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Fabrication and characterization of a granular film consisting of size-selected silver nanoparticles: application to a SERS substrate

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Abstract. Uniform-sized silver nanoparticles with average diameter of 13.7 nm have been prepared in the gas-phase by combining a pulsed laser ablation method with a low pressure-differential mobility analyzer (LP-DMA). By depositing the silver nanoparticles onto a silicon substrate, a granular film consisting of size-selected silver nanoparticles has been fabricated and its morphology and electronic properties have been examined using transmission electron microscopy (TEM) and UV-visible absorption spectroscopy. This granular silver film serves as a highly active substrate for surface-enhanced Raman scattering (SERS).

PACS. 61.46.Df Nanoparticles

1 Introduction

The structure and properties of thin films consisting of metal nanoparticles have attracted much attention recently from the viewpoints of both fundamental science and practical applications [1]. The physical and chemical properties of metal nanoparticle films generally depend on the film nanostructure [2]. In order to fabricate a film with desirable properties, it is important to manipulate the nanostructure of the film, i.e., size, shape, density, and spatial distribution of the metal nanoparticles in the film.

Electrical mobility analysis methods such as a low pressure-differential mobility analyzer (LP-DMA) have recently provided a simple and reproducible tool to achieve the necessary fine classification of metal nanoparticles [3]. By producing metal nanoparticles using a laser ablation method and classifying them with LP-DMA in succession, the creation of uniform-sized metal nanoparticles is possible [4]. In this method, surface morphology of the film can be controlled by adjusting experimental conditions such as laser power, the sheath gas flow rate in LP-DMA, deposition time, and diameter of the selecting nanoparticles. Moreover, this method possesses a great advantage that any metal can be similarly used to create the nanoparticle substrate. Thus, this method could provide a very promising avenue for creating various types of nanostructured films with fascinating and unexpected mechanical, optical, electronic, magnetic and other properties.

In this work, a granular film consisting of size-selected silver (Ag) nanoparticles was fabricated in vacuum using LP-DMA with a laser ablation source, and was characterized by scanning electron microscopy (SEM) and UV-visible absorption spectroscopy. In this film, different morphologies of Ag nanoparticle aggregates were observed at the centre and edge regions of the film. In particular, high quality surface-enhanced Raman scattering (SERS) spectra of isonicotinic acid (INA) were obtained at the edge of the film, even with the concentration of the immersed INA solution being as low as 10^{-8} M, indicating that the granular film consisting of size-selected Ag nanoparticles serves as an excellent SERS-active substrate.

2 Experimental section

The experimental details of the preparation of size-selected metal nanoparticles has been described previously [4], and therefore only a brief description will be given here. Silver (Ag) particles were produced by vaporizing a rotating Ag disk (diameter 50 mm, 2 mm thickness, purity 99.98%) using the second harmonic of a Nd^{3+}:YAG laser (532 nm, 30 mJ/pulse). The produced particles were then carried into a LP-DMA where nanoparticles of a specific diameter have been classified by controlling He sheath gas flow and applied electric field in the LP-DMA.

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The size-selected nanoparticles were then deposited onto a substrate through the outlet nozzle of the LP-DMA (inner diameter: 4.0 mm), and total amount of the deposited nanoparticles were estimated by monitoring the ion current onto the substrate during the deposition. The size distribution and morphology of the Ag nanoparticles were characterized by a field emission-transmission electron microscope (TEM; TECNAI F20, PHILLIPS).

The size-selected Ag nanoparticles were deposited onto a clean surface of a P-doped Si(100) wafer and a glass slide, forming a granular Ag film. The morphology of the film was characterized by Scanning Electron Microscopy (SEM; Hitachi S-4700) and the electronic transmission spectrum of the film and the glass substrate itself were obtained using a UV-visible spectrophotometer (SHIMADZU UV-1650).

