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The fabrication of surface-enhanced Raman spectroscopy (SERS) substrates that are optimized for use with specific laser wavelength-analyte combinations is addressed. In order to achieve large signal enhancement, temporal stability, and reproducibility over large substrate areas at low cost, only self-assembly and templating processes are employed. The resulting substrates consist of arrays of gold nanospheres with controlled diameter and spacing, properties that dictate the optical response of the structure. Tunability of the extended surface plasmon resonance is observed in the range of 520–1000 nm. It is demonstrated that the enhancement factor is maximized when the surface plasmon resonance is red-shifted with respect to the SERS instrument laser line. Despite relying on self-organization, site-to-site enhancement factor variations smaller than 10% are obtained.

1. Introduction

Plasmonic structures are routinely used in Raman spectroscopy to increase the cross-section for the scattering process and augment the signal, particularly when very little sample is available, a technique termed surface-enhanced Raman scattering (SERS).^[1,2] The extreme sensitivity of SERS is achieved through the strong coupling between electromagnetic radiation, plasmon modes of a surface and electronic states of a molecule, which in turn couple to the vibrational modes of the molecule.^[3,4] The SERS substrate, containing the plasmonic structure and often a binding site for the molecule to be analyzed, needs to be tailored precisely (i.e., at the nanoscale) in order to achieve efficient coupling and provide colossal signal enhancement.^[5] In many cases, it is desirable to design the SERS substrate so that its surface plasmon resonance frequency lies between the frequencies of the incident light (the laser of the Raman spectrometer) and the scattered light.^[6-8] The surface plasmon resonance frequency may also need to match approximately an

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electronic transition energy of the molecule or solid being probed to make use of the resonant Raman scattering effect and further increase the enhancement factor.^[9] Self-assembly techniques,^[10-16] nano-lithography techniques,^[8,17–19] and combinations thereof^[20–23] have been employed to fabricate and optimize SERS substrates for the detection of and discrimination between analytes. Each fabrication method for SERS substrates involves a compromise between enhancement factor, cost, active area, reproducibility, and service life.^[15,24] In this article, we describe a fabrication method for SERS substrates that show a unique combination of three highly desirable attributes: These SERS

substrates can be tuned to match the laser wavelength of operation and maximize the enhancement factor for the particular Raman instrument and analyte in use. These SERS substrates have a highly reproducible enhancement factor over macroscopic sampling areas. Furthermore, this is achieved without resorting to expensive, slow nano-lithography tools. The substrates are made entirely through self-assembly and templating techniques, which are cost-effective and scalable to large areas.^[25–28] These attributes make the fabrication process very appealing for mass production.

2. Results and Discussion

The SERS substrates described herein consist of hexagonal arrays of metallic nanospheres with controllable diameters and lattice spacing (Figure 1). By controlling the size and the spacing between the nanospheres, tunable, tailored plasmonic response is achieved.^[29,30] The underlying template for ordering the metallic nanospheres for the SERS substrates is formed through the self-assembly of a thin film of block copolymer (polystyrene-b-poly(4-vinylpyridine), PS-b-P4VP) (Scheme 1). As the polymer solution is spin-cast and the solvent evaporates, the low solubility of the blocks in each other leads to segregation of the blocks into hydrophilic and hydrophobic domains of nanometer dimensions and long range order.^[31] We utilized a PS-b-P4VP block copolymer composition that results in cylindrical domains of P4VP in a matrix of PS (Scheme 1). Following a solvent-annealing step, the P4VP domains become more regularly spaced and aligned perpendicular to the substrate.^[32] Figure 1a shows a representative atomic force microscopy (AFM) topographic image of the self-assembly film. The local environment around the domains has hexagonal symmetry and

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Figure 1. a) AFM image of the THF annealed PS-b-P4VP ordered film. b-h) SEM images of gold nanoparticle arrays on the quaternized PSb-P4VP films after different overgrowth times: b) 0 min, c) 1 minute, d) 3 min, e) 5 min, f) 7 min, g) 10 min and h) 15 min.

the long range order extends on the order of ~800 nanometers. The elevated P4VP domains are approximately 20 nm in diameter and the hexagonal lattice parameter is 42 nm. The center-to-center spacing and the diameter of the P4VP columns are controlled by the choice of the molecular weight of the polymers and the ratio between the number of 4-vinyl pyridine and styrene repeat units. To improve the templating capabilities of the block copolymer film, the pyridine groups of the P4VP block were converted into quaternary pyridinium groups (as well as crosslinked) by exposing the film to 1,4-dibromobutane (DBB) vapor.^[33] XPS analysis of the quaternized films indicated a 66% conversion to the pyridinium bromide (Figure S1).^[34] There are two beneficial consequences to the reaction with DBB. First, the P4VP domains of the film become positivelycharged. The quaternized P4VP domains selectively trap negatively-charged nanoparticles from solution through electrostatic interactions.^[34] As will be shown, the nanoparticle immobilization process is highly localized and effectively irreversible due to the strength of the interaction. Second, each cylindrical P4VP domain of the film becomes crosslinked. This contributes to the stability of the self-assembly structure, reducing swelling and surface-reconstruction upon exposure to various



