Thermal and Chemical Stabilization of Silver Nanoplates for Plasmonic Sensor Application

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Thermal and chemical stabilities of silver nanoplates (AgPLs), which are triangle plate-shaped silver nanoparticles, were improved by coating with titanium oxide. The titanium oxide layer prepared by a dip-coating method was certainly advantageous for the improvement of thermal stability. Furthermore, the overlayering of titanium oxide by a spray pyrolysis method was quite useful for improving the chemical stability against I⁻ exposure. Such a coating exhibited satisfactory refractive index sensitivities.

**Keywords** Silver nanoparticles, plasmonic sensors, localized surface plasmon resonance

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Introduction

Plasmonics is becoming to be promising in optical scientific, and technological fields of the next generation. In particular, engineering applications of localized surface plasmon resonance (LSPR) due to the oscillations of free electrons on the surface of metal nanoparticles have become broad and of practical interests. One of the most fascinating applications of LSPR is an optical sensing device.1,2 LSPR sensors are expected to overcome important problems confronting in conventional surface plasmon resonance (SPR) sensors.3,4 For instance, LSPR sensors offer simpler optical systems as compared with conventional SPR ones, because the LSPR of metal nanoparticles can be directly excited by the incident light irradiation without attenuated total reflection (ATR) systems. Thus, they can be instrumentally simpler and easier to be downsized, and especially the detection (sensing) cells can be easily exchangeable. However, the reproducibility and sensitivity are still poorer than that of the conventional SPR sensors, due to drawbacks concerning the difficulty for precisely controlling the shape (size) and the deposition density of metal nanoparticles on the transparent supports.

Regarding optical sensitivity using LSPR, the metal nanoparticle that has the stronger plasmon absorption peak with a narrower band width at longer wavelength is advantageous to obtain higher sensitivity. In this regards, silver nanoparticles are known to be superior to gold ones due to stronger effects of LSPR. Furthermore, anisotropic shapes can frequently answer to such demands for the plasmon band. Although many types of anisotropic silver nanoparticles, which have plasmon absorption bands in the range of near-infrared (NIR), have been reported,5,6 through the basic problem of their synthesis with uniform size has not yet been overcome for most shapes. As a result, anisotropic silver nanoparticles generally exhibit too broad plasmon absorption peaks to be applied to LSPR sensors due to the random and wide distribution of size and shape in the prepared colloidal solution, yet their precise separation is also difficult.

In this study, we focused on silver nanoplates (AgPLs), which were plate-shaped silver nanoparticles, as a candidate metal nanoparticle for the LSPR sensor. The plasmon absorption bands of AgPLs can be widely tunable in the range of the visible to NIR region by controlling the size and the deposition density of metal nanoparticles on the transparent supports.

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sensitized solar cells.\textsuperscript{20} From these viewpoints, we fabricated an LSPR sensing device consisting of AuNRs that were coated with thin (~5 nm) TiO\textsubscript{2} film on a glass substrate.\textsuperscript{16} In that case, we first deposited negatively-charged AuNRs on the positively-charged glass substrate by electrostatic interactions, and then the surfaces of pre-deposited AuNRs were coated with thin (~5 nm) TiO\textsubscript{2} layers by the dip-coating method. This approach has the following advantages: (1) easy to control the deposition density of the isolated nanoparticles because the nanoparticles are pre-deposited on the substrate by electrostatic interactions, which can prevent appreciable aggregation before inorganic coating, (2) being useful for applying to conductive photoelectrodes because the structure of the nanoparticles and inorganic film can form layer-by-layer alignment on a substrate.

In this study, we employed AgPLs whose surfaces were coated with gold shells, denoted as AgPLs@Au. They have been commercially supplied, intended for improving chemical and thermal stabilities. AgPLs@Au were electrostatically deposited onto a substrate, and then coated with a thin TiO\textsubscript{2} film so as to improve chemical and thermal stabilities in the LSPR performance in this study.

**Experimental**

Planar silver nanoparticles (thickness ~10 nm) with a triangle (some are hexagonal) shape, called silver nano-plates (AgPLs), were supplied from Dainippon Toryo Co., Ltd. (DNT). They were prepared by a chemical reduction of Ag\textsuperscript{+} with sodium citrate and polyvinylpyrrolidone (PVP), and were thus dispersed into an aqueous solution. Furthermore, their surfaces were capped with a thin gold shell, denoted as AgPLs@Au. We used AgPLs@Au without any further surface modification before coating with TiO\textsubscript{2} layer, except for removal of excess PVP by centrifugation (9800g at 15°C for 30 min).