The SERS effect from the Ag granular films thus fabricated was examined using isonicotinic acid (INA) as an adsorbate. The films were immersed in $5\times10^{-8}-5\times10^{-2}$ M aqueous solutions (volume about 2 ml) of INA (Wako Pure Chemical Industries, Ltd.) for 30 minutes. Subsequently, the immersed substrates were rinsed with water and dried in vacuum. Distilled and deionised water (Alpha-Q, Millipore) was used for the preparation of the solution and rinsing of the substrates. Since the SERS signal intensity of the Ag granular films decreases with exposure time to air, the fabrication of the substrate was immediately followed by the SERS measurement [5]. SERS spectra were obtained by a micro-Raman apparatus, consisting of Olympus BX51 microscope, Chromex Raman-One spectrometer and a CCD-detector [6]. The excitation source was provided by 532 nm cw diode laser with a typical laser power of 10 mW reaching the sample.

3 Results and discussion

Figure 1 shows the size distribution of size-selected Ag nanoparticles, which was determined from TEM images of Ag nanoparticles. One of the typical TEM images is given in the inset of the figure. The obtained Ag nanoparticles have an estimated mean particle diameter of 13.7 nm and their full-width-half-maximum is about 15% of the mean diameter. Considering also that the nanoparticles had been size-selected from the original size range of about one nanometer to a few micrometers, LP-DMA proves to be a valuable tool in classifying disperse and uniform metal nanoparticles.

By depositing the nanoparticles onto a silicon substrate, a granular film consisting of size-selected Ag nanoparticles was obtained as seen in the Figure 2a, a CCD-camera image of the film taken using the micro-Raman apparatus. Since singly charged nanoparticles were deposited for 3 min with currency of ~50 pA during the formation of the film, the number of the constituent Ag nanoparticles was estimated to be about 6×10^{10}. Although it is not obvious from the figure, the film thickness is highest in the central part of the circular film, gradually diminishing in height as it recedes away from the centre of the film.

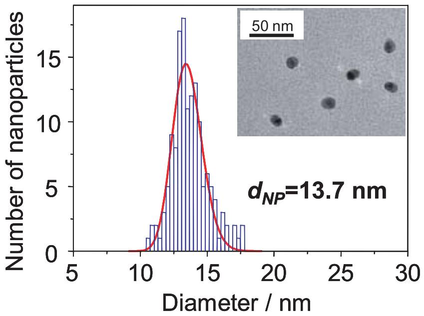

Fig. 1. TEM image and size distribution of ~14 nm Ag nanoparticles in diameter after the classification by the LP-DMA. The histograms of the size distributions were fitted by a log-normal function.

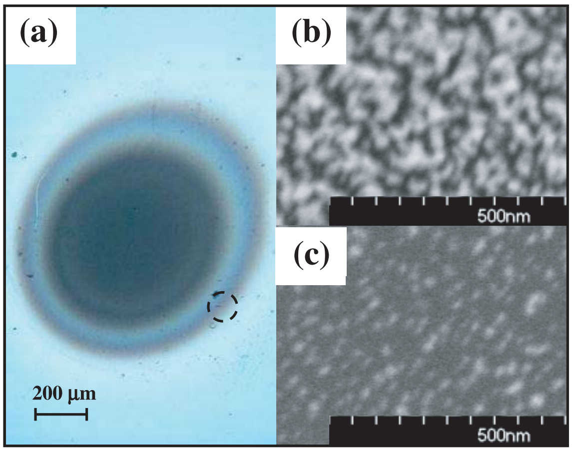

Fig. 2. (a) A CCD-camera image of a granular film consisting of size-selected Ag nanoparticles taken using the micro-Raman apparatus, and higher magnification SEM images of SERS active area of (b) the central part and (c) near the edge of the granular Ag film.

Figure 2b shows a higher magnification SEM image of the central part of the film, here a rough surface of thick multilayered Ag nanoparticles has been observed. The thickness of the central part of the granular film was determined to be about 200 nm by atomic force microscopy [7]. Therefore, it can be deduced that the central region of the film is composed of approximately 14 layers of deposited Ag nanoparticles. Near the edge of the film, on the other hand, nanoparticles are much more dispersed as seen in Figure 2c. Various shaped and sized spots in the figure represent aggregates of 2–10 Ag nanoparticles, forming a fractal-like morphology. As discussed later, it is noted that such fractal structure can be one of the causes of extremely large SERS enhancement [8,9].