Scheme 1. SERS substrate fabrication scheme. i) Solvent annealing. ii) Quaternization. iii) Colloid adsorption. iv) Overgrowth. (key: cyansubstrate; green-P4VP; yellow-PS; red-Au).

solvents.^[33] The quaternization reaction is therefore essential for obtaining a template to build upon a plasmonic structure that has a predictable periodicity and no detectable deterioration during preparation and use.

Upon immersion of the quaternized block copolymer film in a solution of citrate-stabilized gold nanospheres, self-assembly of the nanospheres into a hexagonal array commensurate with the array of P4VP domains was observed (see Figure 1b). The adsorption of the gold nanospheres is complete within 3 h, when 97% of the P4VP domains are covered by particles. The best ordering is achieved when the diameter of the gold nanospheres is slightly larger than the diameter of the P4VP domains, preventing the deposition of 2 gold nanospheres on a single P4VP domain (see defects in Figure 1b). The templating is driven strictly by electrostatic interactions between the positively charged pyridinium groups on the substrate and the negatively charged surface ligands of the nanoparticles. The assembly process was successfully carried out with other nanoparticle types (quantum dots, magnetic nanoparticles, and oxide nanoparticles) carrying negatively charged surface groups (carboxylates, borates, etc.).^[34] An attractive feature of this system is that the nanoparticles adhere strongly to the block copolymer film; therefore, the substrate can be washed and manipulated without the risk of losing the hexagonal order. The robustness of these assemblies sets them apart from other templated structures reported in the literature.^[35–37]

The gap between adjacent nanoparticles is a major factor that determines the surface plasmon resonance frequency and the SERS enhancement factor.^[29,30,38–41] The inter-particle gap size is the difference between the center-to-center spacing (set by the block-copolymer template) and the nanosphere diameter. The

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 $\ensuremath{\textbf{Table 1.}}$ Evolution of the parameters of the nanoparticle arrays as a function of overgrowth time.

Reaction time [min]	NP diameter (average \pm standard deviation) [nm] ^{a)}	Gap size (calculated average) [nm] ^{b)}
0	16.6±1.8	23.0
1	20.2 ± 1.5	18.4
3	24.8 ± 2.0	14.6
5	$\textbf{27.6} \pm \textbf{2.4}$	11.2
7	32.7 ± 3.3	9.5
10	34.3 ± 4.4	6.6
15	36.5 ± 6.3	4.1

 $^{a)}Analysis based on ~700 nanoparticles imaged by SEM in an area of 1.14 <math display="inline">\mu m^2;$ $^{b)}Calculated assuming a hexagonal lattice.$

gap size was tuned by metal overgrowth over the nanoparticles anchored on the surface. Soaking the substrate in an aqueous solution of HAuCl₄, silver nitrate, ascorbic acid and hexadecyltrimethylammonium bromide ("Au growth solution")^[42] resulted in a gradual increase in nanosphere diameter and a concomitant reduction of the gap (Figure 1b-h and Table 1). Since the overgrowth reaction rate slows significantly at the narrow gaps between the particles, growth of individual nanoparticles is favored over coalescence of adjacent nanoparticles. This is advantageous in making the processes highly controllable (by varying the soaking time) and the product uniform. The uniformity of the substrate is manifested in the marked peaks observed in the UV-vis attenuation spectra of SERS substrates fabricated on glass (Figure 2). The spectra contain two absorption peaks. The high photon energy peak is a resonance peak from the localized surface plasmons of the individual nanospheres. The low photon energy peak is from an extended surface plasmon delocalized over the array. These spectral features gradually evolve with overgrowth reaction time. As the particles in the nanosphere array grow larger and the gaps between them narrow, the localized surface plasmon resonance peak at 520 nm gradually red-shifts and the nascent lower-energy peak markedly increases in intensity and red-shifts. These spectral changes are a consequence of the increase in the coupling between plasmons on adjacent nanoparticles. Figure 3 shows a photograph of a series of SERS substrates obtained on silicon with varying overgrowth times, corresponding to the spectra shown in Figure 2. Clearly, the spectral shifts are pronounced also in reflection mode. Thus, the substrates can be tuned to



Figure 2. UV-vis attenuation spectra of SERS substrates fabricated on glass with overgrowth times ranging from 0 to 15 min. The vertical lines indicate the wavelengths of the incident (solid) and the scattered (dash) light utilized in our SERS measurements.

accommodate for Raman spectrometers operating at a range of wavelengths from 500 to 900 nm.