A glass substrate was cleaned by sonication in acetone for 10 min, and further treated with a H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}SO\textsubscript{4} (60:40) solution. It was then immersed into an aqueous solution containing 45 mg mL\textsuperscript{-1} polyethyleneimine (PEI; M\textsubscript{w} = 50000 - 100000) and 0.4 M NaCl at 30°C for 20 – 30 min, followed by being twice sonicated in distilled water for 2 min, resulting in a PEI-modification. The substrate was immersed into the colloidal solution of AgPL or AgPL@Au at 30°C for 4 h so as to obtain a AgPL- or AgPL@Au-deposited glass substrate by using electrostatic interaction.

The substrate with AgPLs@Au was coated with thin a TiO\textsubscript{2} film by a dip-coating method\textsuperscript{16} from a solution consisting of 0.175 g of H\textsubscript{2}O\textsubscript{2}, 8.8 g of tetrahydrofuran, 0.05 g of TiCl\textsubscript{4}, and 8.8 g of ethanol at a constant withdrawal rate of 1.2 mm s\textsuperscript{-1}, at <10% relative humidity, followed by drying at room temperature and heating at 100°C for 30 min. A sub dip-coating procedure was further repeated three times. The total thickness of the dip-coating layer was estimated to be ca. 5 nm.\textsuperscript{16} If necessary, a titanium oxide (TiO\textsubscript{2}) overlayer was further coated on the TiO\textsubscript{2}-coated AgPL@Au-deposited glass substrate by a spray pyrolysis method\textsuperscript{18,21,22} from a 2-propanol solution containing 0.1 or 0.3 M titanium diisoproxide bis(acetylacetonate) with 0.15 MPa N\textsubscript{2} gas for 1 s, and further repeated four times at 200°C. The thickness of the TiO\textsubscript{2} overlayers were estimated to be ca. 30 and ca. 70 nm, respectively, from cross-sectional images of a field-emission scanning electron microscope (FE-SEM; SU8000, HITACHI High-Technologies).

Characterizations of the samples were carried out with a UV-vis-NIR spectrophotometer (V-670, JASCO) for obtaining extinction spectra, an atomic force microscope (AFM; JSPM-5400; JEOL) by using an Al-coating silicon cantilever (NCHR-10, NanoWorld) with a tip curvature radius of 8 nm for the surface morphologies of the samples, and a transmission electron microscope (TEM; JEM-200 CX, JEOL) for observing colloidal AgPLs and AgPLs@Au.

**Results and Discussion**

It has been recognized that a TiO\textsubscript{2}-coating is useful for improving the thermal stability of metal nanoparticles.\textsuperscript{11,15,16} However, bare AgPLs are less stable to halogen ions.\textsuperscript{10} Therefore, we employed AgPLs@Au so as not to be etched by Cl\textsuperscript{-}, which was contained in the precursor solution of TiO\textsubscript{2}. We confirmed that the aqueous colloidal solution of AgPLs@Au had roughly the same geometric and optical properties as AgPLs based on UV-vis-NIR spectra and TEM image (Fig. 1). Furthermore, we confirmed that AgPLs@Au was stable against exposure to Cl\textsuperscript{-}, in contrast to bare AgPL. It has been recognized that TiO\textsubscript{2}-coating is useful for improving the thermal stability of metal nanoparticles.\textsuperscript{11,15,16} However, bare AgPLs are less stable to halogen ions.\textsuperscript{10} Therefore, we employed AgPLs@Au so as not to be etched by Cl\textsuperscript{-}, which was contained in the precursor solution of TiO\textsubscript{2}. We confirmed that the aqueous colloidal solution of AgPLs@Au had roughly the same geometric and optical properties as AgPLs from UV-vis-NIR spectra and TEM images (Fig. 1). Furthermore, we confirmed that AgPLs@Au was stable against exposure to Cl\textsuperscript{-} in contrast to bare AgPLs.

