were prepared by electrochemical alloying using AAO hard templates. The estimated SERS efficiency for the alloy NWs is comparable to the p-Au NWs, and both the NWs show definitely higher molecular sensing activity than the s-Au NWs. This result means that 1D AuAg alloy nanomaterials would be excellent SERS substrates.

Experimental Section

Preparation of AuAg Alloy Nanowires. Firstly AuAg alloy was electrochemically deposited in the nanocylindrical pores of the AAO membrane. The AAO membrane was Pt back-plated using a sputter to use as a working electrode prior to the alloy deposition. A two-electrode cell configuration with a Pt counter electrode was used for the electrochemical deposition using a 20 mL aqueous solution consisting of 0.05 M KAg(CN)$_2$ and 0.25 M Na$_2$CO$_3$ at 2.7 V for 30 s for Ag buffer layer and in a 20 mL solution consisting of 0.02 M KAu(CN)$_2$, 0.05 M KAg(CN)$_2$ and 0.25 M Na$_2$CO$_3$ at 2.7 V for 10 min for the AuAg alloy in constant

potential mode. The AAO template was completely removed by a 10 wt % HF aqueous solution, which resulted in AuAg alloy nanowires. Silver atoms of the AuAg alloy were selectively etched out within 20 min in concentrated nitric acid, leaving porous Au nanowires. For the comparative SERS study, smooth solid Au nanofibers were also synthesized using the electrolyte including 0.02 M KAu(CN)$_2$ and 0.25 M Na$_2$CO$_3$ at 2.7 V for 10 min.

Instrumentations. Scanning electron microscope (SEM) imaging was carried on a microscope (Hitachi, SU-70) equipped with an EDX spectrometer. Raman spectra were measured on a home-built micro-Raman setup with an inverted microscope (Zeiss, Axiovert-40CFL). A He-Ne laser (λ_{ex} = 633 nm, 5 mW) and a TE-cooled CCD (Princeton Instruments, PIXIS: 100B) detector were used to collect the Raman scattered light from the CV probe molecules after removal of Rayleigh scattering. SERS spectra were obtained at multiple locations for each solution sample including CV probes (1 × 10^{-6} M) and the 1D gold and gold-silver nanomaterials with an integration time of 100 s for all measurements. SERS experiment was also examined for pyridine (1 × 10^{-2} M) solution without gold nanomaterials.

References

 1. (a) Tao, A.; Sinsermsuksakul, P.; Yang, P. *Nature Nanotech.* **2007**, *2*, 435. (b) Campion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, *27*, 241. (c) Kneipp, K.; Kneipp, H.; Kneipp, J. *Acc. Chem. Res.* **2006**, *39*, 443. (d) Yoon, K. J.; Seo, H. K.; Hwang, H.; Pyo, D.; Eom, I.-Y.; Hahn, J. H.; Jung, Y. M. *Bull. Korean Chem. Soc.* **2010**, *31*, 1215. (e) Liu, Z.; Searson, P. C. *J. Phys. Chem. B* **2006**, *110*, 4318. (f) Zhang, Y.; Dragan, A.; Geddes, C. D. *J. Phys. Chem. C* **2009**, *113*, 12095. (g) Kondo, Y.; Takayanagi, K. *Science* **2000**, *289*, 606. (h) Rodrigues, V.; Fuhrer, T.; Ugarte, D. *Phys. Rev. Lett.* **2000**, *85*, 4124.

 2. (a) Emory, S. R.; Haskins, W. E.; Nie, S. *J. Am. Chem. Soc.* **1998**, *120*, 8009. (b) Seney, C. S.; Gutzman, B. M.; Goddard, R. H. *J. Phys. Chem. C* **2009**, *113*, 74. (c) Noguez, C. *J. Phys. Chem. C* **2007**, *111*, 3806. (d) Tiwari, V. S.; Oleg, T.; Darbha, G. K.; Hardy, W.; Singh, J. P.; Ray, P. C. *Chem. Phys. Lett.* **2007**, *446*, 77. (e) Jeong, D. H.; Zhang, Y. X.; Moskovits, M. *J. Phys. Chem. B* **2004**, *108*, 12724. (f) Mohanty, P.; Yoon, I.; Kang, T.; Seo, K.; Varadwaj, K. S. K.; Choi, W.; Park, Q.-H.; Ahn, J. P.; Suh, Y. D.; Ihee, H.; Kim, B. *J. Am. Chem. Soc.* **2007**, *129*, 9576. (g) Bae, Y.; Kim, N. H.; Kim, M.; Lee, K. Y.; Han, S. W. *J. Am. Chem. Soc.* **2008**, *130*, 5432. (h) Lu, L.; Eychmüller, A. *Acc. Chem. Res.* **2008**, *41*, 244. (i) Park, J. S.; Yoon, J. H.; Kim, H. J.; Huh, Y.-D.; Yoon, S. *Bull. Korean Chem. Soc.* **2010**, *31*, 819. (j) Brolo, A. G.; Arctander, E.; Gordon, R.; Leathem, B.; Kavanagh, K. L. *Nano Lett.* **2004**, *4*, 2015. (k) Hunyadi, S. E.; Murphy, C. J. *J. Mater. Chem.* **2006**, *16*, 3929.