SERS spectra were collected using a series of SERS substrates with varying thickness of overgrown gold over 15 nm gold nanosphere cores. Prior to the measurement, the substrates were soaked in a dilute solution of 4-aminobenzenethiol, rinsed with ethanol, and dried. The same SERS substrates were studied with 3 different lasers commonly found in Raman spectrometers. All the SERS spectra correspond to that of 4-aminobenzenethiol, however, the SERS signal intensity per molecule varies dramatically from SERS substrate to substrate. For example, in the series of SERS spectra obtained with a He-Ne laser (633 nm) the maximum SERS enhancement is obtained with the substrate that was immersed for 7 min in the Au growth solution (Figure 4). The enhancement factors of the SERS substrates were calculated taking into account the surface area of the plasmonic nanospheres and the focal beam diameter (see definition of SERS substrate enhancement factor in Ref. [43], Eq. 7). The dependence of the SERS substrate enhancement factor on the overgrowth time and the laser wavelength is depicted in Figure 5. To understand the trends in the magnitude of the enhancement factor we consider two guiding principles: i) The enhancement factor increases with the absolute value of the ratio



Figure 3. Photograph of SERS substrates fabricated on silicon with overgrowth times ranging from 0 (far left) to 15 min (far right), under white light illumination. The change in the perceived color implies a variation in the frequency of the surface plasmon resonances.

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Figure 4. Surface-enhanced Raman spectra of 4-aminobenzenethiol on our series of SERS substrates. The meaning of the colors/symbols is the same as in Figure 2. The spectra were shifted vertically for clarity.

of the real to imaginary components of the permittivity of the metal, $|\mathcal{E}'/\mathcal{E}'|$.^[44,45] For gold, this ratio increases with the increase in wavelength in the range 500–900 nm (from ~1 to 33).^[46] As a result, the highest enhancement factors were obtained using the 785 nm laser and the lowest using the 515 nm laser. ii) The optimal SERS performance is anticipated for substrates with surface plasmon resonance peaks slightly red-shifted with respect to the incident laser wavelength.^[47] For a given laser, there is an optimal overgrowth time (i.e., diameter to gap ratio) that maximizes the enhancement factor.^[29] The longer the wavelength of the laser, the longer the optimal overgrowth time. The optimal overgrowth time correlates with the shift in wavelength of the low-frequency (extended) surface plasmon resonance peak



Figure 5. SERS substrate enhancement factors as a function of overgrowth time and probing (incident) laser wavelength.



Figure 6. SERS substrate enhancement factor as a function of overgrowth time. Left: Collection of data from 120 sites probed by a 633 nm laser. Right: Average values and standard deviation. The meaning of the colors/ symbols is the same as in Figure 2.

 $(\lambda_{\text{max}} = 678 \text{ nm at 7 min and } \lambda_{\text{max}} = 768 \text{ nm at 10 min})$. In the case of the 515 nm argon ion laser, the high-frequency surface plasmon resonance peak matches the laser in all of our substrates. As a result, the variations in the structure of the substrate do not achieve any substantial increase in the SERS signal when the 515 nm laser is used. These experimental results are in good agreement with theoretical calculations of field enhancement in periodic 2D arrays.^[29]

The SERS substrates were fabricated on glass and silicon wafers with areas of at least 1 cm². Since the fabrication process is based on self-assembly and templating, errors in the registry of the polymer domains and in the position of the nanospheres are observed (Figure 1). These structural defects may inadvertently produce variations in the SERS enhancement, locationby-location, questioning the utility of these SERS substrates. To mitigate this concern, each substrate was probed on 120 different sites and the SERS enhancement factor distribution was analyzed. As shown in **Figure 6** and **Table 2**, the site-to-site variations within a substrate are small, while the enhancement

 Table 2. Evolution of the enhancement factor as a function of overgrowth time.

Reaction time [min]	Enhancement factor (average \pm standard deviation) ^{a)}
0	720 ± 640
1	3300 ± 1200
3	25300 ± 4900
5	89800 ± 6200
7	91100 ± 10000
10	54100 ± 5200
15	57900 ± 7600

^{a)}Analysis based on measurements on 120 different sites on each substrate, using the 633 nm laser and the 1078 cm⁻¹ Raman peak of 4-ABT.



