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Simple Method for Preparing Controllably Aggregated Silver Particle Films Used as Surface-Enhanced Raman Scattering Active Substrates

Jiawen Hu,[†] Bing Zhao,^{*,†} Weiqing Xu,[†] Yuguo Fan,[†] Bofu Li,[†] and Yukihiro Ozaki^{*,†}

Key Laboratory for Supramolecular Structure and Spectroscopy of Ministry of Education, Jilin University, Changchun 130023, People's Republic of China, and Department of Chemistry, School of Science and Technology, Kwansei-Gakuin University, Sanda, Hyogo 669-1337, Japan

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Silver colloids are one of the extensively employed surface-enhanced Raman scattering (SERS) active substrates. To obtain the SERS effect, their aggregation upon addition of analyte is necessary. However, problems of instability and irreproducibility in the magnitude of the signal are caused by the formation of aggregates. Considering that the aggregation of silver colloids is essential to induce small silver clusters, in the present study, we develop a drying process to prepare silver particle films (silver clusters) that are supported directly on a glass slide. These silver particle films arise through the aggregation of silver colloids occurring in thin water films supported on a solid substrate. With the evaporation of water, silver clusters are left on the solid substrate. Thus, the assembly meets perfectly the requirement of aggregation of silver colloids and, at the same time, possesses the stability of solidlike SERS-active substrates. We can easily obtain excellent SERS spectra from these silver particle films. These substrates show great potential in practical applications such as ultrasensitive microanalysis with micro-Raman spectroscopy and are suitable for studying the optical properties of silver clusters. 4-Mercaptopyridine (4MPY) was used to test the utility of the proposed method and to compare it with the chemically deposited silver film (silver mirror) method. The intensity of SERS signals of 4MPY on the silver particle films is stronger by about 100 times than that of 4MPY on the silver mirror. In addition, the experimental results of SERS reveal that the activation agent, coadsorbed chloride ions, can further enhance the SERS signals from both the silver mirror and the silver colloids.

Introduction

The methods of preparing surface-enhanced Raman scattering (SERS) active substrates have been explored extensively because the development of substrates with high enhancement ability and stability is the key to initiate and/or broaden novel applications of SERS.^{1–20} Moreover, appropriately prepared substrates provide ideal models for investigating the mechanism of this complicated phenomenon. The versatility of SERS techniques is underlined by the variety of methods using different types

of substrates satisfying the requirements of a particular application.

Metal colloids are used most frequently to produce SERS-active media in solutions.^{1–4,9} Metal colloids, in

* To whom correspondence should be addressed. Mailing address: Yukihiro Ozaki, Department of Chemistry, School of Science, Kwansei-Gakuin University, Sanda, Hyogo 669-1337, Japan. Fax: +81-795-65-9077. E-mail: ozaki@kwansei.ac.jp.

[†] Jilin University.

[‡] Kwansei-Gakuin University.

(1) Chang, R. K.; Furtak, T. E. *Surface Enhanced Raman Scattering*; Plenum Press: New York, 1982.

(2) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

(3) Otto, A.; Mrozek, I.; Grabhorn, H.; Akemann, W. *J. Phys.: Condens. Matter* **1992**, *4*, 1143.

(4) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Chem. Rev.* **1999**, *99*, 2957.

(5) (a) Fleischmann, M.; Hendra, D. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163. (b) Jeanmaire, D. L.; Van Duyne, P. R. *J. Electroanal. Chem.* **1977**, *84*, 1.

(6) (a) Aroca, R.; Jennings, C.; Kovacs, G. J.; Loutfy, R. O.; Vincett, P. S. *J. Phys. Chem.* **1985**, *89*, 4051. (b) Sudnik, L. M.; Norrod, K. L.; Rowlen, K. L. *Appl. Spectrosc.* **1996**, *50*, 422.

(7) (a) Ni, F.; Cotton, T. M. *Anal. Chem.* **1986**, *58*, 3159. (b) Wu, Y.; Zhao, B.; Xu, W.; Li, G.; Li, B.; Ozaki, Y. *Langmuir* **1999**, *15*, 1247. (c) Wu, Y.; Zhao, B.; Xu, W.; Li, B.; Jung, Y. M.; Ozaki, Y. *Langmuir* **1999**, *15*, 4625. (d) Boo, D. W.; Oh, W. S.; Kim, M. S.; Kim, K.; Lee, H.-C. *Chem. Phys. Lett.* **1985**, *120*, 301.

(8) (a) Mattei, G.; Quagliano, L. G.; Pagannone, M. *Europhys. Lett.* **1990**, *11*, 373. (b) Pagannone, M.; Quagliano, L. G.; Mattioli, L.; Mattei, G. *J. Raman Spectrosc.* **1991**, *22*, 825. (c) Xue, G.; Dong, J. *Anal. Chem.* **1991**, *63*, 2393.

(9) (a) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 790. (b) Lee, P. C.; Meisel, D. *J. Phys. Chem.* **1982**, *86*, 3391. (c) Nickel, U.; Zu Castell, A.; Pöpl, K.; Schneider, S. *Langmuir* **2000**, *16*, 9087. (d) Ahern, A. M.; Garrell, R. L. *Anal. Chem.* **1987**, *59*, 2813. (e) Neddersen, J.; Chumanov, G.; Cotton, T. M. *Appl. Spectrosc.* **1993**, *47*, 1959. (f) Sibblad, M. S.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4672.

