Adjustment and control of SERS activity of metal substrates by pressure

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Metal pellets of silver and copper for surface-enhanced Raman scattering (SERS) spectroscopy were prepared by compression with different pressures. It was found that the SERS activity of the pellet could be controlled by pressure. Enhanced Raman scattering properties of the metal pellets in the presence of adsorbed 4-mercaptobenzoic acid (4-MBA) with excitation at 632.8 or 514 nm could be obtained by choosing proper pressure of pelletization. The SERS peak intensity of the band at ~1584 cm−1 of 4-MBA adsorbed on the metal pellets varies as a function of applied pressure, and which is about 1.2–32 times greater when it is adsorbed on silver and copper particles. The calculated results of three-dimensional finite-difference time-domain method (3D-FDTD) are in good agreement with the experimental data. Moreover, no spurious peaks appear in the SERS spectra when it is adsorbed on silver and copper particles. The calculated results of three-dimensional finite-difference time-domain method (3D-FDTD) are in good agreement with the experimental data. Moreover, no spurious peaks appear in the SERS spectra when it is adsorbed on silver and copper particles. The calculated results of three-dimensional finite-difference time-domain method (3D-FDTD) are in good agreement with the experimental data. Moreover, no spurious peaks appear in the SERS spectra when it is adsorbed on silver and copper particles. The calculated results of three-dimensional finite-difference time-domain method (3D-FDTD) are in good agreement with the experimental data. Moreover, no spurious peaks appear in the SERS spectra when it is adsorbed on silver and copper particles. Therefore, by controlling the pressure, the SERS activity of metal pellets can be adjusted. This provides a convenient and effective method to adjust the SERS activity of metal pellets, which opens a new way to control the SERS activity of metallic nanoparticles. In the future, this method can be applied in the preparation of SERS-active substrates for analytical purposes.

Keywords: pressure-dependent activity; metal substrate; surface-enhanced Raman scattering spectroscopy; 4-mercaptobenzoic acid; FDTD method

Introduction

Since the discovery of surface-enhanced Raman scattering (SERS),1–3 the optical properties of metal–molecule complexes have attracted considerable interest.4–8 Molecules adsorbed onto roughened Ag and Au surfaces or nanostructured Ag and Au colloids produce a millionfold increase in the intensity of Raman,8,9 absorption,10–12 and fluorescence emission.7,13,14 Recently, it has been reported that even single-molecule spectroscopy can be performed by SERS, suggesting that the enhancement factor (EF) can reach as high as 1014–1015.15–19 Second-harmonic generation at the silver–air interface is also enhanced by surface roughness and it is accompanied by a broad luminescence background extending far beyond the anti-Stokes side of the second harmonic.20 In addition, nonlinear Raman scattering, i.e. hyper-Raman scattering, and two-photon excited luminescence of dye molecules–silver colloidal aggregate complexes are facilitated by the surface-enhancement effect.21 It is commonly agreed that all these phenomena are caused by a strongly enhanced electric field in the vicinity of the metal structure via the excitation of resonant surface-plasmon modes.4–8,16–18,22

To use SERS in routine in situ studies for analytical purposes, the substrates should be stable, reproducibly prepared, inexpensive, and easy to make.23–25 In reality, the enhancement properties of an SERS-active surface are highly correlated to its method of preparation and its nanostructure. Vacuum-evaporated metal island films should be prepared with the evaporation rate and mass thickness of the corresponding metals controlled to obtain the SERS enhancement,26,27 but it always needs expensive and specialized apparatus.28 Optically tunable SERS-active Ag films can be fabricated on glass by the thermal decomposition of layered silver alkane carboxylates under inert conditions,29 but it nonetheless needs fine control of the size of the powdered salt prior to thermal treatment. The extent of aggregation of colloidal sols is difficult to control,30 and the sedimentation of aggregated sols onto solid substrates is not reproducible.31 Nimmo et al.32 reported that Raman scattering signals of some colored compounds could be reliably measured when small amounts of the compounds were diluted in a large excess of silver powder and the mixtures were prepared as compacted discs by using a pressure of 10 tons. Later, Yang and Zhang33 applied the method to measure SERS signals of some humic samples for environmental analysis. The preparation of metal substrates is the prime consideration to obtain the best SERS signals. For certain applications, it is highly desirable to prepare high SERS-active substrates, the activity of which can be easily adjusted and controlled.