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factor variations resulting from varying the overgrowth reaction time are significant. The results are most uniform for substrates with high enhancement factors (overgrowth time of 5–15 min). The standard deviation in the SERS substrate enhancement is only 10% of the average value. For comparison, the same experiment was carried out on an e-beam evaporated thin silver film on a silicon wafer. In this case, the standard deviation was 50% of the average enhancement value. The data demonstrate that the SERS substrates are effectively homogeneous and that tuning the nanoparticle size and the gap size are effective ways to optimize the SERS enhancement factor. The SERS substrate enhancement factor values reported here are significant in magnitude; additional enhancement could be obtained by using silver instead of gold if long-term stability is not critical or by changing the underlying substrate material.^[48-50] The enhancement factor values are lower than those reported for individual dimers of nanoparticles, however, the SERS response of individual dimers is highly anisotropic: strong enhancement is obtained only for a parallel orientation of the dimer axis and the laser polarization.^[23,51–54] Our substrates display a uniform response regardless of orientation, which is extremely convenient for real-world applications. The substrates retained their SERS activity for at least 6 months of storage in air.

3. Conclusions

We have characterized SERS substrates made through the selfassembly of gold nanoparticles, guided by a chemically modified PS-b-P4VP block copolymer template. By controlling the size of the anchored nanospheres, the plasmon resonances of the substrate were tuned and the SERS substrate enhancement factor was maximized for a given type of input laser. These SERS substrates show enhancement factors that are significant in magnitude and highly uniform spatially. Due to their lowcost, reproducibility and tunability these SERS substrates could make Raman the method-of-choice in a wider range of chemical sensing applications.

4. Experimental Section

Materials: PS-b-P4VP block copolymer (number average molecular weight $M_n^{PS} = 47 \text{ kgmol}^{-1}$, $M_n^{P4VP} = 10 \text{ kg mol}^{-1}$, polydispersity index = 1.1) was purchased from Polymer Source, Inc., and used without further purification. Hexadecyl-trimethyl-ammonium bromide (CTAB), ascorbic acid, tetrahydrofuran, and 1,4-dibromobutane (DBB) were purchased from Sigma-Aldrich. Citrate-capped gold colloidal solution with 15 nm mean diameter was purchased from BB International. Silver nitrate (AgNO₃) and hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O) were purchased from Alfa Aesar.

Fabrication of SERS Substrates: PS-b-P4VP block copolymer was dissolved in THF to yield a 0.5 wt% polymer solution. The polymer solutions were filtered through a Millipore 0.45 μ m poly(tetrafluoroethylene) filter. PS-b-P4VP films were prepared by spincoating at 3000 rpm for 30 s on silicon or glass substrates at ~23% RH. As-spun films were annealed in THF at room temperature. The P4VP blocks in the PS-b-P4VP film were quaternized in DBB vapor. The PS-b-P4VP films were immersed in the nanoparticle solutions for 3 hours. Gold growth solutions were prepared by mixing solutions of CTAB (6 mL, 0.2 m), HAuCl₄ (0.384 mL, 0.04 m), AgNO₃ (0.228 mL, 0.01 m), ascorbic acid (0.96 mL, 0.1 m), and deionized water (11 mL) [42].

Thin Film Characterization: Thin film surface morphology was characterized using a Dimension 3000 AFM from Digital Instruments, Inc. Silicon tips on a cantilever with spring constants ranging between 20.0 and 80.0 N m^{-1} (as specified by the manufacturer) were used. The degree of quaternization was measured using XPS on a Kratos AXIS 165 X-ray photoelectron spectrometer using a monochromatic Al K α X-ray source (1486.6 eV). SEM observations were conducted using a Hitachi SU-70 Schottky FE-SEM working at 10 kV accelerating voltage and working distance around 5.5 mm. UV/Vis absorption spectra of the gold nanoparticle array films on glass substrates were measured using a Perkin-Elmer Lambda 25 UV-vis spectrometer. The substrates were immersed in 0.4 mm 4-ABT solution in ethanol for 3 h, rinsed extensively with ethanol, and dried under nitrogen. SERS spectra were measured with a Horiba Jobin-Yvon LabRAM HR-VIS micro-Raman spectrometer equipped with 515 nm, 633 nm, and 785 nm laser sources, a confocal microscope, and an x-y scanning stage. A 50× objective (numerical aperture NA = 0.5) was used for all of the measurements. SERS spectra were obtained with incident laser power of 0.18 mW (515 nm), 0.11 mW (633 nm) and 0.67 mW (785 nm), and acquisition time of 30 sec. The Raman spectrum from a reference solution of 1.0 $\scriptstyle\rm M$ 4-ABT in pentanediol was acquired using the same spectrometer settings. The Raman signal intensity was quantified as the integrated peak area for the carbon-sulfur bond stretch of 4-ABT at 1078 cm⁻¹. The number of molecules probed in each SERS substrate was calculated assuming that all the particles were perfect spheres, a focal diameter of φ 2.2 μ m and a monolayer surface density of 5 molecules nm⁻² for 4-ABT on gold.^[55,56] The number of molecules probed in the reference solution was calculated assuming a cylindrical focal volume of φ 2.2 µm × 16 µm. The substrate enhancement factor is the ratio of the Raman signal intensity per molecule of the SERS substrate and that of the reference solution.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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