(10) (a) Freeman, R. G.; Grabar, K. G.; Allison, K. A.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629. (b) Chumanov, G.; Sokolov, K.; Gregory, B. W.; Cotton, T. M. *J. Phys. Chem.* **1995**, *99*, 9466. (c) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.

(11) (a) Bello, J. M.; Stokes, D. L.; Vo-Dinh, T. *Appl. Spectrosc.* **1989**, *43*, 1325. (b) Bello, J. M.; Stokes, D. L.; Vo-Dinh, T. *Anal. Chem.* **1989**, *61*, 1779. (c) Alak, A. M.; Vo-Dinh, T. *Anal. Chem.* **1989**, *61*, 656.

(12) (a) Liao, P. F.; Bergman, J. G.; Chemla, D. S.; Wokaun, A.; Melngailis, J.; Hawryluk, A. M.; Economou, N. P. *Chem. Phys. Lett.* **1981**, *82*, 355. (b) Hulteen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol., A* **1995**, *13*, 1553. (c) Enlow, P. D.; Buncick, M.; Warmack, R. J.; Vo-Dinh, T. *Anal. Chem.* **1986**, *58*, 1119. (d) Kahl, M.; Voges, E.; Kostrewa, S.; Viets, C.; Hill, W. *Sens. Actuators, B* **1998**, *51*, 285.

(13) Matsui, H.; Pan, S.; Doublerly, G. E., Jr. *J. Phys. Chem. B* **2001**, *105*, 1683.

(14) Tessier, P. M.; Velev, O. D.; Kalambur, A. T.; Rabolt, J. F.; Lenhoff, A. M.; Kaler, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 9554.

(15) Oldenburg, S. J.; Westcott, S. L.; Averitt, R. D.; Halas, N. J. *J. Chem. Phys.* **1999**, *111*, 4729.

(16) (a) Joo, Y.; Suh, S. *Bull. Korean Chem. Soc.* **1995**, *16*, 808. (b) Yao, J.-L.; Xu, X.; Wu, D.-Y.; Xie, Y.; Ren, B.; Tian, Z.-Q.; Pan, G.-P.; Sun, D.-M.; Xue, K.-H. *Chem. Commun.* **2000**, 1627.

(17) (a) Tian, Z. Q.; Ren, B.; Mao, B. W. *J. Phys. Chem. B* **1997**, *101*, 1338. (b) Zou, S.; Weaver, M. J.; Li, X. Q.; Ren, B.; Tian, Z. Q. *J. Phys. Chem. B* **1999**, *103*, 4218.

(18) Dutta, P. K.; Robins, D. *Langmuir* **1991**, *7*, 2004.

(19) Walls, D. J.; Bohn, P. W. *J. Phys. Chem.* **1989**, *93*, 2976.

(20) Yogeve, D.; Efrima, S. *J. Phys. Chem.* **1988**, *92*, 5761.

general, show strong SERS enhancement and are easily prepared and manipulated. To generate greater SERS signals, aggregation of the metal colloids induced by an analyte itself or by the addition of coadsorption ions such as Cl^- and NO_3^- is essential.^{9a,21} However, aggregated metal colloids tend to coagulate. This makes them unstable and difficult to use, resulting in poor reproducibility of SERS signals. The problem can be reduced by the addition of stabilizers such as poly(vinyl alcohol), poly(vinylpyrrolidone), and sodium dodecyl sulfate into the metal colloids to prevent further aggregation.^{21a,22} The flow injection method has been used to prepare metal colloids, and thus flow injection analysis has been applied so as to improve the reproducibility of SERS signals from metal colloids.²³ Supported metal nanoparticles on rigid substrates through hydrosols on filter paper,²⁴ porous silica entrapment of metal nanoparticles,²⁵ and self-assembled metal colloid monolayers¹⁰ exhibit large stability. However, these methods may lose the features of aggregation of metal colloids, a prerequisite for a strong SERS effect.

Such consideration prompts efforts to find methods for preparing assemblies of metal colloidal nanoparticles bearing both partial aggregation characteristics and great stability. In our previous paper,²⁶ we reported such a method, that is, silver particle films trapped at an air–water interface. In the usual way of measuring SERS spectra, a metal colloid solution is kept in a small cuvette and thus a laser beam must pass through the wall of the cuvette to focus on the metal colloids therein. We devised recently a U-shaped capillary device as the colloid sampling device. In this device, we can directly focus the laser beam on the silver colloids from the capillary orifice. Interestingly, from observation with the microscope of a micro-Raman instrument, we found that the analyte-covered silver particles migrate from the bulk solution to the air–water interface and are trapped.²⁶ As more and more particles are trapped at the interface, aggregation occurs among the trapped particles, and two-dimensional silver particle films are thus formed and supported at the interface. These silver particle films combine the necessity of aggregation of silver colloids and practical-application-needed stability. When used as SERS-active substrates, these silver particle films supported at the air–water interface demonstrate excellent enhancing ability with only low laser power used for excitation (less than $40\ \mu\text{W}$).²⁶

