Surface-Enhanced Raman Scattering from Silver-Plated Porous Silicon

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Silver micro- and nanocrystallites are prepared on porous Si substrates by immersion plating, and their activity toward SERS (surface-enhanced Raman scattering) is assessed. Scanning electron microscopy reveals a rough silver film containing randomly spaced dendritic structures. SERS spectra of Rhodamine 6G (R6G) and adenine are obtained using an 18-mW, 488-nm laser. The SERS signal from these analytes is dramatically improved by pretreatment of the silver-plated porous Si samples (Ag−PS) with a 1 mM mineral acid solution. Detection of R6G and adenine from 1 nM solutions is demonstrated, corresponding to (at most) 9×10^5 molecules in the experimental configuration used in the current study. Ag−PS samples that have been stored in air for 10 days still display high sensitivity. The presence of chloride either in the analyte solution or in the pretreatment solution is found to dramatically reduce the limit of detection for R6G.

1. Introduction

Surface-enhanced Raman scattering (SERS) has been shown to be a useful tool for the definitive identification of small quantities of analytes. Although Raman spectroscopy is limited by extremely low scattering cross sections, the surface-enhancement effect can provide cross sections up to 14 orders of magnitude higher than normal Raman spectroscopy.[1−3] In some cases the enhancement is large enough to allow single molecule detection.[4−6] Since the Raman spectrum also yields structural information, SERS holds exciting possibilities for trace analysis in complex matrixes that are encountered in environmental and biomedical applications.[7] For example, the ability to detect and distinguish single DNA bases by SERS could be used for rapid DNA sequencing.[5,8] Compared with the widely used fluorescence labeling technique, Raman spectroscopy provides highly resolved vibrational information and does not suffer from photobleaching effects.[9,10]

There is a need for sensitive SERS substrates that can be stored for long periods of time. The most commonly used SERS-active substrates are aggregated Ag and Au colloids. However, the stability of the colloidal solution and reproducibility of aggregation are two major problems.[11,12] Another common substrate is a roughened metal electrode. Although these substrates are more stable than colloids, they are typically not as sensitive.[7] Metal films evaporated on solid substrates or through shadow masks have also been found to provide controllable and reproducible SERS substrates with promising results,[13−15] and recently it has been found that synthesis of Ag nanostructures inside porous Si templates yields SERS-active substrates.[16] These latter materials were prepared either by immersion plating of Ag within the pores of porous Si or by thermal decomposition of Ag nitrate in oxidized porous Si. It was found that Ag nanostructures formed by thermal decomposition in the oxidized films are superior to the immersion-plated films in that study.[16]

Herein, we report a method for producing a SERS-active substrate based on immersion plating of Ag on porous Si (Ag−PS), following the work of Chan et al. We find that, under the appropriate preparation conditions, roughened Ag films containing dendritic structures are produced, and these are highly SERS-active. Pretreatment with mineral acids is found to dramatically reduce background signals in the SERS spectrum. The substrates in the present work are found to be able to detect adenine at a concentration about 5 orders of magnitude lower than the previously reported porous Si-based substrates[16] and comparable to the detection limits observed from aggregated Ag colloids.[5,17] Additionally, it is found that the Ag−PS substrates stored for 10 days in air show no significant degradation in their sensitivity.

2. Experimental Section

Chemicals. Rhodamine 6G (98%), adenine (99%), and $AgNO_3$ (99.9999%) were purchased from Sigma-Aldrich Co. and used without further purification. Hydrochloric acid (36.5−38%) and sulfuric acid (95.0−98.0%) were purchased from EM Science, Inc., and ethanol (200 proof) was purchased from AAPER Alcohol. Water was distilled twice before use. All of the solutions used in the Ag deposition and analyte exposure experiments were prepared with a 1:1 (v:v) mixture of ethanol and water to allow better wetting of the silicon surface. The analyte solutions with different concentrations were prepared by successive dilution of stock solutions.

