Naturally Inspired SERS Substrate Properties of Silver Nanoparticles Deposited on TiO_2-Coated Insect Wings

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Abstract— **Ag nanoparticles were photocatalytically deposited on TiO_2-coated insect wings (Ag/TiO_2-coated insect wings). Wings of dragonfly, cicada and butterfly with different micro/nanostructured surfaces were investigated as substrates based on natural materials. We have investigated the surface enhanced Raman scattering (SERS) substrate properties of the six types of Ag/TiO_2-coated insect wings. The size and shape of the deposited Ag nanoparticles were influenced by the surface structures of the insect wings. The SERS signal intensities of Rhodamine 6G adsorbed on the Ag/TiO_2-coated insect wings with spherical-shaped Ag nanoparticles of 100-250 nm diameter and flake-shaped Ag nanoparticles were more than one order of magnitude larger than those on the Ag thin film grown by sputtering on glass slides.**

Keywords-metal nanoparticle; silver; SRES; insect; wing.

I. INTRODUCTION

In recent years, surface-enhanced Raman scattering (SERS) has attracted much attention because of its application in the detection of trace amount of chemical and biological agents. As the SERS-active materials, roughened metal films and metal nanoparticles have been investigated [1][2]. In the case of metal nanoparticles, the local electromagnetic field enhancement induced by the excitation of the localized surface plasmon resonance (LSPR) is the major mechanism for SERS. It is known that the size and shape of the metal nanoparticles affect their LSPR properties. In particular, silver (Ag) nanoparticles with clear LSPR absorption are the most suitable candidate for SERS-active materials. However, the appropriate size and shape of the Ag nanoparticles for SERS-active materials are still not clear.

The size and shape of the deposited metal nanoparticles on the substrates are also largely affected by the surface structures of the base substrates. The artificial base substrates such as glasses, ceramics and plastics are widely used. On the other hand, some biological surfaces of insect wings are structured at the micro/nanometer scale. Thus, scientists have been trying to develop the new types of SERS-active substrates using natural biological materials such as cicada and butterfly wings [3][4]. In our previous studies [5], we have reported the preparation and SERS properties of the Ag nanoparticles on TiO_2-coated cicada wings with nanopillar array structures. However, it is not clear what types of micro/nanostructured surfaces of insect wings are more suitable for the naturally inspired SERS-active substrates. In this paper, we have reported the characterization, optical and SERS properties of the six types of Ag/TiO_2-coated insect wings.

II. EXPERIMENTAL DETAILS

We used three species of dragonflies, two species of butterflies and one species of cicada. All the investigated insects were captured in the Kansai region of Japan. Wing samples were collected from *Sympetrum darwinianum* (Summer Darter, small to medium-sized skimmer dragonfly with clear and transparent wings): denoted as dragonfly (a), *Mnais costalis* (small-sized one with orange color wings): dragonfly (b), *Mnais pruinosa* (small-sized one with clear and transparent wings): dragonfly (c), *Panantica sita* (Chestnut Tiger, the Danaid group butterfly, black and bluish-white subhyaline markings on the forewings): butterfly (d), *Parnassius citrinarius* (the Parnassiinae one, white and subhyaline markings on the forewings): butterfly (e) and *Cryptotympana facialis* (a black cicada with clear and transparent wings): cicada (f). The male dorsal forewings of the samples were used in the experiments.

The detailed preparation processes of the Ag/TiO_2-coated insect wings have been described previously [5]. By using TiO_2 (Ishihara Sangyo Kaisha, ST-K211) as a photocatalyst, Ag metal was produced by photoreduction of Ag^+ ions.

Photographs of the insect specimens and prepared samples were taken using a digital camera. Scanning electron microscopy (SEM) analysis, X-ray diffraction (XRD) and UV-Vis absorption spectra measurements were carried out to characterize the bare insect wings and Ag/TiO_2-coated insect wings.

SERS measurements were performed by irradiating the sample with 50 mW of 514.5 nm line of an Ar^+ laser in back scattering geometry at room temperature. The laser beam was focused on a spot with a diameter of 2 μm and the data acquisition time was 1 s. The intensities of Raman spectra of

10^{-3} mol L^{-1} Rhodamine 6G (R6G, 2 μL) adsorbed on various samples were compared. As a reference, R6G (2 μL) adsorbed on a mirror-like smooth surface Ag thin film prepared by an RF magnetron sputtering system was used.