Keeping in mind that transferring the silver particle films from the air–water interface to a solid substrate reinforces their structure, in the present study, we have developed a simple way to form controllably aggregated silver particle films supported on a glass slide. We have found that when a drop of silver colloids is placed directly on a glass slide and dried naturally, silver particle films with micrometer scales are generated. With a micro-Raman instrument, the silver particle films can be distinguished easily as small bright flakes on the glass slide. SERS spectra obtained from the silver particle films compared with those from silver colloids and chemically

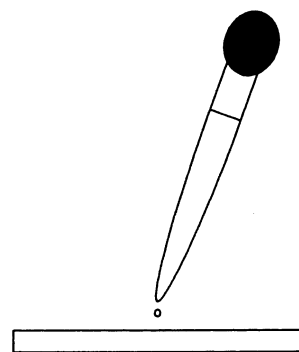


Figure 1. Schematic of the formation of silver particle films supported on a glass slide.

deposited silver films (silver mirror) reveal their excellence and convenience as SERS-active substrates. Small silver particle films, namely, silver clusters, which were reported previously, could be gravitationally deposited from the silver colloid/adsorbate system under carefully controlled conditions, and a single aggregate can be formed with a micropreparative technique.²⁷ As we report here, the drying process forming silver particle films is a convenient method. Moreover, most previous studies concentrated on aqueous silver colloid/adsorbate systems. The silver clusters should, however, deserve more attention since aggregation-induced silver clusters are the main source of the enormous SERS enhancement of colloid systems. Therefore, the SERS process emerging on the silver clusters themselves can help to better understand various SERS phenomena associated with silver colloids. However, the importance of the method of measuring SERS spectra from silver clusters has not been well recognized. The present study offers a feasible way of investigating the relationship between the detailed nanostructure of silver clusters and their strong SERS signals or other optical properties.

Experimental Section

AgNO_3 , trisodium citrate, and 4-mercaptopyridine (4MPY) were all obtained from Aldrich. Sodium chloride was of spectral grade. Aqueous solutions of analytical grade formaldehyde (HCHO) and ammonia (NH_3) were employed for preparing silver mirrors. The SERS enhancement ability of active substrates was tested by 4MPY as has been employed extensively for SERS studies.²⁸ Before use, the 4MPY was recrystallized from methanol and a 1×10^{-4} mol/L aqueous solution of 4MPY was prepared. Triply distilled water was used throughout the present study.

The method of preparing silver colloids was the standard citrate-reduction procedure.^{9b} To 0.9 mL of a silver colloid solution, 100 μL of the 1×10^{-4} mol/L 4MPY solution was added. For activating the silver colloids, 10 μL of a 0.1 mol/L NaCl solution was introduced to the mixture. The final concentration of the analyte in the sample was 1×10^{-5} mol/L. A glass capillary was used as the sampling device for measuring SERS from the silver colloid substrates. Figure 1 shows a schematic of the formation of silver particle films supported on a glass slide. Prior to deposition, the 20 mm \times 10 mm glass slide was successively sonicated in chloroform, absolute ethanol, and distilled water and then dried. One drop of the colloid with the analyte concentration of 1×10^{-5} mol/L was deposited on the glass and dried naturally in a desiccator to form the silver particle films.

(21) (a) Siiman, O.; Bumm, L. A.; Callaghan, R.; Blatchford, C. G.; Kerker, M. *J. Phys. Chem.* **1983**, *87*, 1014. (b) Siiman, O.; Feilchenfeld, H. *J. Phys. Chem.* **1988**, *92*, 453. (c) Dou, X.; Jung, Y. M.; Cao, Z.; Ozaki, Y. *Appl. Spectrosc.* **1999**, *53*, 1440.

(22) (a) Heard, S. M.; Grieser, F.; Barraclough, C. G. *Chem. Phys. Lett.* **1983**, *95*, 154. (b) Lee, P. C.; Meisel, D. *Chem. Phys. Lett.* **1983**, *99*, 262.

(23) (a) Berthod, A.; Laserna, J. J.; Winefordner, J. D. *Appl. Spectrosc.* **1987**, *41*, 1137. (b) Ni, F.; Sheng, R.; Cotton, T. M. *Anal. Chem.* **1990**, *62*, 1958.

(24) Tran, C. D. *Anal. Chem.* **1984**, *56*, 824.

(25) Liu, F. X.; Xiao, Y.; Li, Y.-S. *J. Raman Spectrosc.* **2001**, *32*, 73.

(26) Hu, J.; Zhao, B.; Xu, W.; Fan, Y.; Li, B.; Ozaki, Y. *J. Phys. Chem. B* **2002**, *106*, 6500.

(27) Vlckova, B.; Gu, X. J.; Tsai, D. P.; Moskovits, M. *J. Phys. Chem.* **1996**, *100*, 3169.

