9554 *J. Am. Chem. Soc.* **2000,** *122,* 9554−9555

Assembly of Gold Nanostructured Films Templated by Colloidal Crystals and Use in Surface-Enhanced Raman Spectroscopy

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Received June 26, 2000
Revised Manuscript Received August 18, 2000

This communication describes how thin porous films of metals on glass substrates can be conveniently and easily fabricated by the use of colloidal crystal templates and how these structures can find analytical applications in surface-enhanced Raman spectroscopy (SERS). Since the method of forming macroporous materials by templating with colloidal crystals was introduced a few years ago,[1] it has been extended to the fabrication of structures from inorganic oxides,[2] polymers,[3] carbon,[4] semiconductors,[5] and metals.[6] Most of the efforts in this area are currently focused on the formation of photonic crystals, structures with 3D periodicity on a length scale comparable to that of light, which may be used in microscopic lasers, efficient light-emitting diodes, and miniature waveguides or mirrors.[7] However, the fabrication of high-quality, defect-free photonic crystals via colloidal crystallization poses a significant technological challenge, and the practical feasibility of this method remains unproven. Nevertheless, as we report here, materials being developed as photonic crystals can find immediate use in applications such as SERS when they are fabricated in the form of thin films supported on flat surfaces.

The key to the wider application of Raman spectroscopy using roughened metallic surfaces[8] is the development of highly enhancing substrates for analytical purposes,[9] i.e., for better detection sensitivity of trace contaminants and pollutants. To use SERS in routine, on-line studies, the substrates should also be stable, reproducibly prepared, inexpensive, and easy to make. The methods developed to date cannot satisfy all of these requirements. Substrates that are produced by adsorption[10,11] or sol-gel entrapment[12] of metallic nanoparticles lack advanced features, e.g., periodicity. The enhancement can be increased by creating a long-ranged pattern with a submicrometer periodicity on the substrate,[13] but the present techniques used for surface patterning such as electron-beam lithography[13] or nanosphere lithography[14] are limited by the relatively high cost of fabrication and the low surface area of the metal structure.

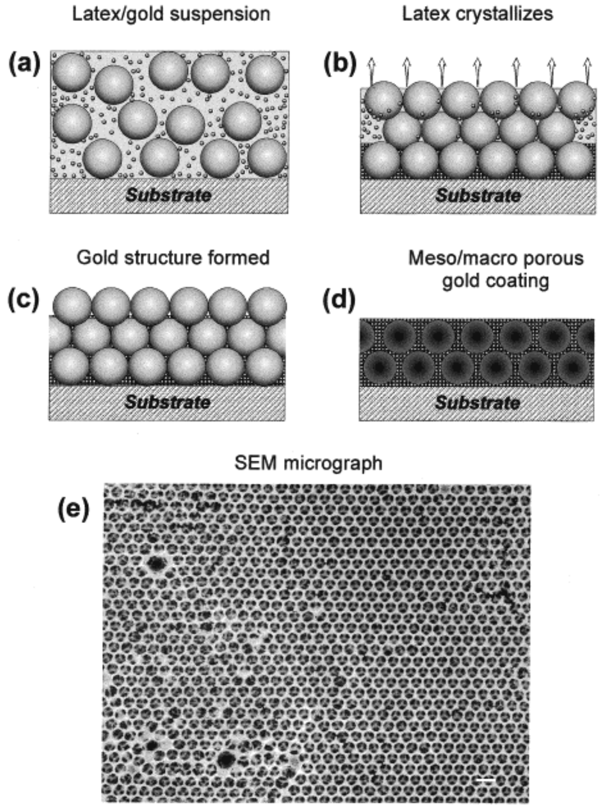

Figure 1. Schematic diagram (a−d) of the formation of mesoporous-macroporous gold films templated by colloidal crystals. The porous structure of the resulting material was observed by SEM (e) using a JEOL JXA-840 operating at 20 kV. Scale bar = 1 μm.

The simple procedure that we have developed for depositing structured macroporous metallic films on flat substrates is shown schematically in Figure 1a−d. Concentrated gold nanoparticles (25 nm) and latex microspheres (630 nm) were mixed together and deposited on a microscope slide (Figure 1a). A second slide was used to drag a meniscus of the colloidal suspension along the lower slide, depositing a film of latex particles (Figure 1b). This procedure is somewhat similar to the process of convective assembly of 2D crystals,[15] although the films obtained with our coating method were much thicker than those in the previous experiments. Thick multilayer latex crystals grew upon drying of the films, probably due to the combination of the increasing latex volume fraction and convective assembly. The gold particles were trapped in the interstitial voids of the latex crystal and upon further evaporation assembled around the bottom latex layers

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10.1021/ja0022831 CCC: $19.00

(Figure 1c). The latex/gold composite was then immersed in toluene to dissolve the latex template, leaving behind the gold structure immobilized on the glass slide (Figure 1d). A more detailed description of the method is described elsewhere.[16]

The SEM image in Figure 1e shows a gold film of a thickness corresponding to two layers of latex particles, with hexagonally ordered pores. The lower layer of the nanostructure can be seen through the holes of the upper layer. Monocrystalline domains of hundreds of identical pores are seen on the surface, usually corresponding to stacked close-packed planes of hexagonal or square symmetry. The individual gold particles forming the macroporous material were also observed by AFM, confirming the second level of porosity for these structures.