In this paper, we report a pelletization method to prepare activity-tunable substrates, which is very simple. The results show

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that SERS activity of the metal pellet varies with the pressure used to make it. Since no chemical process is involved in the preparation of the metal pellets using a hydraulic press, this must be advantageous in preparing chemically pure SERS-active substrates. Moreover, by controlling the required pressure, the as-obtained metal pellets show enhanced Raman scattering in the presence of adsorbed 4-mercaptobenzoic acid (4-MBA) with excitation at 632.8 or 514 nm. The SERS peak intensity of the 4-MBA band at ∼1584 cm⁻¹ adsorbed on the metal pellets varies as a function of the applied pressure, and is about 1.2–32 times greater than when it is adsorbed on Ag and Cu particles. As a result, the SERS-active metal pellets can be produced by a simple and cost-effective method, and is expected to play an important role in the development of SERS-based analytical devices.

Experimental
Materials
The silver powder (99.9 ± %) and copper powder (99.9 ± %) with a particle size of 2.0–3.5 µm were purchased from Aldrich and used as received. 4-MBA, silver nitrate (> 99.8%), ammonia solution (28.0–30.0 wt%), potassium hydroxide (≥ 82%), ethanol (99.9%), and glucose used were of reagent grade, and were used without further purification. Highly pure water with a resistivity higher than 18.0 MΩ·cm was used in all the preparations.

Preparation of the activity-tunable pellets
Potassium hydroxide aqueous solution (2.6 wt%, 0.2 ml) was mixed with silver nitrate aqueous solution (2 wt%, 3 ml) to form a fine brown precipitate of Ag₂O. An aqueous ammonia solution (8 wt%) was added to the above mixture drop by drop until the precipitate completely dissolved to form [Ag(NH₃)₂]⁺. Then silver nitrate aqueous solution was added to the mixture until the solution became pale brown/yellow. When one drop of ammonia solution (2 wt%) was added to the solution and the solution became transparent again, further addition of ammonia solution to the mixture is stopped.[34] Subsequently, the above [Ag(NH₃)₂]⁺ solution was put into a polypropylene container with continuous magnetic stirring and kept for 5 min. Then, glucose aqueous solution (1 ml, 35 wt%) and pure ethanol (0.5 ml) were added to this mixture. This mixture was kept at 35 °C in a water bath for 1 h. The silver powder was finally washed with water and ethanol, and then dried at room temperature under vacuum for 4 h. In order to adsorb 4-MBA on Ag or Cu powder, the respective powders (0.4500 g) were immersed in an ethanol solution of 4-MBA (18 ml, 1 mmol l⁻¹) for 1 h. After thoroughly washing with water and ethanol to remove the excess reactants, the products were dried at room temperature under vacuum for 4 h. Subsequently, Ag (0.050 g) and Cu (0.0425 g) powders with the adsorbed 4-MBA were weighed and then introduced into a chamber of a pressure press (Shimadzu Corporation, Japan) used for preparation of KBr pellets for IR spectroscopy, its pressure ranging from 0 to 1000 kgf cm⁻². Pressures of 50, 100, 300, or 500 kgf cm⁻² were applied and maintained for 2 min. In this way, metal pellets with a diameter of 12.7 mm were obtained.

Characterization
Raman spectra were obtained with a Renishaw inVia micro-Raman spectroscopy system. Laser radiation of 632.8 or 514 nm was used for excitation. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer. Scanning electron microscope (SEM) images of samples were recorded by using an S-570 SEM operating at 15.00 kV. The thickness of the metal pellets was measured three times by a screw micrometer.

Theoretical simulations
The three-dimensional finite-difference time-domain (3D-FDTD) method was used for the theoretical simulation of the local electric field on the particles (the diameter of the silver particle is fixed at 200 nm). In the FDTD method, the space containing the simulated model is discretized using elements called ‘yee cells’. [35] The yee cell size was 2 nm × 2 nm × 2 nm, and the total number of time steps was 6000 to ensure convergence, which could be judged by checking whether the near-zone electric field values had reached a steady state. The amplitude of the sinusoidal plane wave was set at 1 V m⁻¹ in the calculation, and the excitation wavelengths were 632.8 nm and 514.5 nm, respectively.