Then, the thermal stabilities of AgPLs in the presence or absence of a Au shell, and further TiO\textsubscript{2}-coating were compared by AFM and UV-vis-NIR measurements. AgPLs and AgPLs@Au were electrostatically deposited on the glass substrate, as described before.\textsuperscript{21} Regarding the AgPL@Au-deposited glass substrate, dip-coating with TiO\textsubscript{2} was carried out (Fig. 2). After annealing the substrates with AgPLs, AgPLs@Au, and TiO\textsubscript{2}-coated AgPLs@Au at 200°C for 1 h, the plasmon extinction peaks showed blue-shifts by 354 ± 9, 137 ± 7, and 83 ± 4 nm (n = 3), respectively. These peak shifts were due to the heat-induced shape change of AgPLs, as was confirmed from AFM images. It is noteworthy that AgPLs@Au exhibited a higher thermal stability than bare AgPLs. This might be caused by the fact that the Tamman temperature, at which atoms from the bulk metal may exhibit mobility, of gold is higher than that of silver, because the melting point of bulk gold is higher than that of silver.\textsuperscript{24} Hence, the Au shell improve the toughness against a heat-induced shape change of AgPLs, even after annealing. On the other hand, TiO\textsubscript{2}-coated AgPLs@Au exhibited the highest thermal stability among them. This reveals that the TiO\textsubscript{2}-coating can function as a shape template of AgPLs and, as a result,
Next, we have investigated the chemical stabilities of the TiO2-coated AgPLs@Au. It is known that bare AgPLs can be easily etched by halogen ions, such as Cl− and Br−, followed by dissolution into a solution.10 Although the Au shell was able to prevent the oxidation of AgPLs by Cl− and by plasmon-induced charge separation, which was observed in the case of resonant light-irradiated Ag nanoparticles with TiO2,25 the AgPL@Au was still unstable against I−, which oxidizes even gold. Here, AgPLs@Au with and without a TiO2-coating were immersed into an ethylene glycol solution containing 0.05 M LiI and 0.5 M I2, which has been commonly used as an electrolyte for dye-sensitized solar cells, so as to investigate their chemical stabilities against I− exposure (Figs. 3a, 3b). After immersion, the extinction peak based on LSPR of AgPLs almost disappeared, even with the TiO2-coating. This indicates that the TiO2 layer prepared by the dip-coating method is not dense enough to prevent etching with I−. Hence, the TiOx overlayer was further coated on the TiO2-coated AgPL@Au-deposited glass substrate by a spray pyrolysis method that could make a dense and smooth film, although being applicable to only heat-resistant substrates, in order to improve the chemical stability. When 0.1 M titanium diisopropoxide bis(acetylacetonate) was sprayed onto the TiO2-coated AgPL@Au-deposited glass substrate at 200°C, the extinction peak based on LSPR of AgPLs did not completely disappear, even after exposure to I− (Fig. 3c). On the other hand, when 0.3 M titanium diisopropoxide bis(acetylacetonate) was sprayed, the oxidative dissolution of AgPLs upon immersion into the electrolyte containing I− could be completely prevented (Fig. 3d). These results indicate that the TiOx overlayer obtained by the spray pyrolysis method is useful for improving the chemical stabilities of AgPLs.

In all cases, the sensing performance of the substrates with AgPLs was investigated. Since the extinction peak (Δλmax) it can improve the thermal stability of AgPLs.
based on the LSPR of metal nanoparticles shifts with an environmental refractive index change, this property has been applied to biosensors and chemical sensors.1,2 Here, we measured the extinction spectra of the substrates in various liquids with different refractive indices (Table 1, Fig. 4). It revealed that AgPLs@Au exhibit superior sensitivity to AgPLs prepared by colloidal lithography (19 nm RIU–1)26 and AuNRs (231,15 252,17 and 20628 nm RIU–1) even after TiO2-coating with the thermal stability. Although the sensitivity of the TiO2-coated AgPL@Au-deposited glass substrate decreased after TiOx-overcoating with the chemical stability, the substrate could show satisfactory performance of LSPR sensing.

Conclusions

AgPLs@Au that were electrostatically deposited on a glass
substrate were successfully coated with a thin TiO2 film by the dip-coating method, resulting in toughness against etching with Cl–. The TiO2-coating was also useful for improving the thermal stability. A TiO overlayer prepared by the spray pyrolysis method could suppress the corrosion of AgPLs@Au, even upon exposure to I–. Accordingly, both the thermal and chemical stability of AgPLs@Au was remarkably improved. Applying those surface-protection procedures were quite advantageous for improving the performance of LSPR sensing using AgPLs. Accordingly, AgPLs@Au with appropriate titanium oxide-coatings can be applicable to LSPR sensors under severe conditions.