III. RESULTS AND DISCUSSION

In the SEM micrographs, the wings of the dragonfly (a), (b) and (c) showed sub-micrometer-scale relief structures. The pitch of the concavo-convex pattern of the dragonfly (a), (b) and (c) increased in that order. The wing membrane (bluish-white subhyaline marking part) of the butterfly (d) had a wrinkle-like irregular shape surface. A small number of scales were observed on the bluish-white subhyaline markings. The wing scales of the butterfly (e) possessed uniform ordered ridge structure. The wings of the cicada (f) had a dense nanopillar array structure [5].

In all the investigated six types of Ag/TiO_2-coated insect wings, the color of the wings was changed to metallic gray after the UV irradiation indicating the formation of Ag metal on the insect wings. In the case of the Ag/TiO_2-coated insect wings of the dragonfly (a) shown in Fig. 1, (c) and cicada (f), densely stacked Ag nanoparticles with 100-250 nm in diameter were seen. The mean diameter of Ag nanoparticles of the Ag/TiO_2-coated insect wing of the dragonfly (c) was smaller than those of the dragonfly (a) and cicada (f). In the case of the Ag/TiO_2-coated insect wings of the butterfly (d) (membrane) and dragonfly (b) shown in Fig. 1, flake-shaped Ag nanoparticles with various sizes were seen.

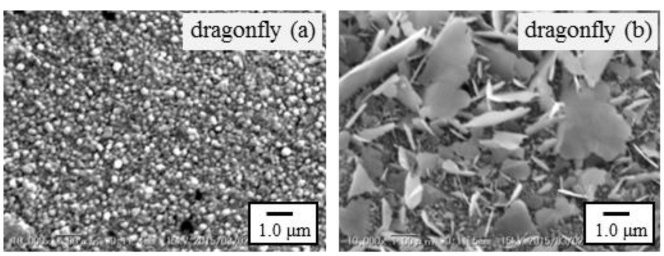

Figure 1. SEM micrographs of Ag/TiO_2-coated insect wings of the dragonfly (a) and (b).

On the other hand, the uniform ordered ridge structures of the Ag/TiO_2-coated insect wings of the butterfly (e) (scales) were covered with the Ag films and small number of nanoparticles. Among the investigated six types of insect wings, the size and shape of the Ag nanoparticles deposited on the TiO_2-coated insect wings were largely influenced by the surface structures such as sub-micrometer-scale relief and nanopillar array ones.

In the XRD patterns of the six types of Ag/TiO_2-coated insect wings, it was seen that the peak at $2\theta = 38.1^\circ$ which was assigned to the (111) reflection line of cubic Ag. From the results of the XRD, the TiO_2-coated insect wings were successfully covered by the metallic Ag.

In the optical absorption spectra of the Ag/TiO_2-coated insect wings of the dragonfly (a), (c) and cicada (f), the broad absorption band peaking at about 430 nm was observed. The band was due to the LSPR absorption of the Ag nanoparticles. These results were in accordance with the SEM observations. Thus, the Ag nanoparticles could be made on the TiO_2-coated sub-micrometer-scale relief and nanopillar array structured wings by the photoreduction.

SERS spectra of R6G adsorbed on the six types of Ag/TiO_2-coated insect wings and the Ag thin film sputtered on a glass slide were measured. In the SERS measurements, R6G (10^{-3} mol L^{-1}) as standard remarks was dripped and dried on the surface of the Ag/TiO_2-coated insect dorsal forewings and the Ag thin film. In all the SERS spectra, the distinct peaks and a broad band from 600 to 1800 cm^{-1} were seen. The observed Raman peaks were characteristic of R6G [6]. The peak intensities at ca. 1649 cm^{-1} (the C-C stretching mode) of the six types of Ag/TiO_2-coated insect wings were compared with that of the Ag thin film. The intensities of the Ag/TiO_2-coated insect wings of dragonfly (c), butterfly (d) and (e) were about 1-4 times larger than that of the Ag thin film. On the other hand, the intensities of the Ag/TiO_2-coated insect wings of dragonfly (a), (b) and cicada (f) were respectively about 15, 10 and 10 times larger than that of the Ag thin film.

The Ag/TiO_2-coated insect wings with large-area, low-cost and high-SERS performance seem to be a promising candidate for the naturally inspired SERS-active substrates.

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