Results and Discussion
Micrometer-sized Ag (µAg) powders are very efficient substrates for both the infrared and Raman spectroscopic characterization of molecular adsorbates assembled on silver. In particular, the Raman spectrum of organic monolayers on µAg powders is an SERS spectrum.[36,37] For this reason, we chose commercially available µAg powders to prepare activity-tunable pellets by controlling the pelletizing pressure.

The morphologies of the metal pellets are shown in Fig. 1. It can be clearly seen from the images of the metal pellets that the morphologies and the distances between particles vary with pressure. The distances between the particles decrease with increase in pressure. The higher the pressure applied, the more planar were the morphologies of the particles. The thickness of the metal pellets composed of the µAg powder is 0.060 ± 0.003, 0.055 ± 0.001, 0.052 ± 0.004, and 0.040 ± 0.004 mm when the applied pressure is 50, 100, 300, and 500 kgf cm⁻², respectively.

The SERS activity of the metal pellets was evaluated by using 4-MBA as the probing adsorbate, and their SERS activity was compared with that of the µAg powders with excitation at 632.8 nm. All the peaks in Fig. 2a can be attributed to 4-MBA adsorbed on silver substrates. The strong Raman signal at about 1584 cm⁻¹ arises from ν₁₄, aromatic-ring vibrations,[158] and the Raman band at about 1077 cm⁻¹ is due to ν¹₂ aromatic-ring vibrations possessing C–S stretching characteristics.[158] Moreover, the relative intensity ratios are nearly the same for the metal pellets prepared at different pressures and µAg powder.

Surprisingly, the SERS peak intensity of the ∼1584 cm⁻¹ band of 4-MBA adsorbed on the metal pellets prepared by 50, 100, 300, and 500 kgf cm⁻² of pressure, respectively, In Fig. 2b is about 2–7 times greater than when it is adsorbed on the µAg powder by using 632.8 nm radiation as excitation source. This suggests that the metal pellets not only have the merit of ease of use but also give enhanced SERS signals. As shown in Fig. 2b, the SERS peak intensity of the ∼1584 cm⁻¹ band of 4-MBA adsorbed on metal pellets varies as a function of the applied pressure, which indicates that the SERS activity of the metal pellets can be easily adjusted and controlled by pressure. It is found that the SERS peak intensity of the ∼1584 cm⁻¹ band of 4-MBA adsorbed on the metal pellet prepared by 100 kgf cm⁻² of pressure shows the maximum value; it then decreases...
Figure 1. SEM images of the metal pellets composed of μAg powder made with (a) 50, (b) 100, (c) 300, and (d) 500 kgf cm$^{-2}$ pressure, respectively.

with further increase of the pressure from 100 to 500 kgf cm$^{-2}$. This phenomenon can be attributed to the different gaps among the particles, the change of the number of effective gaps, the different numbers of adsorbates irradiated by the laser light, and different morphologies of the particles. It is well known that the crevices or gaps between two or three particles in contact with one another are hot sites for the induction of SERS via an electromagnetic enhancement mechanism.[19,39] For a gap of 1 nm between two Ag spheres with the diameter of 90 nm, the EF was estimated to be $\sim 10^{10}$ in a volume that could contain only a few molecules.[18] When two particles approach each other, their transition dipoles are expected to couple in such a way that the enhanced electromagnetic fields around each particle can create a pattern of coherent interference. When the gaps among the particles decrease with the increase in pressure, the coupled plasmon resonance shifts to red and the enhanced electromagnetic field increases at the junction of the particles.[40] Moreover, the numbers of effective gaps will also increase along with the decrease of the gaps. In addition, the signal increase observed is thought to occur likely from the increase in the number of adsorbates irradiated by the laser light. Because the gaps among the particles in the metal pellets prepared by using a hydraulic press are smaller than those of μAg powders in a man-pressure accumulation, the SERS peak intensities of the $\sim 1584$ cm$^{-1}$ band of 4-MBA adsorbed on the metal pellets decreases when the applied pressure is varied from 100 to 500 kgf cm$^{-2}$. This indicates that the gaps among the particles predominates the electromagnetic enhancement when the applied pressure is below 100 kgf cm$^{-2}$, while the particle morphology of the metal pellets plays the important role in the case of the pressure varied from 100 to 500 kgf cm$^{-2}$. Another reason (that the SERS peak intensity of the $\sim 1584$ cm$^{-1}$ band of 4-MBA adsorbed on the metal pellets decreases when the pressure is varied from 100 to 500 kgf cm$^{-2}$) may be from the tunneling charge transfer (TCT) between particles,[42–44] since the excitation of particle plasmon emission by tunneling electrons could decrease the enhancement of SERS when the gap among the particles was decreased to below 1 nm. With charge difference density,[45] the phenomenon of TCT has been clearly visualized in metal–molecule–metal junctions when the gap is below 1 nm.[42] When the applied pressure is large enough, the particles will be flattened and connected to each other (the distance of gaps is 0 nm), and the number of effective gaps will decrease, which will also decrease the lightning rod effect and decrease the intensity of SERS spectroscopy.