Preparation of Porous Silicon. The Si wafers used in this study were p-type, boron-doped, $<0.005\ \Omega\cdot$cm resistivity, ⟨100⟩ orientation, and $525 \pm 25\ \mu$m thick, obtained from Silicon Materials Inc. The wafers were cut into squares and placed in a Teflon etch cell using a piece of aluminum foil as a back contact and a small O-ring to seal the wafer to the cell, exposing an area of approximately 1.3 cm^2 to solution. The cell was filled with a 3:1 (v/v) mixture of 48% aqueous HF (Fisher Scientific, Inc.) and absolute ethanol. A platinum mesh was immersed in the solution as the counter electrode. An anodic current (100 mA) was passed between the electrodes for 30 s in the dark. The cell and sample were then washed with ethanol and

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dried under a stream of nitrogen. This preparation results in a 2-μm-thick mesoporous structure.[18]

Immersion Plating of Silver on Porous Si. In a typical preparation, approximately 2 mL of a 0.01 M $AgNO_3$ solution in 1:1 ethanol:water was added into the Teflon cell containing the freshly etched porous silicon sample for 5 min. After thoroughly rinsing with ethanol and water, the sample was dried under a stream of nitrogen and removed from the etching cell.

Acid Pretreatment of Ag−PS Samples. Samples designated as "acid pretreated" were rinsed with a solution of 1 mM HCl or H_2SO_4 in a 1:1 ethanol:water mixture for a few seconds. They were then thoroughly rinsed with ethanol and water and dried under a stream of nitrogen.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were obtained as secondary electron images with 20-keV electrons using a Cambridge (LEO) S360 electron microscope equipped with an Oxford energy-dispersive X-ray (EDS) analyzer.

Raman Spectroscopic Measurements. The Ag−PS sample was incubated in 10 mL of the analyte solution. The solvent for all the analytes used in this work was 1:1 water:ethanol. After incubation for a few (>2) hours, the sample was thoroughly rinsed with ethanol and water and dried in a stream of nitrogen. Raman spectra were obtained using a cooled Princeton Instruments CCD detector (1300 × 1030) mounted to a Spex 270M spectrometer. The high-resolution grating in the spectrometer (1200 grooves/mm) allowed acquisition of a spectral region ~25-nm wide at the desired wavelength. The samples were mounted under a Nikon Optiphot microscope equipped with a 50× DF/BF long working distance objective. Laser illumination was performed by focusing a 0.3 kW/cm^2 488-nm argon ion laser beam onto the top surface of the Ag film, at glancing incidence. The sample was brought into focus with the microscope and the Raman signal was passed through a 488-nm notch filter (~10^6 rejection, Omega Optics) to remove the scattered laser light. The microscope was also equipped with an adjustable image plane aperture, which was set at 500-μm diameter. After passing through the aperture, the Raman signal was re-focused onto the 200-μm slit of the spectrometer mounted above the microscope.

3. Results and Discussion

3.1. Preparation of Silver SERS Substrates by Immersion Plating on Porous Silicon. Exposure of porous silicon to solutions containing metal ions such as Ag^+, Au^+, Pd^{2+}, or Cu^{2+} leads to spontaneous deposition of the corresponding metal.[19−22] Under the conditions used in the present work, reduction of Ag by porous Si results in rough Ag films (Figure 1), according to eqs 1−3. The roughened Ag morphology is confirmed by scanning electron microscopy (SEM) and the elemental composition is confirmed by microprobe analysis (energy-dispersive X-ray spectroscopy, EDS). Au is also known to display a strong SERS enhancement effect and it is compatible with many biological applications.[8] However, under similar conditions, immersion plating with Au leads to a smooth film on the porous Si substrate that has no features larger than 20 nm and no observable SERS signal.

$$2Si_{(surface)} + H_2O \rightarrow Si{-}O{-}Si_{(surface)} + 2H^+_{(aq)} + 2e^- \quad (1)$$

$$2Si{-}H_{(surface)} + H_2O \rightarrow Si{-}O{-}Si_{(surface)} + 4H^+_{(aq)} + 4e^- \quad (2)$$

