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Long-term stabilization of mixed silver nanoparticles on an Al surface with poly(2-vinylpyridine) films

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ABSTRACT

Surface-enhanced Raman scattering active substrates were prepared by the chemical assembly of Co, Ni and Ag nanoparticles on 3-aminopropyltriethoxysilane-functionalized Al surface. Poly(2-vinylpyridine) films were also deposited on the Al substrates by electrochemical polymerization in aqueous solution. Raman intensities were measured with respect to pyridine. Although silver has very desirable physical properties, good relative abundance, and low cost, gold nanoparticles have been widely favored because of their proved stability and ease of use. Unlike gold, silver is notorious for its susceptibility to oxidation (tarnishing), which has limited the development of important silver-based nanomaterials. However, the substrates with poly(2-vinylpyridine) films were exceptionally stable as they produced spectra that did not change even after much more than one year.

1. Introduction

Surface enhanced Raman scattering (SERS) is a useful technique for structure analysis of trace substances and observation of cell transport [1]. In recent years, cell transport has been observed and their organic secretions have been analyzed using gold and silver nanoparticles [1–10]. Development of a SERS substrate comprising an assembled nanoparticle film on an indium tin oxide (ITO) coated glass slide with 3-aminopropyltrimethoxysilane(APTMS),as well as observation of cell transport under irradiation were reported [1,11]. The aim of this study, was to reduce the amount of irradiation required for Raman spectroscopy, as well as investigate and modify the surface of the nanoparticle material, to increase its stability over long periods of time. Because Ag nanoparticles are very unstable and cannot keep activity for long time, Al surface was used to keep Ag nanoparticles for increasing the stability of Ag nanoparticles over long periods of time. Nanoscale spatial confinement of the electric field can be achieved by localized surface plasmon (LSP) polaritons of metal nanostructures, which strongly enhance photophysical and photochemical processes. One promising structure is a dimer of metal nanoparticles with a nanometer-sized separation, which can produce an intense electric field within the nanogap, known as the hotspot. The extreme field enhancement and localization effects are caused by strong interaction between the plasmonic resonances of the two particles. The hotspot provides an enormous spatial gradient in the electric field, inducing strong radiation pressure on even single molecules. When the spot size is comparable to the spread of the molecular electric wave functions, anomalous excited-state dynamics appear that break the long wavelength approximation. These applications of the hotspot could be improved if the spatial pattern of the gap-mode LSP field could be externally controlled [12]. As such, the interaction between dissimilar metals, was investigated.

In this study, Al plates were used in place of ITO glass slides to create a substrate with high SERS activity. Al was used as it is inexpensive, has excellent conductivity, and is able to be processed into thin films. The Raman intensity was measured with respect to pyridine [1,13]. SERS is believed to cause attached metal nanoparticles to coordinate to the pyridine through lone pair on the nitrogen. Raman shifts were observed around 1032 cm^{-1} and 1008 cm^{-1} when pyridine was adsorbed [14]. Moreover, the polymer coating on the surface of the nanoparticle material investigated for its ability to increase the stability of the substrate. [15] Although silver has very desirable physical properties, good relative abundance, and low cost, gold nanoparticles have been widely favored because of their proved stability and ease of use. Unlike gold, silver is notorious for its susceptibility to oxidation (tarnishing), which has limited the development of important silver-based nanomaterials. Silver nanoparticles are inert or have long-term stability so difficult to realize. Special procedure is need [16,17]. In this study, for stabilization of silver nanoparticles tried the electrolytic polymerization of 2-vinyl pyridine. The substrate

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remained stable even for more than one year after coating 2-vinyl pyridine on the surface of the Al plate to maintain the SERS activity. As a result, this allowed for a long term SERS activity of unstable silver nanoparticles. Moreover, the Raman shift of carboxylic acids [18] on succinic acids was measured.

2. Experimental

2.1. Preparation of SERS-active substrates

SERS-active substrates were prepared by the chemical assembly of Ag nanoparticles on the APTMS-functionalized Al plates [1,19–21].

Ag nanoparticles were synthesized according to a typical protocol [1]: aqueous $AgNO_3$ solution (200 mL, 0.01%) was heated to boiling under vigorous string, and aqueous trisodium citrate solution (1.0 mL, 1%) was added. The color of the solution changed within the first several minutes. A final yellow solution was obtained and used for chemical assembly (solution 1).

Co nanoparticles were synthesized according to the same procedure: aqueous $Co(NO3)_2$ solution(100 mL, 0.01%) was heated to boiling with vigorous stirring, and aqueous trisodium citrate solution(1.0 mL, 1%) was added, and the resultant solution was heated with stirring for 10 min (solution 2).

Ni nanoparticles were synthesized according to the same procedure: aqueous $Ni(NO3)_2$ solution(100 mL, 0.01%) was heated to boiling with vigorous stirring, and aqueous trisodium citrate solution(1.0 mL, 1%) was added. The resultant solution was heated with stirring for 10 min (solution 3).

