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SERS on Silver Formed in Anodic Aluminum Oxide Nanotemplates

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A strong SERS effect has been observed on silver surfaces which were prepared by Ag deposition in anodic aluminum oxide nanotemplates and subsequent partial removal of the oxide layers. The advantage of these surfaces for SERS studies is that the controlled size and dispersion of Ag particles can be achieved.

Introduction

Surface-enhanced Raman Scattering (SERS) spectroscopy[1,2] is a well-established method for studying properties of molecules adsorbed on specially prepared surfaces of metals, such as silver, gold, and copper. For SERS experiments, various SERS-active surfaces have been used. Examples of these are surfaces of colloidal metal particles,[3] vacuum-deposited metal films,[4] electrochemically roughened electrodes,[5] chemically prepared films,[6] and HNO_3-roughened metal foils.[7] However, surfaces with controlled particle size and dispersion have not been reported. When anodized in an electrolytic acid solution, aluminum forms a porous oxide with highly uniform-size and parallel pores open only on one end.[8] Its pores can function as nanotemplates in which small metal or semiconductor particles can be electrochemically deposited. As electrodeposition continues, metal fills the pore from the bottom upward.[9] Metal wires can be fabricated in this manner with lengths in excess of 2 μm and with diameters between approximately 10 and 200 nm. Surfaces prepared in this way have been studied in a wide spectrum of scientific and technological fields, from catalysis to magnetic data storage.[8,10]

In this paper we present a strong SERS effect observed on surfaces of silver particles deposited in anodic aluminum oxide pores whose oxide layers were partly removed after the deposition of silver.

Experimental

0.25 mm-thick aluminum sheet was used as a substrate material. Prior to the anodization, several steps were taken to ensure a clean non-oxidized surface of the aluminum. The air-oxidized surface of the aluminum sheet was etched in an aqueous solution of sodium carbonate (25 g/L) at 80 ℃ for 1 minute.

The sheet was then rinsed in distilled water for 30 seconds, dipped into 1:1 nitric acid/water solution for 15 seconds in order to neutralize the sodium carbonate, and finally rinsed in distilled water for 1 minute.

Cleaned aluminum sheets were anodized in an aqueous solution of H_3PO_4 (10% (w/w)) at room temperature (20-25 ℃) for 30 minutes at 20 V DC. [The porous anodic aluminum oxide is made during this anodization process.] The cathode of the electrochemical cell was a graphite sheet.

Silver/alumina/aluminum sheets were prepared from an aqueous mixture of silver nitrate (1.51 g/L) buffered with boric acid (45 g/L). The silver metal was deposited in the anodic aluminum oxide pores using a sinusoidal 20 V AC for 40 seconds. The counterelectrodes were graphite sheets. The silver/alumina/aluminum sheet was then rinsed in distilled water for several minutes.