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)} \quad (3)$$

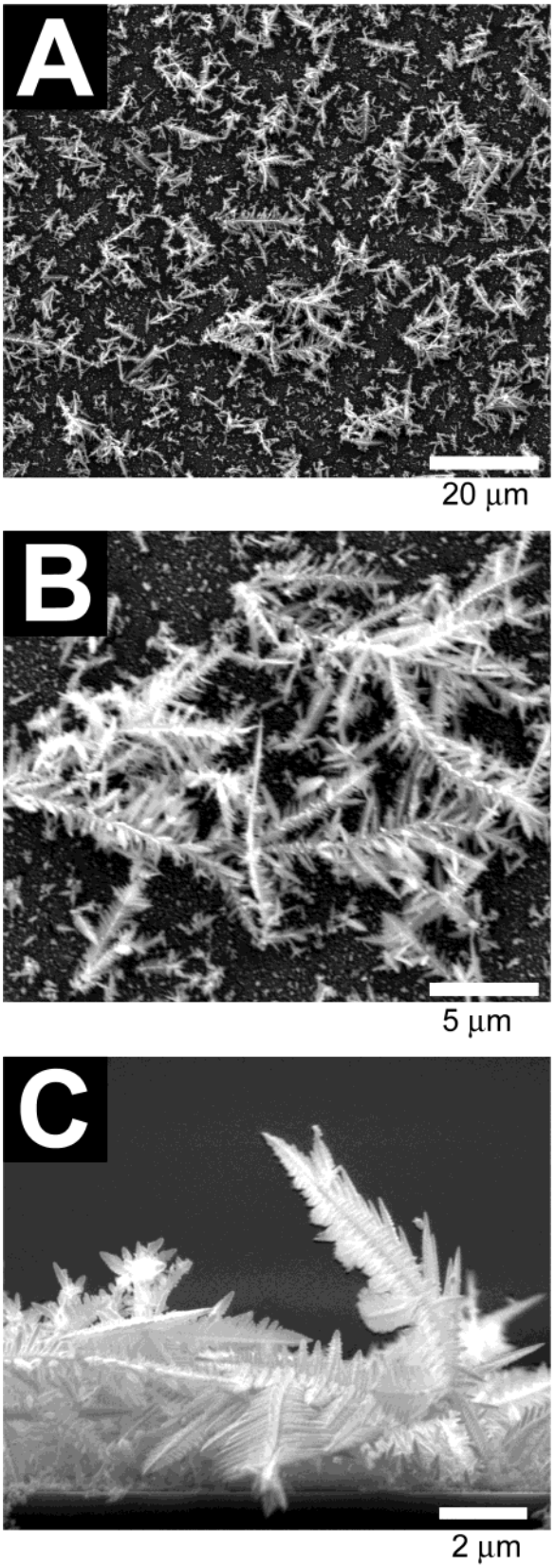

Figure 1. Scanning electron microscope (SEM) images of the Ag-coated samples (Ag−PS) used in this study. (A) Plan-view image representative of the surface. (B) Plan-view image showing the dendritic structure of the Ag deposit. (C) Cross-sectional image showing the Ag dendrites on top of the porous Si layer.

A local cell model has been proposed by Ogata and co-workers to explain metal deposition onto porous Si substrates during immersion plating.[23] In this reaction, oxidation of surface

silicon atoms and silicon hydride species (eqs 1 and 2, respectively) provides the reducing equivalents for $Ag^{+}_{(aq)}$. It is proposed that reduction and oxidation do not necessarily occur at the same physical location, allowing for nucleation and growth of Ag islands. The present results are consistent with the model of Ogata et al.[23] The simultaneous formation of SiO_2 and metallic Ag has been reported[23,24] and is confirmed in the present work by electron microprobe and infrared absorption measurements. Semiquantitative EDS measurements indicate about 10 atom % Ag is present on the Ag−PS substrates. In the literature there is a disagreement about whether hydrogen gas is evolved in the deposition reaction.[23,24] Some gas bubbles were observed during immersion plating in the present experiments, but the gas was not identified.