To account for the change of electromagnetic enhancement qualitatively in our experiments, we use the 3D-FDTD method to calculate the electromagnetic field distribution around the illuminated particles by numerically solving Maxwell’s equations. We built a model with three particles with different distances...
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Figure 2. (a) SERS spectra of 4-MBA adsorbed on the μAg powder and on metal pellets composed of μAg powder made with 50, 100, 300, and 500 kgf cm\(^{-2}\) pressure, respectively using 632.8 nm radiation as an excitation source. (b) The normalized SERS peak intensity of the ∼1584 cm\(^{-1}\) band of 4-MBA adsorbed on the metal pellets composed of μAg powder and μAg powder using 632.8 nm radiation as an excitation source.

between them in order to simulate quantitatively our experiments. The calculated results can be seen in Figs. 3a–g. The distances between the particles are 100, 60, 30, 10, and 2 nm, which correspond to the surface of particles from being slightly connected to strongly connected to each other in the form of a new larger particle, respectively. The 632.8-nm laser, irradiated perpendicularly to the surface plane, has the electric field vector as indicated in Fig. 3h. The pressure-dependent SERS enhancement according to the calculation at the incident light of 632.8 nm can be seen in Fig. 3i. The calculated data show that the maximum field enhancement at the junction of particles is about 76 when the gap is 2 nm for case (e), corresponding to 3.3 × 10\(^7\) SERS enhancement. When the distance between the particles is 100 nm, there is no coupling among the particles, and electromagnetic enhancements are contributed by the isolated particles. With the decrease of distance among the particles, the coupling effect of electromagnetic will be gradually enhanced for cases (b)–(d). When the surfaces of particles are slightly connected to each other (f), the electromagnetic enhancement will be decreased compared to that for case (e). Furthermore, when the surfaces of particles are strongly connected to each other as a new larger particle, the electromagnetic enhancement will be further decreased. Our qualitatively calculated results support strongly the experimental observations. It has been pointed out that when particles approach each other, the electromagnetic theory predicts that a coherent interference of the enhanced field around each particle will result in a dramatic increase in the electric field at the junction between them. Accordingly, the calculated electromagnetic field is highly localized at the junction of three particles, as shown in Fig. 3. It can be seen clearly that the magnitude of the electric field reaches a maximum in the gap region of the trimer. Since the SERS signal obtained in the experiment should average over all the surfaces, therefore, the enhancement obtained in the experiment may be substantially lower than the calculated value. To study the SERS enhancement for the fabricated structures as a function of the excitation wavelength, we also qualitatively described pressure-dependent SERS enhancement at the incident light of 514 nm by the model calculations, as shown in Fig. 3j. Comparing Fig. 3i with Fig. 3j, the qualitative tendencies of the pressure-dependent SERS enhancement are the same at the incident light of 632.8 and 514 nm.

