Proceedings of the 5th International Conference on Nanotechnology: Fundamentals and Applications
Prague, Czech Republic, August 11-13, 2014
Paper No. 71

Silver Nanoparticles Deposited on Cicada Wings as Naturally Inspired SERS Substrates

Ichiro Tanahashi, Yoshiyuki Harada
Nanomaterials and Microdevices Research Center, Osaka Institute of Technology
5-16-1 Omiya, Asahi-ku, Osaka, 535-8585, Japan
tanahashi@chem.oit.ac.jp; harada@ge.oit.ac.jp

Extended Abstract

Surface-enhanced Raman scattering (SERS) has been studied intensively because of its applications in trace detection of biological and chemical analytes. A lot of studies have been carried out focusing on the fabrication of larger-area, low-cost, and high-performance SERS-active substrates. The most investigated SERS-active metal nanoparticles are silver (Ag) and gold (Au) nanoparticles because of their clear localized surface plasmon resonance (LSPR) absorption. The LSPR properties of the metal nanoparticles are primarily responsible for the SERS effect (Haynes et al., 2003) and they are strongly dependent on the metal nanoparticle's size and shape. Especially, the surface nanostructures of the substrates affect the size and shape of the deposited metal nanoparticles. In order to obtain stable and immobilized metal nanoparticles on the substrates, photocatalytic deposition of metal onto TiO_2 films seems to be a convenient and desirable method. We have reported that the photocatalytically prepared Au nanoparticles deposited on TiO_2 films showed the SPR sensing properties (Tanahashi et al., 2008).

In this paper, we have reported the properties of the photocatalytically deposited and SERS-active Ag nanoparticles on the cicada and butterfly wings with and without uniform ordered nanopillar array structures. Usually, the nanopillar structured substrates with tunable gap size are fabricated by electron-beam lithography, which requires a high fabrication cost. On the other hand, the chitin of some kinds of insects is a self-assembled nanocomposite material.

The typical preparation processes of the Ag nanoparticles deposited on TiO_2-coated insect wings (Ag/TiO_2-coated wings) are outlined as follows. Cicadas (*Cryptotympana facialis* and *Graptopsaltria nigrofuscata*) and butterfly (*Parnassius citrinarius*) wing samples were collected from Kansai region of Japan. On both sides of a forewing was coated with TiO_2 from anatase sol by using a dip-coating technique. The resulting wing was soaked in a mixture of $AgNO_3$ aqueous solution and ethyl alcohol (1.67×10^{-2} mol L^{-1} of Ag^+ ions) in a petri dish and exposed to UV light, Ag^+ ions were photoreduced on the surface of TiO_2. Ag^+ ions were also photoreduced on the surface of the wings (chitin) without TiO_2. For SERS measurements, the sample was irradiated with 50 mW of 514.5 nm excitation line (Ar^+ laser) in back scattering geometry. A 50× long distance objective and a cooled CCD detector were employed. The Raman spectra of 10^{-4}-10^{-3} mol L^{-1} Rhodamine 6G (2 μL) adsorbed on various samples were compared.

Densely stacked Ag nanoparticles (150-300 nm) were successfully obtained on TiO_2 coated cicada (*Cryptotympana facialis*) wings. In the optical absorption spectra of the Ag/TiO_2-coated cicada wings, the absorption peak due to the LSPR peak of Ag nanoparticles was observed at 440 nm. By using the Ag/TiO_2-coated cicada (*Cryptotympana facialis*) wings, the strongest SERS signals of R6G could be observed among the investigated insect wings. Therefore, the photocatalytically deposited Ag nanoparticles on TiO_2-coated cicada wings with nanopillar structures seem to be a promising candidate for naturally inspired SERS substrates.

References

Haynes C. L., Duyne R. P. V. (2003). Plasmon-sampled surface-enhanced Raman excitation spectroscopy. J. Phys. Chem. B, 107, 7426-7433.

Tanahashi I., Iwagishi M., Chang G. (2008). Localized surface plasmon resonance sensing properties of photocatalytically prepared Au/TiO_2 films. Mater. Lett., 62, 2714-2716.