(28) (a) Baldwin, J.; Schühler, N.; Butler, I. S.; Andrews, M. P. *Langmuir* **1996**, *12*, 6389. (b) Baldwin, J. A.; Vlckova, B.; Andrews, M. P.; Butler, I. S. *Langmuir* **1997**, *13*, 3744. (c) Jung, H. S.; Kim, K.; Kim, M. S. *J. Mol. Struct.* **1997**, *407*, 139.

Silver mirrors were prepared by Tollen's method.^{7b,c} Formaldehyde-reduced silver particles were randomly deposited on a cleaned glass slide to generate the silver mirror. A monolayer range of coverage was produced through immersing the silver mirror into a 1×10^{-4} mol/L 4MPY solution for about 15 min. A SERS spectrum of 4MPY without coadsorbed chloride ions was measured from this silver mirror first, and it was subsequently dipped into a 1×10^{-4} mol/L NaCl solution so as to adsorb chloride ions. Both SERS spectra with and without coadsorbed chloride ions were obtained from the same spot on the silver mirror with the aid of the microscope of the Raman instrument.

SERS spectra were measured with a confocal microscopy Raman spectrometer (Renishaw 1000 model) equipped with a CCD detector and a holographic notch filter. Radiation of 514.5 nm from an air-cooled argon ion laser (Spectra-Physics model 163-C4260) was used for excitation. Laser power at the sample position was not more than a few milliwatts. The microscope attachment was based on a Leica DMLM system, and a $50\times$ objective was used to focus the laser beam onto a spot of approximately $1 \mu\text{m}$ in diameter. Optical images of the silver particle films and silver mirror were measured with a CCD camera and displayed on a computer. All the spectra reported were the results of a single 10-s accumulation. Atomic force microscope (AFM) images were obtained with a Nanoscope IIIa (Digital Instruments) using the tapping mode.

Results and Discussion

The Formation of Silver Particle Films. Figure 2a–c shows optical images of silver particle films supported on a glass slide prepared by the present method and an optical image of a silver mirror, respectively. Bright flakes, which we call silver particle films, can be distinguished easily from the glass slide at the edge (Figure 2a) or at the central region (Figure 2b) of the wetted area of the drop of silver colloids. At the edge of the wetted area, a lot of silver particle films with a scale of a few micrometers are connected via clusters. Meanwhile, at central locations silver particle films are usually separated from each other. From the edge to the center, many small, bright spots can be discerned (Figure 2a). The optical image of the silver mirror was obtained for comparison (Figure 2c), on which no bright locations can be seen. Figure 3a depicts an AFM image of silver particle films supported on a glass slide. It can be seen from the image that the films are tightly compacted aggregates consisting of more than hundreds of silver particles. On the other hand, on the parts of the wetted area where no silver particle films are present most particles exist as separated, single nanocrystals with a few dimers and trimers emerging. Typical detailed images of such places are depicted in Figure 3b,c. Figure 3d shows an AFM image of the silver mirror. The silver particles on the silver mirror are randomly deposited, although compacted closely.

The aggregation of metal colloid systems is a complex process. It depends on the surface potential of the colloids, the chemical nature and charge of an analyte, the concentration of the analyte in the system, and any electrolytes added intentionally as preaggregating agents.^{27,29} However, in the present case, the aggregation process seems to proceed mainly during drying; even without the addition of an analyte and preaggregating agent such as sodium chloride to silver colloids, silver particle films are formed spontaneously on a glass slide through the drying process. The driving force producing the aggregation may be the capillary force. It has been reported that when colloid particles are immersed in a thin liquid film supported on a solid substrate, the capillary force between the particles could lead to their aggregation with the evaporation of the liquid.³⁰