The oxide surface prepared by anodization on silver/alumina/aluminum sheet was partly removed by etching in an aqueous solution of sodium carbonate (25 g/L) at 80 ℃ for
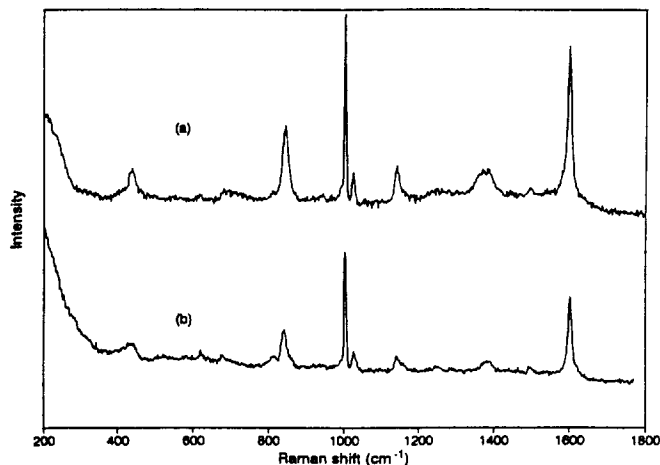
Figure 1. SERS spectra of benzoic acid adsorbed on (a) silver colloid surfaces and (b) the Ag/alumina/aluminum surfaces whose oxide layers were partly removed after the deposition of silver.
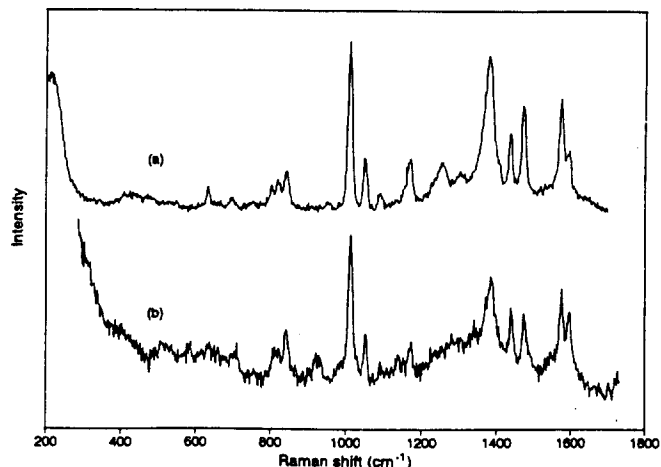
Figure 2. SERS spectra of picolinic acid adsorbed on (a) silver colloid surfaces and (b) the Ag/alumina/aluminum surfaces whose oxide layers were partly removed after the deposition of silver.

10-20 seconds. The sheet was then rinsed in distilled water. Their surface may appear such that silver pillars stand up on the alumina. The sheet was dipped into the adsorbate solution for at least 5 minutes, taken out, and dried for Raman scattering measurements. In order to minimize any laser-induced effects, the sample sheets were spun at a 2500 rpm during spectral measurements using an ac motor.

A 1×10^{-2} M aqueous solution of benzoic acid was prepared by dissolving benzoic acid in NaOH solution. A 1×10^{-3} M aqueous solution of picolinic acid was prepared.

Spectral data were collected using a SPEX 1403 monochromator equipped with a *dc* detection device, and the excitation source was a Lexel Model 95 argon ion laser. The laser wavelength used was 488 nm and the laser power was 20 mW at the sample position.

Results and Discussion

Reliable SERS spectra could not be obtained from the surfaces of Ag deposited in anodic aluminum oxide pores without the partial removal of the oxide layers after Ag deposition. After a partial removal of the oxide layers of anodic aluminum oxide pores, however, intense SERS spectra were observed on the surfaces of Ag/alumina/aluminum.

A SERS spectrum of benzoic acid adsorbed on the surfaces of Ag/alumina/aluminum is shown in Figure 1b. For comparison, the SERS spectrum of benzoic acid adsorbed on silver colloid surfaces is also presented in Figure 1a. The two spectra are almost the same with each other in their signal-to-noise ratio and shape, and are in good accordance with the literature.[11]

The strongest band at 1002 cm^{-1} is due to the ring breathing mode of benzene ring. Another strong band at 1602 cm^{-1} is due to the ring stretching vibration which is the e_{2g} mode of benzene. The intense band at 842 cm^{-1} is due to the C-H deformation which is the e_{1g} mode of benzene. The band at 1384 cm^{-1} is due to the symmetric stretching of COO^{-}.

Even with the sample spinning during the laser irradiation, a small amount of photodecomposition was still observed,

as evident in the SERS spectrum of picolinic acid (see Figure 2b). There is a strong background intensity near 1300 and 1550 cm^{-1}. This background is known to be due to disordered graphite.[12] Without the sample spinning, a severe photodecomposition was observed. The SERS spectrum of picolinic acid adsorbed on silver colloid surfaces which is in good accordance with the literature[13] is shown in Figure 2a for comparison.