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References

1. K. M. Mayer and H. F. Hafner, Chem. Rev., 2011, 111, 3828.
2. J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. van Duyne, Nat. Mater., 2008, 7, 442.
3. S. Lofås and B. Johnsson, J. Chem. Soc. Chem. Commun., 1990, 21, 1526.
4. Q. Zou, N. Menegazzo, and K. S. Booksh, Anal. Chem., 2012, 84, 7891.

| Substrate | Refractive index sensitivity/nm RIU–1 |
|-----------|-------------------------------------|
| AgPLs@Au  | 354 ± 9a                           |
| TiO2-coated AgPLs@Au | 293 ± 17a                       |
| TiOx-overcoated (0.1 M) TiO2-coated AgPLs@Au | 219 ± 20a            |
| TiOx-overcoated (0.3 M) TiO2-coated AgPLs@Au | 97 ± 20a              |

a. Mean ± standard error (n = 3).

b. Mean ± standard error (n = 2).

Fig. 4 Typical extinction spectra of AgPLs@Au (a), TiO2-coated AgPLs@Au (b), TiOx-overcoated (0.1 M) TiO2-coated AgPLs@Au (c), and TiOx-overcoated (0.3 M) TiO2-coated AgPLs@Au (d) onto glass substrates immersed in various liquids with different refractive indices (water (1.333), acetonitrile (1.344), hexane (1.388), chloroform (1.447), and toluene (1.497)).
5. M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin, and Y. Xia, *Chem. Rev.*, 2011, **111**, 3669.

6. N. E. Motl, A. F. Smith, C. J. DeSantis, and S. E. Skrabalak, *Chem. Soc. Rev.*, 2014, **43**, 3823.

7. D. E. Charles, D. Aherne, M. Gara, D. M. Ledwith, Y. K. Gun’ko, J. M. Kelly, W. J. Blau, and M. E. Brennan-Fournet, *ACS Nano*, 2010, **4**, 55.

8. K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668.

9. B. Tang, S. Xu, X. Hou, J. Li, L. Sun, W. Xu, and X. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 646.

10. B. H. Lee, M. S. Hsu, Y. C. Hsu, C. W. Lo, and C. L. Huang, *J. Phys. Chem. C*, 2010, **114**, 6222.

11. A. Antonello, E. D. Gaspera, J. Baldauf, G. Mattei, and A. Martucci, *J. Mater. Chem.*, 2011, **21**, 13074.

12. N. A. Joy, B. K. Janiszewski, S. Novak, T. W. Johnson, S. H. Oh, A. Raghunathan, J. Hartley, and M. A. Carpenter, *J. Phys. Chem. C*, 2013, **117**, 11718.

13. N. Omura, I. Uechi, and S. Yamada, *Anal. Sci.*, 2009, **25**, 255.

14. Y. Imura, S. Hojo, C. Morita, and T. Kawai, *Langmuir*, 2010, **30**, 1888.

15. Y. Takahashi and T. Tatsuma, *Nanoscale*, 2010, **2**, 1494.

16. Y. Takahashi, N. Miyahara, and S. Yamada, *Anal. Sci.*, 2013, **29**, 101.

17. C. X. Xiaodong, C. S. J. Hurst, and C. A. Mirkin, *Adv. Mater.*, 2007, **19**, 4071.

18. P. Du, L. Ma, Y. Cao, D. Li, Z. Liu, Z. Wang, and Z. Sun, *ACS Appl. Mater. Interfaces*, 2014, **6**, 8853.

19. A. Fujishima, K. Hashimoto, and T. Watanabe, “*TiO2 Photocatalysis, Fundamentals and Applications*”, 1999, BKC, Tokyo.

20. B. O’Regan and M. Grätzel, *Nature*, 1991, **353**, 737.

21. Y. Takahashi and T. Tatsuma, *Appl. Phys. Lett.*, 2011, **99**, 182110.

22. T. Kawawaki, Y. Takahashi, and T. Tatsuma, *Nanoscale*, 2011, **3**, 2865.

23. J. You, Y. Takahashi, H. Yonemura, T. Akiyama, and S. Yamada, *Jpn. J. Appl. Phys.*, 2012, **51**, 02BK04.

24. J. A. Moulijn, A. E. van Diepen, and F. Kapteijn, *Appl. Catal. A*, 2001, **212**, 3.

25. Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, and A. Fujishima, *Nat. Mater.*, 2003, **2**, 29.

26. A. J. Haes and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2002, **124**, 10596.

27. S. M. Marinakos, S. Chen, and A. Chilkoti, *Anal. Chem.*, 2007, **79**, 5278.

28. Y. Takahashi, N. Ide, and S. Yamada, *Bunseki Kagaku*, 2014, **63**, 551.