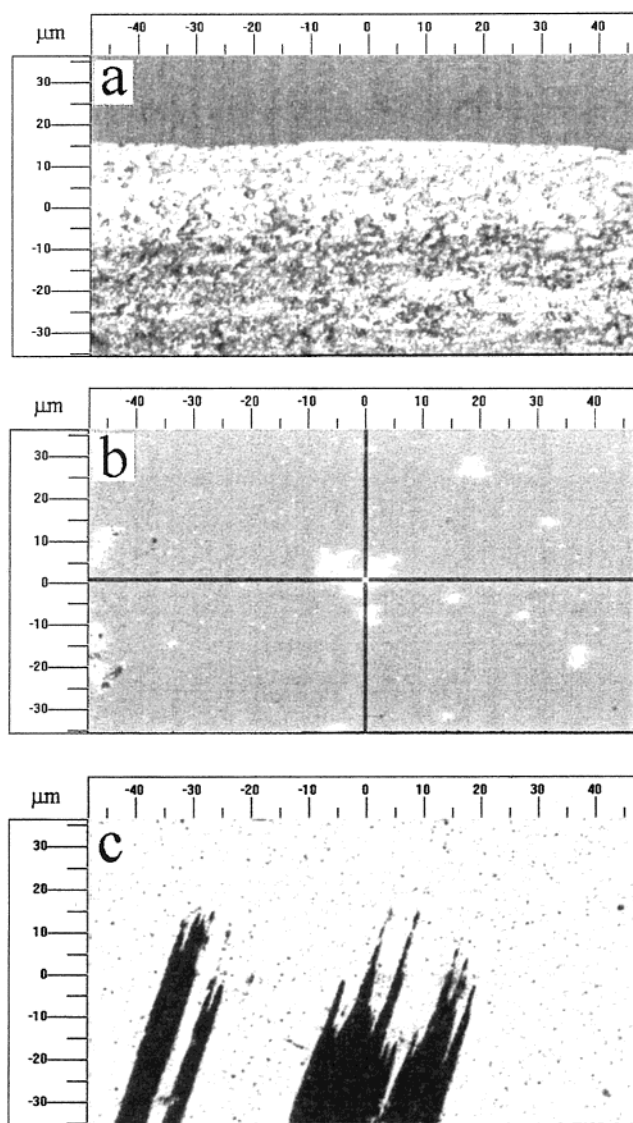


Figure 2. Optical images of the silver particle films (a) at the edge and (b) at the central location, where one drop of silver colloids was spread and dried, and (c) an optical image of a silver mirror.

Surface-Enhanced Raman Scattering. With the use of the confocal micro-Raman system, we obtain a diameter of $1 \mu\text{m}$ for the laser beam spot. Therefore, it is easy to measure a SERS spectrum from silver particle films with scales of a few micrometers. Figure 4a shows the strong SERS spectrum of 4MPY obtained from the silver particle films shown in Figure 2b and positioned by the crosswire of the microscope from the optical mode. Figure 4b,c shows the SERS spectra of 4MPY obtained from the places of the wetted area with no obvious silver particle films discerned with the microscope but probably with some silver film or something like that present. Typical AFM images of such places are presented in Figure 3b,c. The silver particle films give much stronger Raman signals compared with those in Figure 4b,c. On the silver particle films, many more silver particles can be illuminated in the laser spot than on the places where only separated, single particles exist, resulting in the markedly enhanced Raman signals observed. However, the great enhancement of Raman

(29) Weitz, D. A.; Oliveria, M. *Phys. Rev. Lett.* **1984**, *52*, 1433.

(30) Kralchevsky, P. A.; Denkov, N. D.; Paunov, V. N.; Velev, O. D.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *J. Phys.: Condens. Matter* **1994**, *6*, A395.

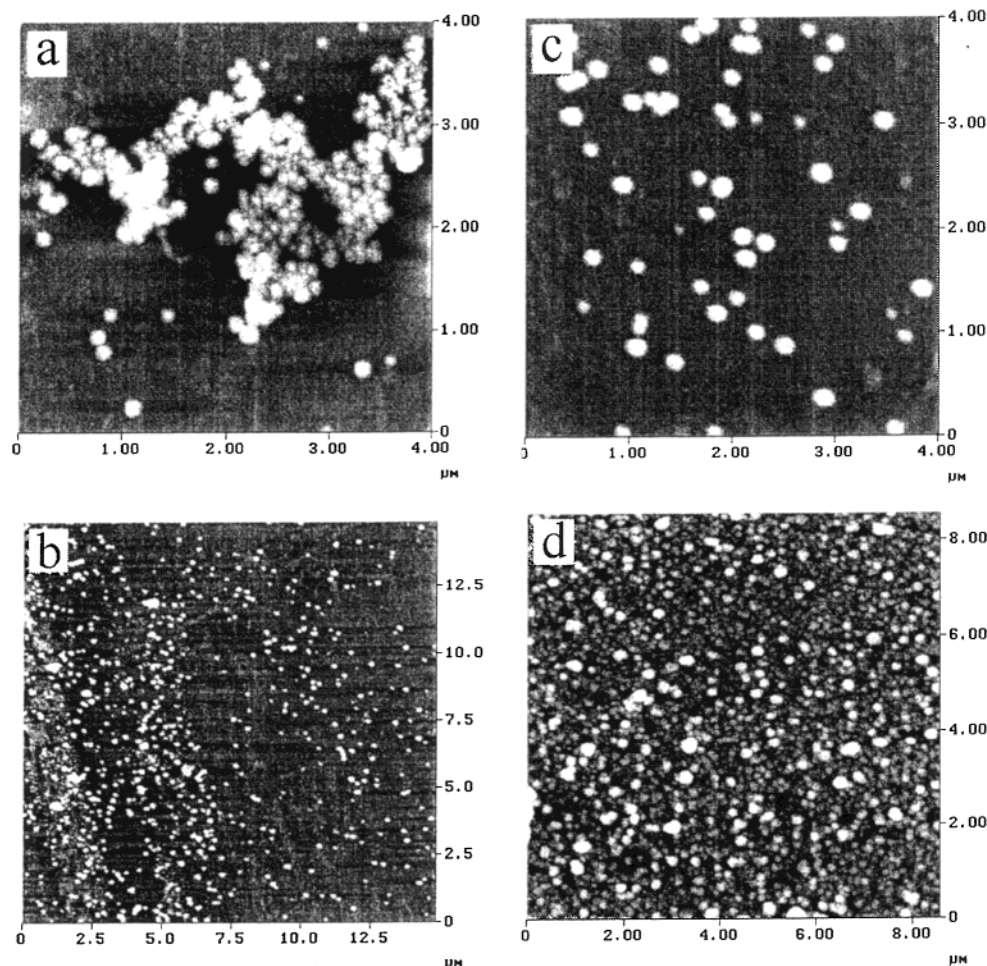


Figure 3. AFM images of (a) the silver particle films, (b,c) the parts of the wetted area of the silver colloids where no silver particle films can be discerned with the microscope, and (d) a silver mirror.