Figures 3a and 3b show UV-vis absorption spectra of fabricated Ag granular films on a glass slide and the glass slide itself, respectively. In Figure 3a, strong absorption is observed around 380 nm together with a broad absorption curve ranging about 400 to 800 nm. The absorption around 380 nm is assignable to surface plasmon modes of Ag nanoparticles, because a blank glass substrate exhibits no absorption band as shown in Figure 3b [10]. On

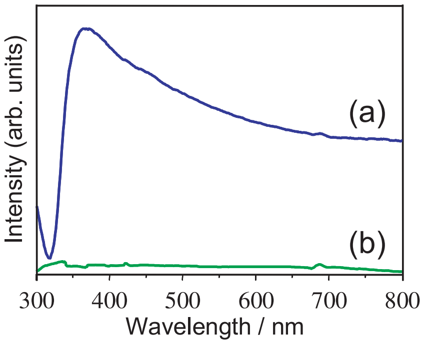

Fig. 3. UV-visible absorption spectra of (a) the fabricated Ag granular film on a glass slide and (b) the glass slide itself.

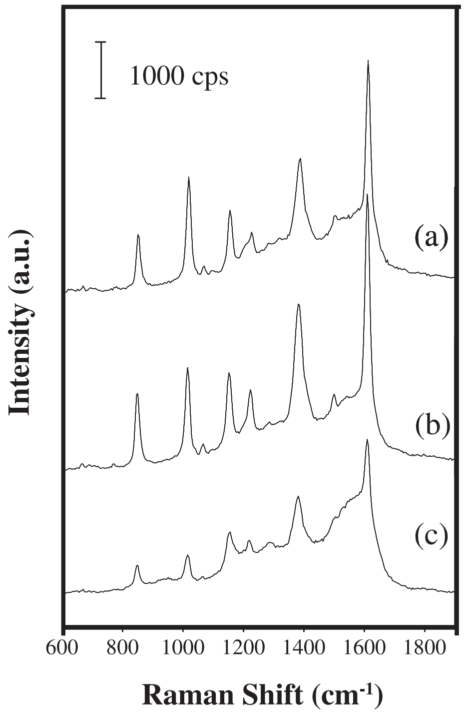

Fig. 4. A series of SERS spectra of isonicotinic acid deposited onto a Ag granular film substrate in which preparation, the concentration of the immersing solution was varied; (a) 5×10^{-2} M, (b) 5×10^{-4} M and (c) 5×10^{-6} M.

the other hand, the very broad absorption is seemingly attributed to the Ag nanoparticle aggregates having fractal like structures in the granular film, because remarkable broadening of the surface plasmon band has been reported for colloidal Ag aggregates having fractal structures [11].

Figure 4 shows a series of SERS spectra of INA deposited onto a Ag granular film substrate, in which the concentration of the immersing solution was varied; (a) 5×10^{-2} M, (b) 5×10^{-4} M, and (c) 5×10^{-6} M. Through the measurements, the detection limit of INA was found to be lower than 5×10^{-7} M, signifying that the Ag granular film fabricated in the present study has a high SERS activity. As smooth Ag films do not exhibit strong SERS enhancement, this prominent enhancement of the SERS activity is most likely caused by peculiar morphologies of the nanoparticle assembly, i.e. the fractal-like structure of the supported Ag nanoparticles. In every spectrum, the ratio of vibrational peaks was kept almost identical, suggesting that the adsorption orientations of INA were preserved, even when varying the concentration of the solution. Besides, the peak intensities were not greatly changed.