By the scanning electron micrographs observed by Al-Mawlawi *et al.*,[14] after the partial removal of the aluminum oxide layers, the side view of the surface of metal/alumina/aluminum is such that the pillars of metal stand on aluminum oxide surfaces. The top view of the surface is similar to island films. There are some advantages of this surface morphology over others, such as those of island films and other SERS-active surfaces. In practice, we can change the size of silver pillars and the distance between silver pillars. The size of silver pillar is defined by its diameter and length. The length of a silver pillar can be controlled by changing the deposition time of silver in anodic aluminum oxide pores. The height of the silver pillar is determined by the extent of the oxide layer removal. The diameter of the silver pillar can be enlarged by widening the anodic alumina pores prior to the silver metal deposition therein. Al-Mawlawi *et al.*[9] have widened the pores of the anodic alumina by immersing the samples in a solution of 0.085-M phosphoric acid and measured the pore diameters by varying pore widening time. They have found a quadratic dependence of the mean pore diameter on the pore widening time.[10]

The distance between silver pillars can be changed by changing the pore density in anodic aluminum oxide films. The pore density can be controlled by an applied DC voltage, temperature, and the kind of the electrolyte employed in the anodization process. It is known[8,10] that the pore density (ρ_{pore}) expressed in number per Å^{2} is a simple function of the anodizing voltage (V) of the form

$$\rho_{pore} = \alpha/(D_p + \beta V)^2,$$

where α is a constant approximately equal to 1.15, D_p is

the pore diameter, and β is a constant. Values of the parameters D_p and β for some acid media and temperatures are known.[8] In most cases pore densities fall in the range 10^{10}-10^{11} pores/cm^2. This technique allows one to make a well-defined surface. These surfaces of well-defined particle dimensions can then be used to study the SERS enhancement effect as functions of the particle size and the distance between particles.

In conclusion, we have demonstrated that highly-enhanced Raman spectra can be observed from the surfaces of silver deposited in anodic aluminum oxide pores whose oxide layers were partly removed after the deposition of silver. This preparatory method for new SERS-active surfaces may have advantages in that the size of and the distance between Ag particles can be controlled.

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CARS Spectra of HCl, N₂, and C₂H₂ in the Gas Phase

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Coherent anti-Stokes Raman scattering (CARS) spectra of HCl, N₂, and the ν_1 fundamental of C₂H₂ have been measured in the gas phase. The measured spectra show rotational structures which originate from the Q-branch transitions. The spectra have successfully been simulated with proper selection rules, line positions, and relative intensities from room temperature Boltzmann population distributions. The vibration-rotation interaction constant α of HCl in the ground electronic state has been measured from the rotationally resolved CARS spectra which is α=0.3076 cm^{-1}. Possibilities of optical pumping and of measuring state specific energy distributions of molecules are discussed.

Introduction

Rovibrational spectra of molecules in the gas phase provide rich information about molecular structures and the dynamics when the spectra can particularly be observed in a chemically changing system. Absorption or Emission of light due to spectroscopic transitions between the rovibrational states in the ground electronic state of the molecules would produce such spectra in the infrared.[1] However, it is not easy to obtain the IR absorption spectra of the molecules in the gas phase because of intrinsically low absorption coefficients of the molecules in this spectral region. Since the

radiative lifetime in the excited rovibrational states are in general long (longer than 1 ms in many cases), it is even more difficult to measure the emission spectra of the molecules in IR.[2] Moreover, the fact that the blackbody radiation at ambient temperatures peaks in near IR decreases the signal-to-noise in the IR emission spectra. Vibrational Raman spectra may be alternatives to study the molecular structures but the Raman scattering signals from the molecules in the gas phase are too small to be measured in the rotationally resolved spectra. However, with a recent advent of coherent high power lasers, a stimulated Raman scattering technique greatly enhances the signal. Various laser Raman spectro-