 3. (a) Mulvaney, P. *Langmuir* **1996**, *12*, 788. (b) Evanoff, D. D.; Chumanov, G. *J. Phys. Chem. B* **2004**, *108*, 13948. (c) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80. (d) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano Lett.* **2003**, *3*, 1229.

 4. (a) Gao, J.; Bender, C. M.; Murphy, C. J. *Langmuir* **2003**, *19*, 9065. (b) Chen, H. M.; Peng, H.-C.; Liu, R.-S.; Asakura, K.; Lee, C.-L.; Lee, J.-F.; Hu, S.-F. *J. Phys. Chem. B* **2005**, *109*, 19553.

 5. (a) Qian, L. H.; Yan, X. Q.; Fujita, T.; Inoue, A.; Chen, M. W. *Appl. Phys. Lett.* **2007**, *90*, 153120. (b) Gao, W.; Xia, X.-H.; Xu, J.-J.; Chen, H.-Y. *J. Phys. Chem. C* **2007**, *111*, 12213. (c) Zhang, X.; Li, D.; Bourgeois, L.; Wang, H.; Webley, P. A. *Chem. Phys. Chem.* **2009**, *10*, 436.

 6. (a) Ji, C.; Searson, P. C. *Appl. Phys. Lett.* **2002**, *81*, 4437. (b) Bok, H.-M.; Shuford, K. L.; Kim, S.; Kim, S. K.; Park, S. *Nano Lett.* **2008**, *8*, 2265. (c) Lee, H.-O.; Kim, E.-M.; Yu, H.; Jung, J.-S.; Chae, W.-S. *Nanotechnol.* **2009**, *20*, 325604.

 7. (a) Mallin, M. P.; Murphy, C. J. *Nano Lett.* **2002**, *2*, 1235. (b) Ji, C.; Searson, P. C. *J. Phys. Chem. B* **2003**, *107*, 4494. (c) Chen, J.; McLellan, J. M.; Siekkinen, A.; Xiong, Y.; Li, Z.-Y.; Xia, Y. *J. Am. Chem. Soc.* **2006**, *128*, 14776.

 8. Wang, A.; Hsieh, Y.-P.; Chen, Y.-F.; Mou, C.-Y. *J. Catal.* **2006**, *237*, 197.

 9. Link, S.; Burda, C.; Wang, Z. L.; El-Sayed, M. A. *J. Chem. Phys.* **1999**, *111*, 1255.

10. Tong, L.; Cobley, C. M.; Chen, J.; Xia, Y.; Cheng, J.-X. *Angew. Chem. Int. Ed.* **2010**, *49*, 3485.

11. Kim, K.; Kim, K. L.; Lee, S. J. *Chem. Phys. Lett.* **2005**, *403*, 77.

12. (a) Lu, L.; Eychmller, A.; Kobayashi, A.; Hirano, Y.; Yoshida, K.; Kikkawa, Y.; Tawa, K.; Ozaki, Y. *Langmuir* **2006**, *22*, 2605. (b) Kumar, G. V. P.; Shruthi, S.; Vibha, B.; Reddy, B. A. A.; Kundu, T. K.; Narayana, C. *J. Phys. Chem. C* **2007**, *111*, 4388.

13. (a) Hunyadi, S. E.; Murphy, C. J. *J. Mater. Chem.* **2006**, *16*, 3929. (b) Huang, Y.; Yang, Y.; Chen, Z.; Li, X.; Nogami, M. *J. Mater. Sci.* **2008**, *43*, 5390. (c) Zhu, J. *Nanoscale Res. Lett.* **2009**, *4*, 977.

14. Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450.