In order to examine the universality of the method which can be used to prepare activity-tunable substrates for SERS spectroscopy, we also chose silver nanoparticles prepared by the well-known mirror reaction\(^{[46]}\) and commercially available 2-μm-sized copper (μCu) powder to prepare metal pellets (Fig. 4). The experimental results were similar to those the μAg powder. Silver nanoparticles prepared by the well-known mirror reaction with a size range of 300 to 600 nm were used to prepare metal pellets, and the thickness of the metal pellets obtained was 0.075 ± 0.006, 0.063 ± 0.003, 0.050 ± 0.003, and 0.048 ± 0.001 mm for 50, 100, 300, and 500 kgf cm\(^{-2}\) pressure, respectively. The SERS peak intensity of the ∼1584 cm\(^{-1}\) band of 4-MBA adsorbed on the metal pellets composed of silver nanoparticles varies as a function of the applied pressure and is about 1.7–32 times greater than when it is adsorbed on the original silver nanoparticles by using 632.8 nm radiation as the excitation source. The maximum value of the SERS peak intensity appears at 100 kgf cm\(^{-2}\) pressure, and it then decreases with the increase of the pressure from 100 to 500 kg fcm\(^{-2}\). For comparison between the metal pellets and silver nanoparticle films coated on a dielectric support, silver nanoparticle films were also prepared on a borosilicate cover glass (diameter = 12 mm, Deckglaser) by the well-known mirror reaction.\(^{[46]}\) Initially, the cover glass was soaked in a piranha solution [30% H\(_2\)O\(_2\); 98% H\(_2\)SO\(_4\) (1:3)] for 30 min and then sonicated in distilled water for 10 min, followed by rinsing with ethanol, and then finally dried in an oven at 70 °C for 20 min. The cleaned glass was dipped in the reaction mixture and incubated for 1 h at 35 °C with vigorous stirring. The silver-coated glass substrate was finally rinsed with ethanol and dried in air. The size of the silver nanoparticles coated on the glass substrate is in range of 300 to 600 nm and the particles are approximately spheroidal.\(^{[37,46]}\) Subsequently, we measured the relative SERS signals of 4-MBA molecules adsorbed on the silver nanoparticles coated on a glass substrate under the same experimental condition. The SERS peak intensity of the ∼1584 cm\(^{-1}\) band of 4-MBA adsorbed on the metal pellets composed of the silver nanoparticles varies as a function of the applied pressure, and which is about 8–259 times greater than when it is adsorbed on the silver nanoparticle films coated on a glass substrate by using 632.8 nm radiation as the excitation source. When μCu powder, which has very low SERS activity,\(^{[47]}\) was used to prepare metal pellets, the thickness of the metal pellets was 0.082 ± 0.003, 0.062 ± 0.001, 0.060 ± 0.003, and 0.048 ± 0.006 mm with 50, 100, 300, and 500 kgf cm\(^{-2}\) pressure, respectively. The
SERS peak intensity of the $\sim 1584$ cm$^{-1}$ band of 4-MBA changes as a function of applied pressure. The maximum value of the SERS peak intensity appears at 300 kgf cm$^{-2}$ of pressure, and this value is about 26 times greater than when it is adsorbed on the $\mu$Cu powder, using 632.8 nm radiation as an excitation source. This indicates that the method of preparing activity-tunable substrates by pressure for SERS spectroscopy is applicable over a wide range.

We explored the SERS effect for 4-MBA adsorbed on the metal pellets composed of $\mu$Ag powder and $\mu$Ag powder by comparing the results with 514.5 and 632.8 nm laser excitation. The spectra using 514 nm radiation as an excitation source are little different from those using 632.8 nm radiation as an excitation source; the strong Raman signal arising from $\nu_{8a}$ aromatic-ring vibrations shifts from 1584 to 1586 cm$^{-1}$.[38] Although the SERS peak intensities of the $\sim 1586$ cm$^{-1}$ band of 4-MBA were smaller when using 514 nm radiation as an excitation source than those excited with 632.8 nm, the SERS activity also varied as a function of applied pressure. For 514-nm excitation, a maximum value of the SERS peak intensity also appears at 100 kgf cm$^{-2}$ pressure, and then decreases with the increase of pressure from 100 to 500 kgf cm$^{-2}$ in Fig. 5. This is similar to the case with 632.8 nm.