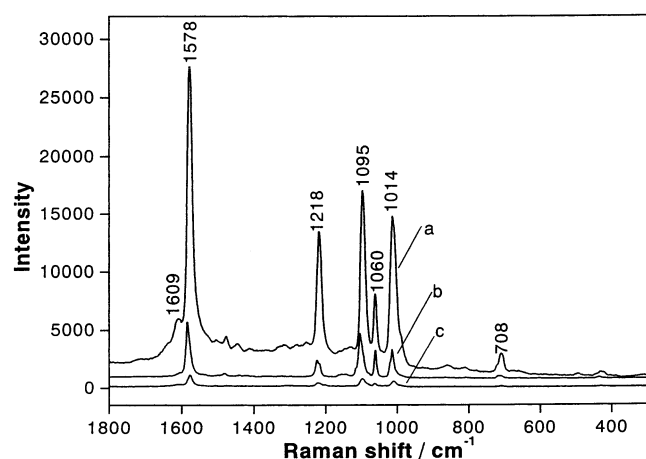


Figure 4. SERS spectra of 4MPY obtained from (a) the silver particle films (shown in Figure 2b) and (b,c) the parts of the wetted area of silver colloids where no silver particle films can be discerned with the microscope. The laser power was 40 μW for all three spectra. The concentration of the analyte in the silver colloids for generating the silver particle films was 1×10^{-5} mol/L.

signals for the silver particle films may be attributed mainly to the coupling between silver particles.

The aggregation of silver colloids is crucial for a strong SERS effect. Two characteristic features are seen in the UV-vis spectra of an aggregated aqueous silver colloid system. One is a surface plasmon band of the usual silver

particles themselves, and the other is a new red-shifted peak arising from the coupling of surface plasmons of adjacent particles.^{9a,21} Aggregation of metal colloids leads usually to fractal clusters.²⁹ Theoretical and experimental studies on the silver clusters have revealed that greatly enhanced electric fields exist in aggregated silver particles, especially in the junctions between the particles, resulting in the enhancement of Raman signals of the molecules adsorbed at these locations.^{31,32} In the present case, the Raman signals on the silver particle films arise from the particles in a micrometer range (the diameter of the laser spot). It is difficult to obtain a micro-UV-vis spectrum from the silver particle films on which the laser beam is focused to confirm whether coupling between silver particles occurs in these illuminated silver particles. However, an ordinary UV-vis spectrum from periodic gold films which were assembled by gold nanoparticles showed a "red-shift" band.¹⁴ Therefore, it was concluded that the coupling between silver particles could be responsible for the strong SERS signals from silver particle films.^{9a,21} A theory about the optical properties of fractal clusters of colloidal gold and silver particles shows that the SERS

(31) (a) Markel, V. A.; Shalae, V. M.; Zhang, P.; Huynh, W.; Tay, L.; Haslett, T. L.; Moskovits, M. *Phys. Rev. B* **1999**, *59*, 10903. (b) Bozhelvolnyi, S. I.; Markel, V. A.; Coello, V.; Kim, W.; Shalae, V. M. *Phys. Rev. B* **1998**, *58*, 11441.

(32) (a) Kneipp, K.; Wang, Y.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *78*, 1667. (b) Michaels, A. M.; Nirmal, M.; Brus, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 9932. (c) Michaels, A. M.; Jiang, J.; Brus, L. *J. Phys. Chem. B* **2000**, *104*, 11965. (d) Xu, H.; Bjerneld, E. J.; Käll, M.; Börjesson, L. *Phys. Rev. Lett.* **1999**, *83*, 4357.

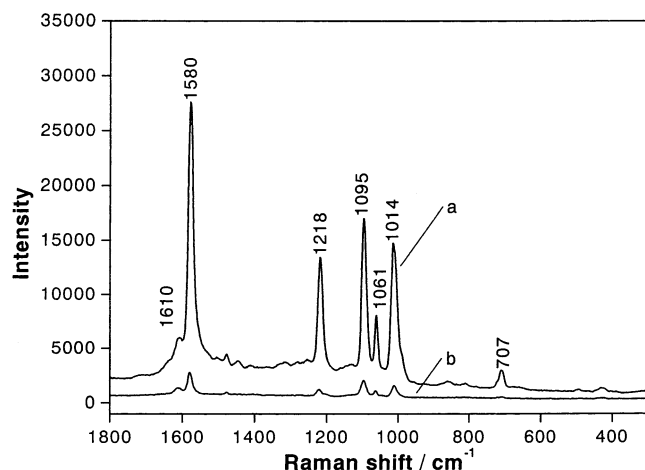


Figure 5. SERS spectra of 4MPY obtained from (a) the silver particle films and (b) the silver colloids. The laser power on the silver particle films was $40\ \mu\text{W}$, while that on silver colloids was about 10 times higher (the laser power on the sample stage was about $4.0\ \text{mW}$, and with penetration through the capillary wall and focusing on the silver colloids, it was estimated to decrease by about 10 times). The concentrations of 4MPY in the silver colloids and in those for forming the silver particle films were both $1 \times 10^{-5}\ \text{mol/L}$.

enhancement of N analyte-covered colloidal particles forming a fractal cluster will be greatly enhanced over the equivalent number of analyte-covered independent colloid particles.³³ In the following section, we will further discuss the effect of the increase in the number of probed molecules on the SERS through the comparison of Raman signals from the silver particle films with those from a silver mirror.