3.2. Morphology of Ag Deposited on Porous Si. The deposition of metal onto flat semiconductor surfaces follows a 3-D island (Volmer−Weber) growth mechanism due to a weak interaction energy between the adsorbed metal atom and the semicondutor.[25] Apparently, this mechanism applies to the porous Si system as well,[23] although the high surface area of porous Si provides a larger number of hydride-reducing equivalents. It is generally reported that immersion plating of metals on porous Si results in the formation of small metal particles.[23] In the present case, larger Ag dendrites are observed in addition to these small features. Figure 1A,B shows SEM plan view images of the Ag−PS samples representative of those prepared in the present study. Ag dendrites of dimensions in the micrometer range are randomly dispersed on top of a film with submicrometer features. The cross-sectional SEM image (Figure 1C) indicates that the entire Ag structure is about 4-μm thick. EDS measurements indicate that most of the Ag deposition occurs on the top of the porous Si layer, while only a very small amount of Ag appears inside the porous Si film, consistent with the previous observations of Chan et al.[16] If the porous Si sample is prepared using a lower etching current while keeping all the other reaction conditions the same, the resulting Ag structures appear as densely packed particles, similar to those previously reported.[23] Usually, lower etching currents produce smaller pores and a lower porosity in the porous Si substrates.[26] These results suggest that the morphology of the porous Si substrate determines the microstructure of the Ag deposits. The dendritic Ag structures of Figure 1 are observed with highly doped (<5 mΩ·cm) p-type porous Si substrates and relatively high current densities (>70 mA/cm^2) are used. Although a variety of approaches to synthesize dendritic Ag structures have been reported,[27−30] the present work represents the first example of the spontaneous synthesis of this morphology on a Si surface by immersion plating.

It has been reported that the enhancement of the Raman signal encountered in SERS arises mainly from so-called "hot" sites on the metal surface.[31−33] Theoretical calculations support the postulate that a large and spatially confined electromagnetic enhancement effect exists on sharp protrusions and sites between two particles in proximity.[34,35] Thus, the existence of many sharp protruding dendrites and the roughly corrugated underlying surface in the Ag−PS samples is expected to provide a highly SERS-active substrate.

3.3. Pretreatment of Ag−PS with Mineral Acids. The high surface area of Ag−PS leads to the adsorption of contaminants during preparation and storage. Spectra obtained from the as-formed Ag−PS films contain a large, slightly structured, and broad background emission signal (Figure 2). This background spectrum overwhelms the Raman signal from the analytes of interest, especially when they are at low concentrations. It was found that simply rinsing the as-formed Ag−PS samples with a mineral acid removes this background signal, resulting in a low and flat baseline (Figure 2). Rinsing for a few seconds with either sulfuric or hydrochloric acids at a concentration of 1 mM in a 1:1 (v:v) mixture of ethanol:water was found to be effective. The results represented by Figure 2 were reproduced >10 times on different samples. In some cases the SEM data indicate that some of the small branches of the Ag dendrites are removed during the rinse. However, there is no significant difference in the quality of the Raman spectra from these samples. Thus, even if some highly SERS-active sites are destroyed by the acid-rinsing step, apparently enough of them remain to provide substrates with high sensitivity. The acid rinsing step can be performed on Ag−PS samples that have been stored in air for several days with the same results.

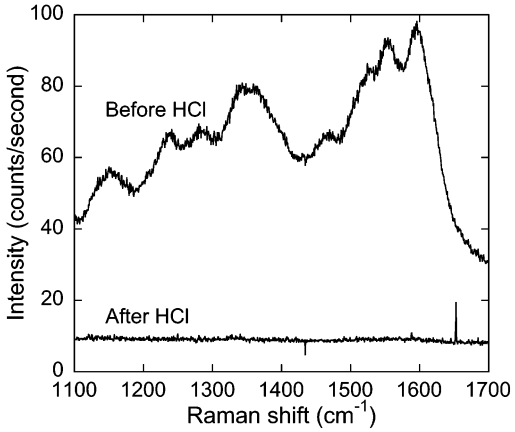

Figure 2. Background spectra obtained from Ag−PS before and after rinsing with 1 mM HCl solution. The integration time for both spectra is 20 s.

3.4. Surface-Enhanced Resonance Raman Scattering (SERRS) of Rhodamine 6G. Rhodamine 6G (R6G) was chosen as an analyte in the present study because it has been well-characterized by SERS and by resonance Raman spectroscopy. Most of the prominent Raman bands have been assigned,[36] and SERS spectra of single R6G molecules have been obtained.[4] The 488-nm line from an argon ion laser is used in the present study. This wavelength corresponds to a resonant excitation of R6G, so the surface-enhanced resonance Raman spectrum (SERRS) is acquired.[36] Although porous Si is known as a photoluminescent material,[37] the porous Si samples used in the present experiments are prepared from highly doped (boron) p-type silicon, which typically displays no detectable visible fluorescence. Thus, no background fluorescence was observed from the substrate in the SERS spectrum of the materials in this study.