Macroscopically, the gold films were semitransparent and showed multicolored domains in reflected illumination. Two characteristic features were seen in the IR−vis spectra,[16] corresponding to the surface plasmon band of individual gold particles and a second "red-shifted" band. The "red-shifted" mode, which arises from the coupling of surface plasmons between adjacent particles,[11] gives rise to locally strong electric fields and causes the enhancement of the Raman spectrum for molecules close to the surface.[17,18]

We evaluated the performance of our gold structures as SERS substrates using *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as a model compound (Figure 2). All samples for which the spectra are shown, except the one for solid BPE (spectrum 3), were prepared similarly to those of Grabar et al.[11] The templated gold substrates (spectrum 1) gave a strong Raman signal with little background noise. This can be compared to the weaker spectrum of BPE (spectrum 2) obtained from gold particles deposited under similar experimental conditions, but without the latex template. Spectrum 3 was obtained from solid BPE flakes without gold, and exhibits slightly shifted peaks compared with the SERS spectra, as is commonly observed in the absence of surface interactions.

For comparison, Figure 2b shows the BPE spectra for several reference surfaces. The weak spectrum 7 was taken on a smooth layer of gold deposited on glass by evaporation. The same surface, after being electrochemically roughened,[19,20] showed a more intense, but still relatively weak, Raman spectrum.[4] No distinguishable peaks were observed for BPE on either bare glass (spectrum 6) or the structured gold sample after being heated to 500 °C (spectrum 5) where the nanoparticles had fused together, yielding larger, SERS-inactive gold droplets.

To estimate the enhancement factor for our substrates, we compared our thin film samples to a glass substrate without gold that had a layer of BPE 100 times thicker than the samples with gold. By comparing the Raman intensity for two peak positions[21] we obtained an average enhancement of 10^4 for a typical structured gold sample relative to glass. This enhancement is an order of magnitude greater than what we observed for gold particles randomly absorbed on glass (spectrum 2), or what is typically reported for samples prepared by random particle adsorption.[11] Also, our signal-to-noise ratio (>100) is better than those of substrates prepared by adsorption, even though we integrated the Raman signal for an order of magnitude less time.[11] The SERS performance of our substrates is similar to that of two-dimensional silver gratings produced by e-beam lithography[13] and thus could result from the ordering and monodispersity of the macropores. However, our method of template-directed assembly provides the significant advantages of being much simpler, faster, and less expensive than lithography. Another reason for the high activity of our samples may be their much larger surface area than those of previously reported substrates prepared by colloidal crystal lithography,[14,22] due to the second level of porosity produced by the gold nanoparticles. Substrates with large metallic surface area are likely to be advantageous for detecting small concentrations of a target compound by SERS.

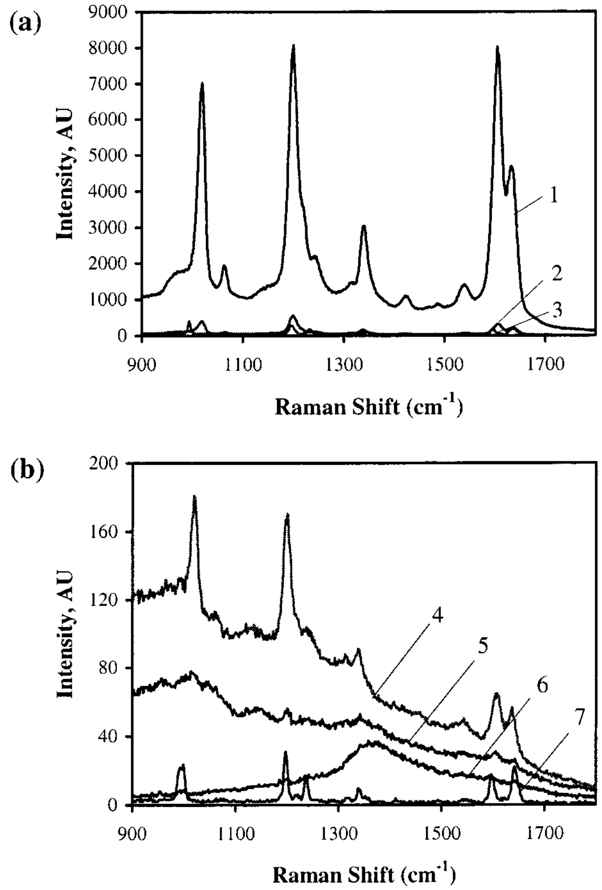

Figure 2. Raman spectra of BPE deposited on various gold and glass substrates: (1) gold particles (25 nm) on glass templated by colloidal crystals; (2) same as (1) without latex template; (3) bulk spectrum from a thick BPE layer; (4) electrochemically roughened gold on glass; (5) same as (1), but after heating to 500 °C; (6) glass slide without metal; and (7) smooth, 200 nm thick gold film evaporated onto glass. Experimental conditions: 5 µL of 1 mM BPE; 60 mW of laser power at 784.6 nm focused on a 15 µm diameter spot; 10 × 10 s integration time. Raman spectrograph system: Kaiser Optical Inc. HoloSpec F/1.8 connected to an Olympus BX-60 microscope by a fiber optic cable.

In conclusion, we have introduced a convenient colloidal crystal templating method to deposit structured porous metallic films on flat substrates. The three-dimensional, highly ordered gold films supported on glass slides are formed by a simple procedure, and could be particularly useful as SERS substrates. The porous structures have clear practical advantages over materials produced by other more complex and expensive methods. Future modifications of our method can create many other types of macroporous films and coatings.

Supporting Information Available: Figures of the deposition process, SEM and AFM images, and IR−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] The roughening procedure used is described by Bryant et al.,[19] except that 10 instead of 20 potential sweeps were used.

[21] The Raman peaks used were at 1196 and 993 cm^{-1}. The latter peak was shifted to 1019 cm^{-1} on the gold substrate.

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