Figure 5a,b compares the SERS spectrum of 4MPY obtained from the silver particle films (the same spectrum as that in Figure 4a) with that of 4MPY on a silver colloid substrate. The SERS spectrum from the silver colloids was measured by using a capillary as the sampling device. Note that even if the excitation laser power is lowered by about 10 times, the Raman signals from the silver particle films are much stronger (Figure 5a). When the silver colloids with $1 \times 10^{-5}\ \text{mol/L}$ of 4MPY generate silver particle films, the number of probed molecules is significantly increased compared to that in the silver colloids. This may be one of the reasons for the enormously enhanced SERS signals observed from silver particle films. In our previous study, to compare the enhancement ability of the silver particle films with that of silver colloids,²⁶ we tried to eliminate the influence of the number of probed molecules. We adjusted the number of probed molecules on the silver particle films trapped at an air–water interface and in the silver colloids so as to be of the same order. Under these conditions and also with a weaker laser power by about 10 times, the SERS signals from the silver particle films and the silver colloids are nearly equal. These results revealed that the enhancing ability of the silver particle films trapped at the air–water interface is higher by about 10 times than that of silver colloids since the intensity of Raman signals is proportional to the laser power. The present silver particle films supported on the glass slide may behave in the same way. Although these two kinds of silver particle films are formed by different methods, both are formed from silver clusters and therefore should have similar SERS enhancement ability. As we discussed previously, their enormously enhancing

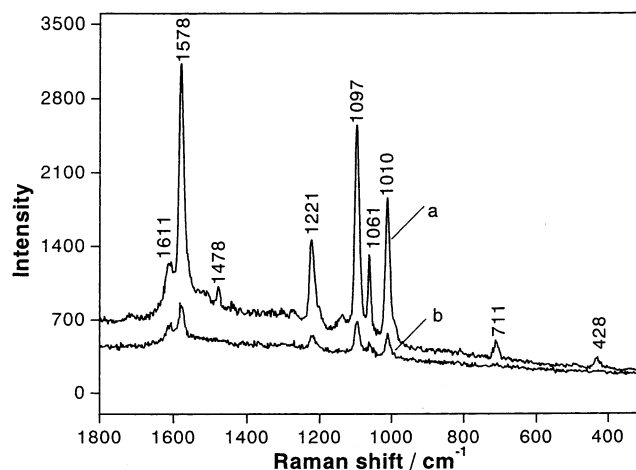


Figure 6. SERS spectra of 4MPY obtained from a silver mirror with a laser power of $40\ \mu\text{W}$ and integration time of 10 s: (a) with and (b) without the coadsorbed chloride.

ability is then understood to be even greater field enhancement that originates from electromagnetic interactions among the constituent small metal particles.³³

When aqueous metal colloid systems are used as SERS substrates, clusters with different sizes move out of and into the probed range of the laser as a result of Brownian motion. This may give the ensemble average of the SERS signals from the clusters with different SERS enhancement abilities and may be one of the reasons for the irreproducibility of SERS spectra. Moreover, aggregation is irreversible; once occurring, the aggregated clusters will become larger and larger and finally be deposited from the solution. By immobilizing the silver clusters on the glass slide, we can directly focus the laser beam on the silver clusters to get the strongest SERS signals.

Comparison of Enhancing Ability between Silver Particle Films and a Silver Mirror. A silver mirror is a type of silver film formed by randomly depositing chemically reduced silver particles on a glass slide, which exhibits excellent SERS enhancement.⁷ The AFM image (Figure 3d) shows that the particles in the silver mirror are closely packed. To evaluate the enhancement ability of the silver particle films, we compare a SERS spectrum from the silver particle films with that from the silver mirror. Since coadsorbed chloride ions are commonly used as preaggregation agents for additional enhancement in the metal colloid systems, here we investigate the effect of chloride ions on SERS spectra from the silver mirror. Figure 6a,b compares the SERS spectra of 4MPY on the silver mirror with and without coadsorbed chloride ions. Note that with coadsorbed chloride ions, the relative intensities of the weaker peaks at 1611 , 1578 , 1221 , 1097 , 1061 , and $1010\ \text{cm}^{-1}$ in Figure 6b are significantly increased and three “new” peaks appear at 1478 , 711 , and $428\ \text{cm}^{-1}$ in Figure 6a. As described in the Experimental Section, the comparison was made for the same mirror and for the same spot that showed higher enhancement than any other places. The spot was selected with the aid of the microscope of the Raman instrument. Moreover, 4MPY binds tightly to the silver surface through a covalent S–Ag bond,²⁸ so that the number of adsorbed molecules would be little changed after the immersion of the silver mirror in a NaCl solution. Therefore, the only difference between the spectra in parts a and b of Figure 6 is the presence or absence of the coadsorbed chloride ions. Accordingly, the additional enhancement in the spectrum in Figure 6a should largely arise from the coadsorbed chloride ions. The particles on the silver mirror are packed

(33) Stockman, M. I.; Shalae, V. M.; Moskovits, M.; Botet, R.; George, T. F. *Phys. Rev. B* **1992**, *46*, 2821.