Another complication often encountered in SERRS is fluorescence from the analyte, which can overwhelm a weak Raman signal. In the present experiments, no strong R6G florescence is observed in the SERRS spectra from the Ag−PS samples, except for the samples exposed to high concentration (≥ 100 nM) R6G solutions in the absence of chloride ion (see below, 2.5). This lack of a strong fluorescence background is somewhat unexpected, and experiments designed to understand this observation were performed. On Ag−PS samples there are three different types of surface: Ag, H-terminated porous Si, and oxidized porous Si. It is well-known that fluorescent molecules undergo efficient energy transfer quenching when in close proximity to metals such as Ag,[4] and so the fluorescence contribution from R6G molecules near or adsorbed to the Ag features is expected to be small. A control experiment in which

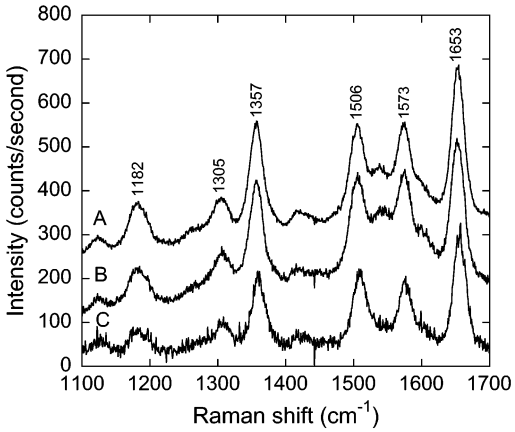

Figure 3. SERRS spectra of Ag−PS substrates after soaking in 1:1 water:ethanol solutions of Rhodamine 6G (R6G) containing 1 mM NaCl. (A) 100 nM R6G, 5-s spectral integration time; (B) 10 nM R6G, 15-s spectral integration time, multiplied by 5; (C) 1 nM R6G, 30-s spectral integration time, multiplied by 25. The Ag−PS samples used in this figure were pretreated with HCl. All annotated peaks can be assigned to R6G based on published spectra. Spectra are offset along the *y*-axis for clarity.

a freshly etched (H-terminated) porous Si sample is exposed to R6G and then the Raman spectrum is acquired shows neither a SERS spectrum nor any detectable fluorescence from R6G. Apparently, either the H-terminated surface efficiently quenches fluorescence from R6G or the dye does not efficiently bind to Si−H such that it is removed at the sample rinsing stage. If the porous Si substrates used in this study are thermally oxidized (600 °C, 30 min, in air) prior to exposure to R6G, an extremely strong fluorescence background from the analyte is observed. Since Si oxides are clearly present on the Ag−PS samples used in this study, it is interesting that fluorescence is not observed from the R6G molecules. Presumably R6G preferentially adsorbs to the Ag or Si−H surfaces, the Si oxide is formed in regions that are not accessible to the R6G molecules, or the oxide is thin enough that energy transfer quenching to the highly doped porous Si substrate or the Ag features still occurs.

The SERRS spectra of R6G at concentrations ranging between 1 and 100 nM are shown in Figure 3. The samples were prepared by first rinsing the Ag−PS wafer with a 1:1 (v:v) water:ethanol solution containing 1 mM HCl. After this pretreatment step, they were soaked in the analyte solution for a few (>2) hours. The solvent for all the analytes used in this work was 1:1 water:ethanol, to allow consistent wetting of the Ag−PS samples and reproducible measurements. Raman spectra obtained from analyte solutions consisting of 100% double-distilled water were not significantly different from those reported here. The samples were removed, rinsed with pure water and ethanol several times, and dried under a stream of nitrogen. A disposable plastic tube (Corning) was used for each of the incubation solutions. The Raman bands assignable to R6G based on published spectra[4,36] are quite evident (Figure 3). Control spectra, obtained from samples incubated in a 1:1 (v:v) mixture of double-distilled water and ethanol for the same period of time as the analyte samples, display no discernible features other than a weak, broad background.