To verify whether the substrate itself becomes more SERS-active simply by the applied pressure, we checked the SERS effect after adsorbing 4-MBA following the application of pressure for $\mu$Ag powder using both 632.8 and 514 nm radiation as excitation sources. The SERS spectra of 4-MBA are collectively shown in Fig. 6. Compared to those excited with 632.8 nm in Fig. 6a, the SERS peak intensities when using 514 nm radiation as excitation source in Fig. 6b are smaller, and the peak positions from aromatic-ring vibrations shift slightly from 1584 and 1077 cm$^{-1}$ to 1589 and 1079 cm$^{-1}$, respectively. In any case, it is worth mentioning that the SERS activity still varies as a function of the applied pressure, and the pelletized substrates can be claimed to be highly SERS active. The maximum value of the SERS peak intensity appears at 50 kgf cm$^{-2}$ pressure, and then decreases with the increase of the pressure from 50 to 500 kgf cm$^{-2}$ when using both 632.8 and 514 nm radiation as excitation sources in Figs 6c and d. The SERS peak intensity of the $\nu_{8a}$ aromatic-ring vibrations of 4-MBA adsorbed on the metal pellets composed of $\mu$Ag powder is about 4.6–12 or 1.5–3.9 times greater than when it is adsorbed on the $\mu$Ag powder by using 632.8 or 514 nm radiation as excitation source, respectively.

We attempted to estimate the SERS EF using the following equation:

$$ EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{NR}}/N_{\text{NR}}} $$

where $I_{\text{SERS}}$ denotes the SERS intensity of the $\nu_{8a}$ band of 4-MBA adsorbed on the metal pellets composed of $\mu$Ag powder with a 50, 100, 300, and 500 kgf cm$^{-2}$ pressure, respectively, using 632.8 nm radiation as the excitation source, $I_{\text{NR}}$ denotes the normal Raman (NR) scattering intensity of the same band of dry 4-MBA powder, and $N_{\text{SERS}}$ and $N_{\text{NR}}$ are the numbers of 4-MBA molecules effectively excited by the laser beam to obtain the corresponding SERS and NR.

Figure 3. The calculated electromagnetic enhancement for the cases (a)–(g): the distances between the particles are 100, 60, 30, 10, and 2 nm, the surface of particles being slightly connected and strongly connected to each other as a new larger particle, respectively. The 632.8-nm laser was irradiated perpendicular to the surface plane for the cases (a)–(g), and the electric field vector is indicated in (h). The strongest electromagnetic enhancements according to the calculation at the incident light of 632.8 nm and 514 nm can be seen in (i) and (j), respectively.

Figure 4. SERS peak intensity of the $\sim 1584$ cm$^{-1}$ band of 4-MBA changes as a function of applied pressure. The maximum value of the SERS peak intensity appears at 300 kgf cm$^{-2}$ of pressure, and this value is about 26 times greater than when it is adsorbed on the $\mu$Cu powder, using 632.8 nm radiation as an excitation source. This indicates that the method of preparing activity-tunable substrates by pressure for SERS spectroscopy is applicable over a wide range.
the density of 4-MBA was 1.5 g cm$^{-3}$ and the penetration depth ($\sim$ 6 µm) of the metal pellets occupied 75–98% of the total surface.

Excited by the laser beam was calculated to be 3 band of 4-MBA adsorbed on (a) the metal pellets composed of the silver nanoparticles and (b) on the metal pellets composed of µCu powder and on µCu powder using 632.8 nm radiation as an excitation source.

Figure 4. The normalized SERS peak intensity of the $\sim$ 1584 cm$^{-1}$ band of 4-MBA adsorbed on (a) the metal pellets composed of the silver nanoparticles and on silver nanoparticles, and (b) on the metal pellets composed of µCu powder and on µCu powder using 632.8 nm radiation as an excitation source.