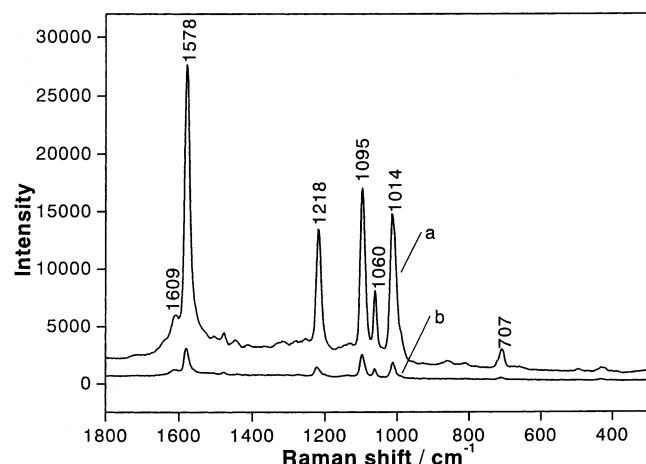


Figure 7. SERS spectra of 4MPY obtained from (a) silver particle films and (b) the silver mirror with coadsorbed chloride ions. The concentration of 4MPY in the silver colloids for forming the silver particle films was 1×10^{-5} mol/L, and a 1×10^{-4} mol/L solution of 4MPY was used for the dipping of the silver mirror. The laser power was $40 \mu\text{W}$ for both substrates with an integration time of 10 s.

tightly, and so surface morphology is not likely to be changed by the coadsorbed chloride ions as much as it is with metal colloids where aggregation of silver colloids shows a characteristic red-shifted peak in the UV-vis spectrum. This means that the coadsorbed chloride ions on the silver mirror cannot move the surface plasmon peak of the latter dramatically. If the present additional enhancement for 514.5 nm excitation is originating from an “electromagnetic mechanism”, that is, the 514.5 nm incident light is in resonance with the surface plasmon, then the 1064 nm laser line would not excite the surface plasmon and we could not obtain additional enhancement. However, when we changed the 514.5 nm excitation to the 1064 nm, we measured additional enhanced Raman signals from the mirror with chloride ions. Therefore, the additional enhancement may be due to a “chemical mechanism”. This activation may occur either by generating unique “SERS-active sites” or by stabilizing the chemisorbed molecules.^{34,35}

Figure 7a,b shows the SERS spectra of 4MPY on silver particle films and a silver mirror with the coadsorbed chloride ions, respectively. The AFM images of the silver

mirror and the silver particle films (Figure 3, parts d and a) reveal that the average particle size of the silver mirror is a little larger than that of the silver colloids. Consequently, a 1×10^{-4} mol/L 4MPY solution was used to prepare the silver mirror sample, while the concentration of 4MPY in the silver colloids for generating the silver particle films was 1×10^{-5} mol/L. Under these conditions, the number of probed molecules in the laser spot on the silver mirror is comparable to or even more than that on the silver particle films. With the same excitation laser power ($40 \mu\text{W}$) and integration time (10 s), the SERS signals from the silver particle films (Figure 7a) are about 10 times higher than those from the silver mirror (Figure 7b). As a result, we conclude that the enhancement ability of silver particle films supported on a glass slide is at least 1 order larger than that of a typical silver mirror substrate. This result is consistent with our previous results for the silver particle films trapped at an air-water interface.²⁶ In our previous study, we found that the SERS enhancement ability of the silver particle films is larger by 1–2 orders than that of the usual active silver substrates.

Conclusions

This paper has demonstrated that the process of drying silver colloids in a thin water film on a glass slide provides a simple method of preparing silver particle films. These silver particle films, in fact, silver clusters, are generated from the aggregation of silver colloids emerging in the thin water films. With the evaporation of water, silver clusters are left on the solid substrate. Thus, the problems of instability and poor reproducibility of silver colloids often encountered as SERS-active substrates can be largely overcome. Combining the aggregated characteristics of silver colloids with the stability of solidlike SERS-active substrates, the silver particle films exhibit excellent enhancement ability and thus are very suitable as SERS-active substrates. Moreover, as we have shown here, the silver particle films can be prepared very easily. The present study also reveals that coadsorbed chloride ions can function as active reagents on silver mirrors as well as in silver colloids.

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(34) Hildebrandt, P.; Stockburger, M. *J. Phys. Chem.* **1984**, *88*, 5935.

(35) Schneider, S.; Grau, H.; Halbig, P.; Freunscht, P.; Nickel, U. *J. Raman Spectrosc.* **1995**, *27*, 57.