3.5. Effect of Anions on the SERRS Spectrum of Rhodamine 6G. It has been noted that the presence of anions, especially halides, significantly increases the SERS intensity of R6G by factors of hundreds to thousands, though the mechanism is not well-understood.[4,11,38−40] This anion effect has been observed in the SERRS spectra both from roughened Ag electrodes[41] and from Ag colloids.[36] Presumably, Cl^-

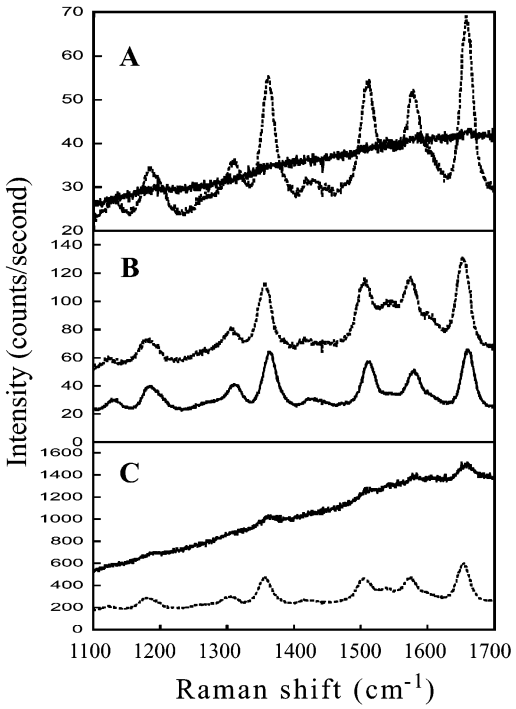

Figure 4. SERRS spectra of Rhodamine 6G (R6G) from Ag−PS substrates pretreated with different acids, showing the different effects of adding 1 mM NaCl into the R6G incubation solution. The solid lines represent spectra of Ag−PS substrates incubated in R6G solution without NaCl, and the dashed lines represent spectra of Ag−PS substrates incubated in R6G solution with 1 mM NaCl. (A) Ag−PS pretreated with 1 mM H_2SO_4, showing the strong enhancement of the Raman signal in the presence of 1 mM NaCl. The concentration of R6G is 10 nM, and the integration time for both spectra is 30 s. (B) Ag−PS pretreated with HCl showing that addition of 1 mM NaCl to the R6G solution has no significant influence on the Raman spectra obtained. The concentration of R6G is 10 nM, and the integration time is 15 s for the experiment with 1 mM NaCl added and 30 s for the experiment without added NaCl. (C) Ag−PS pretreated with HCl, but using a higher concentration of R6G (100 nM). The data show that addition of 1 mM NaCl significantly reduces background fluorescence from R6G. The integration time is 5 s for the experiment with 1 mM NaCl added and 2 s for the experiment without added NaCl.

adsorbs to the Ag surface, creating "active sites" for Raman enhancement. A similar enhancement is observed in the present study. Ag−PS samples pretreated with H_2SO_4 display a SERRS signal that increases by several orders of magnitude if NaCl is included in the analyte solution (Figure 4A), comparable to the previous reports.[36,40,41] If the acid used in pretreatment is HCl, it is not necessary to add NaCl to the analyte solution to obtain the large enhancement (Figure 4B). Thus, addition of NaCl to the analyte solution has no significant effect on the (already strong) Raman signal obtained from HCl-pretreated Ag−PS. Another distinct phenomenon observed with addition of NaCl is a quenching of the fluorescence background observed when high R6G concentrations are analyzed (Figure 4C, dashed line). In the absence of NaCl, fluorescence obscures the Raman spectrum from Ag−PS incubated with 100 nM R6G (Figure 4C, solid line). Other authors have suggested that the presence of Cl^- facilitates the interaction between Ag and R6G in a chemical configuration that quenches the R6G fluorescence.[40,42] The anion effect on the SERRS spectrum from Ag colloids has been attributed to aggregation of colloidal particles, resulting in increased electromagnetic enhancement.[11,39] This interpretation is probably not applicable in the present work or in the studies of roughened Ag electrodes[41] because in these cases the Ag structures are immobilized.