Figure 5. The normalized SERS peak intensity of the $\sim$ 1586 cm$^{-1}$ band of 4-MBA adsorbed on the metal pellets composed of µAg powder and on µAg powder using 514 nm radiation as excitation source.

spectra, respectively. We assumed that the sampling volume from which the NR spectrum of dry 4-MBA powder in Fig. 7 was obtained was the product of the area of the laser spot ($\sim$ 2 µm in diameter) and the penetration depth ($\sim$ 2 µm) of the focused beam. Since the density of 4-MBA was 1.5 g cm$^{-3}$ and its molecular weight was 154.19 g mol$^{-1}$, the number of 4-MBA molecules effectively excited by the laser beam was calculated to be $3.68 \times 10^{10}$ (i.e. $6.11 \times 10^{-14}$ mol). On the other hand, the bonding density of 4-MBA molecules in a self-assembled monolayer is $\sim$ 0.5 nmol cm$^{-2}$.[48]

As can be seen in the SEM image in Fig. 1, the µAg particles in the metal pellets occupied 75–98% of the total surface coverage with 50–500 kgf cm$^{-2}$ of pressure. The total number of molecules sampled in the SERS experiments using the metal pellets composed of µAg powder as a substrate will be $7.09 \times 10^{6}$ (i.e. $1.18 \times 10^{-17}$ mol), $8.03 \times 10^{6}$ (i.e. $1.33 \times 10^{-17}$ mol), $8.51 \times 10^{6}$ (i.e. $1.41 \times 10^{-17}$ mol), and $9.26 \times 10^{6}$ (i.e. $1.54 \times 10^{-17}$ mol). In this estimation, we ignored the surface roughness of the samples. The intensity ratio of the $\nu_{28}$ aromatic-ring vibration bands in Fig. 7 was measured to be 244:286:134:95:1 and was taken using 632.8 nm radiation as the excitation source and normalized with respect to the absolute intensity from a silicon wafer. The EFs of the metal pellets composed of µAg powder with 50, 100, 300, and 500 kgf cm$^{-2}$ of pressure, estimated using 4-MBA as a probing adsorbate, reached $\sim$ 1.27 × 10$^{6}$, $\sim$ 1.31 × 10$^{6}$, $\sim$ 5.79 × 10$^{5}$, and $\sim$ 3.78 × 10$^{5}$, respectively. Their EF values are higher than the values of $\sim$ 2 × 10$^{5}$ and $\sim$ 2 × 10$^{4}$ for benzenethiol adsorbed on silver films prepared using butylamine as a reductant with particle sizes of 71 and 25 nm, respectively.[49] To extend the application of the activity-tunable pellets, we also estimated the EFs based on the SERS spectra of pyridine. The EFs of the metal pellets composed of µAg powders with 300 kgf cm$^{-2}$ of pressure and µAg powder, estimated using pyridine as a probing adsorbate and 514 nm radiation as an excitation source, reached $\sim$ 5.30 × 10$^{4}$ and $\sim$ 1.64 × 10$^{4}$, respectively.

It has to be emphasized that one of the valuable advantages of the method is that no chemical contaminations that could bring about spurious peaks and hinder the use of the SERS-active substrate for analytical purposes are involved in the process. Chemical contamination frequently affects the reproducibility of the SERS activity particularly when chemical adsorbates are used to control the extent of aggregation of colloidal particles.

Conclusions

We have presented a very simple pelletizing method to prepare activity-tunable substrates for SERS spectroscopy. The SERS activity of the substrates prepared by this method varies as a function of pressure. The metal pellets obtained show enhanced Raman scattering in the presence of adsorbed 4-MBA with excitation at 632.8 or 514 nm and also have the advantage of ease of use. Particularly, the preparation processes of the metal pellets do not use any chemicals, which could make the measurements free from interference of spurious peaks and suitable for analytical purposes. The method is easy to control, applicable over a wide range, and cost effective, and it is expected to facilitate the development of SERS-based analytical devices.

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Figure 6. SERS effect after adsorbing 4-MBA following application of pressure for µAg powder using both (a) 632.8 and (b) 514 nm radiation as excitation source. The normalized SERS peak intensity of the $\nu_{8a}$ aromatic-ring vibrations after adsorbing 4-MBA following the application of pressure for µAg powder using both (c) 632.8 and (d) 514 nm radiation as excitation source.

Figure 7. Raman spectrum of dry 4-MBA powder using 632.8 nm radiation as excitation source.

References

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