The Al plate was cleaned with deionized water, heated to boiling in deionized water for approximately 10 min and immersed in a 2%(v/v) aqueous APTMS solution for 30 h at room temperature for functionalization. The substrates were then rinsed with ultrapure water and annealed at 110 °C. The substrates were then immersed in solution 1 for 24 h to obtain a SERS substrate with an assembled Ag nanoparticle film on the Al plate through APTMS. Other substrates were immersed in mixture of solution 1: solution 2: solution 3 (2:1:1) for 24 h. Incidentally, the APTMS solution was alkaline (pH 11), which dissolved Al surface. Therefore to prevent this, the APTMS solution was neutralized by diluted HCl during silanization with APTMS. This solution was then used in the same manner as the original APTMS solution.

For comparison, SERS of the assembled Ag nanoparticle film on the Al plate surface with APTMS. For cleaning glass surface. Glass slide were ultrasonically cleaned in deionized water, isopropyl alcohol, acetone, and ultrapure water for 15 min, each, followed by cleaning in H_2O:H_2O_2 (30%):NH_4OH(5:1:1) for 30 min. The slides were further cleaned by sonication in ultrapure water for 20 min and immersed in a 2% (v/v) aqueous APTMS solution for 12 h at room temperature for functionalization. According to that suggested by Ming-De Li et al. [1].

2.2. Electrolytic polymerization

The assembled substrates were prepared following the literature procedure for polymerization of Zn and Fe [22,23] to the surface of an Al plate with 2-vinyl pyridine, with a slight modification. The Al plate (prepared in the same manner as described in Section 2.1, 1250 mm^2) was formed into a cathode. The anode was a stainless steel plate of the same size. The electrolytic polymerization of 2-vinyl pyridine at room temperature was performed for 55 min at 0.05 A. The electrolytic solution comprised water: methanol in a ratio of 9:1 and included ammonium perchlorate 0.05 mol/L and 2-vinyl pyridine 0.25 mol/L.

A reagent 3-aminopropyltrimethoxysilane and all other reagents were of analytical reagent grade.

2.3. Apparatus

In this study, a few drops of pyridine or a few drops of carboxylic acids were placed on the Al plate or the Al plate with poly(2-vinylpyridine) films and covered with a glass slide, which was then sealed with Teflon tape. The concentration of pyridine was set according to that suggested by Ming-De Li et al. [1].

Raman spectra and images were obtained using a Raman system (NRS2100), a triple spectrometer instrument equipped with a holographic notch filter and charge-coupled device detector. A solid-state laser (532 nm wavelength) was used for Raman measurements. Moreover, the laser power at the sample was ~19 mW. The laser spot was ~4 μm in diameter.

Scanning electron microscope (SEM) images were taken with a field emission microscope (JSM6500F) operated at an accelerating voltage of 15 kV.

3. Results and discussion

To characterize the uniformity of the surface SERS signal, a Raman experiment was performed following adsorption of pyridine on the surface. Fig. 1 shows the Raman spectra of the substrates, using the most intense pyridine bands at 1008 cm^{-1} and 1032 cm^{-1} as the Raman signal.

Those on the APTMS coated Al were immobilized with a mixture of silver, cobalt, and nickel nanoparticles, giving the best Raman intensity. The same Raman intensity could be seen when glass slides were used. As compared with those immobilized on the glass, the intensity of the symmetric ring stretching modes at 1008 cm^{-1} and 1032 cm^{-1} of the pyridine ring had a tendency to reverse. This is considered to be caused by the interaction between Al and pyridine. By adding Co and Ni nanoparticles, the SERS signal became stronger as it may be enhanced by the interaction of the cobalt and nickel nanoparticles. Compared with silver nanoparticles alone, Raman intensity is considered to have improved nearly double by the interaction of particles.

The 2% (v/v) aqueous APTMS solution was alkaline (pH 11). As the Al surface was dissolved in solution, to prevent this, the APTMS solution was neutralized by diluted HCl during silanization with APTMS.

Fig. 2 shows SEM images of the Al surface. String-like substance were observed on the Al surface. (Fig. 2 b)

Poly (2-vinylpyridine) films were deposited on the Al substrate by electropolymerization using galvanostatic techniques at room temperature in an aqueous solution containing methanol (pH 5).

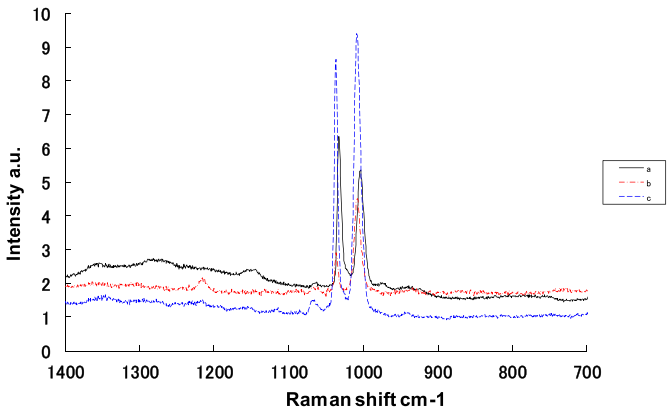

Fig. 1. SERS of pyridine.
(a) SERSs of the (Ag/Glass) substrate, (b) the (Ag/Al) substrate, and (c) the (Ag, Ni, and Co/Al) substrate using pyridine as the probe molecule. The collection times of (a), (b), and(c) were 20 s.