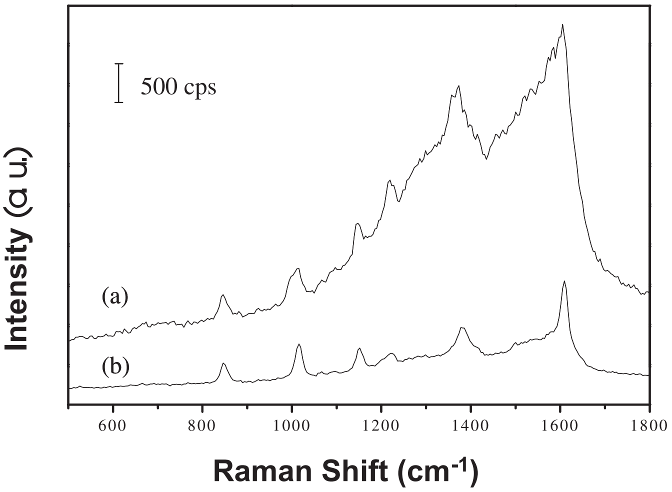

Fig. 5. SERS spectra of 5×10^{-3} M isonicotinic acid obtained at (a) the central part and (b) near the edge of a size-selected Ag granular film substrate.

The vibrational features such as relative intensities and absorption frequencies observed in the SERS spectra are in good agreement with those reported on a silver-modified silver electrode [12]. In particular, strong enhancement of 1386 cm^{-1}, assigned to the COO^- symmetric stretching, clearly indicates that chemical adsorption of INA occurs via a carboxyl group [12]. Significantly, the great enhancement of 1605 cm^{-1} (C-C stretching of pyridine ring), reinforces the existence of charge transfer between Ag granular film and INA (i.e. chemical mechanism), because this band appears only weakly in ordinary Raman spectra of isonicotinic acid in aqueous solution and in solid state [12,13].

Except for the peak at 844 cm^{-1} (out-of-plane ring vibration), most of the sharp peaks obtained were totally symmetric in-plane vibrational modes [12]. According to surface selection rules, if vibration modes have a transition dipole moment perpendicular to the surface, they can usually show strong SERS enhancement. Therefore, most of INA molecules are probably adsorbed on the surface of the Ag granular film, with its molecular plane perpendicular to the surface through the chemical bonding between carboxylate and silver [13].

Figures 5a and 5b show SERS spectra of INA adsorbed at different parts of the Ag granular film. In the SERS spectrum of Figure 5a, obtained at the central part of the film (see Fig. 2a), a strong broad background signal appears in the region of 1100 to 1700 cm^{-1} together with the sharp peaks assigned to INA. Meanwhile, as shown in Figure 5b, this broad background was not strongly observed when the SERS spectrum was measured at the near edge of the film (see Fig. 2c). In previous studies [14–16], similar broad background of 1100–1700 cm^{-1} has often been observed and ascribed to SERS signal from amorphous carbon formed by laser-induced degradation of the adsorbate and/or organic impurities presented on the surface. As mentioned above, multilayered porous structure was formed at the central region, while there were dispersed two-dimensional fractal aggregates near the edge of the film (see Fig. 2c). Since the former morphology in the central region can provide a much larger number of adsorption sites, the remarkable laser-induced degradation effect would be expected. In the edge region, in contrast, high quality SERS spectrum can be obtained even if only a trace amount of adsorbate is present. Therefore, it can be deduced that the high SERS activity in the edge region resulted from that (1) the background signal from amorphous carbon is negligible and that (2) the fractal aggregates (i.e. hot spots) provide a great SERS enhancement.

4 Conclusions

By using LP-DMA, uniform-sized silver nanoparticles with average diameter of about 13.7 nm were deposited onto a silicon substrate. A granular film consisting of size-selected Ag nanoparticles have been fabricated and it was revealed that this granular film exhibits high SERS activity toward isonicotinic acid, especially at the edge region of the deposited area. Optimizing the surface morphology of the film will enable greater region of the substrate to be thoroughly applicable for sensitive detection of adsorbates in SERS studies. This result demonstrates clearly that naked metal nanoparticles provide a very promising avenue for creating nanostructured films with SERS activity.

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