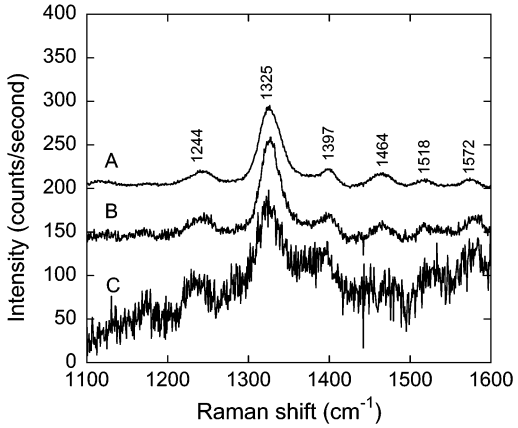

Figure 5. SERS spectra of adenine obtained from HCl-pretreated Ag−PS samples. (A) Sample incubated in 100 nM adenine, 20-s spectral integration time. (B) Sample incubated in 10 nM adenine, 30-s spectral integration time (intensity multiplied by 5). (C) Sample incubated in 1 nM adenine, 30-s spectral integration time (intensity multiplied by 20). All annotated peaks can be assigned to adenine based on published spectra. Spectra are offset along the *y*-axis for clarity.

3.6. Surface-Enhanced Raman Scattering of Adenine. One important potential application of SERS in the biophysical/biochemical and biomedical field is the rapid detection, quantification, and characterization of DNA and DNA fragments. Compared with the fluorescence technique currently used for DNA analysis, SERS provides a convenient method to identify a single DNA base without any labeling steps.[7] Detection of a single adenine molecule absorbed on Ag colloidal clusters has been demonstrated by Kneipp et al.[5] The Ag−PS substrates in the present study were found to be capable of detecting low adenine concentrations. Figure 5 displays the SERS spectra of adenine on HCl-pretreated Ag−PS. Within the error limits of the experiment, the peak positions are in agreement with the literature values.[43]

It is hard to quantify the sensitivity of these samples relative to other substrates reported in the literature such as Ag and Au colloids because the experimental setup (in particular, the laser power and wavelength) has a large influence on the signal-to-noise level. For instance, using an 830-nm near-infrared laser instead of a 407- or 514-nm laser, Kneipp et al. reported increased enhancement factors by 6−7 orders of magnitude for colloidal Ag clusters[5] and about 11 orders of magnitude for colloidal Au clusters, allowing detection of single adenine molecules.[8] Detection of single adenine molecules on Ag colloids has also been reported by Maruyama et al.[17] 488-nm excitation was used in both the work of Maruyama et al. and in the present study, though the laser intensity is almost 30 times lower in the present set of experiments.

The detection limit (2:1 signal:noise level) for adenine in the present study is 1 nM (Figure 5), while the study of Maruyama et al. reports that detection of adenine could only be achieved at concentrations of 1 μM or higher.[17] Kniepp et al. report detection limits as low as 30 pM using a near-infrared excitation source. Although other differences in experimental setup may greatly affect the signal quality, we estimate that the Ag−PS samples in the present study are at least comparable to Ag colloids in terms of sensitivity. Chan et al. used a near-infrared laser source (785 nm, 600 mW) in their experiments with Ag-coated porous Si prepared by thermal decomposition.[16] The lowest concentration of adenine detected in that work was 90 μM, almost 5 orders of magnitude higher than the 1 nM detection limit obtained from the Ag−PS substrates in the present work (using a 488-nm, 18-mW laser source). If it is assumed that all the adenine in the incubation solution is absorbed on the Ag-plated porous Si surface and none of it is removed in the rinsing step, the Raman spectra in the present work are collected from an area containing at most 9×10^5 adenine molecules.

4. Conclusions

Ag films containing dendritic structures can be prepared on porous Si by immersion plating. As a SERS-active substrate, Ag−PS is sensitive and stable. High-quality SERS spectra of Rhodamine 6G and adenine can be obtained on these substrates. A simple acid pretreatment step provides significant reduction of background signals that presumably arise from impurities incorporated into the material during preparation. A detection limit of 1 nM, corresponding to 9×10^5 molecules (at most), is achieved for adenine, which is comparable to that reported for Ag colloids, and about 5 orders of magnitude better than Ag-coated porous Si prepared by thermal decomposition.[16]

Compared with Ag colloids, the Ag microstructures in the present work are immobilized on the porous Si substrate and are not susceptible to further aggregation. The immersion plating technique provides a simple method for preparation of SERS-active substrates. Ag−PS substrates can be prepared in a few minutes at room temperature using mild reaction conditions. They can be stored for several days and then activated prior to analysis by an acid dip. Thus, they are suitable for in situ preparation of SERS-active substrates in the field. This method is also amenable to mass production and integration with well-developed silicon microfabrication technologies.

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