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Silver nanocrystal superlattice coating for molecular sensing by surface-enhanced Raman spectroscopy

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A nanotechnique to assemble silver nanocrystals and control the gaps precisely in the sub-10 nm regime is demonstrated on an active coating exhibiting surface-enhanced Raman scattering (SERS). The silver nanocrystal superlattice coating boasts a high SERS enhancement factor, large dynamic range, and universal SERS activity. The observed SERS efficiency can be explained in terms of interparticle-coupling-induced Raman enhancement. © *2006 American Institute of Physics*.
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Noble metal nanoparticles such as Ag and Au with strong localized surface plasmon resonance have attracted great interests in fields such as nanoscale photonics and biological sensing.[1,2] The fact that particle plasmon allows direct coupling of light to resonant electron plasmon oscillation has spurred tremendous efforts to design and fabricate highly surface-enhanced Raman scattering (SERS) active substrates for molecular sensing.[1–6] The most studied and best established systems are substrates sprayed with Ag or Au colloids that give high SERS signals at some local "hot junctions."[1,2] However, a reliable, stable, and uniform SERS signal with large dynamic range cannot be easily achieved using this method. Theoretical studies have shown that very localized plasmon modes created by strong electromagnetic coupling between two adjacent metallic objects in an array of nanostructures dominate the SERS response, and the effective Raman cross section of a molecule placed between two metal nanoparticles can be enhanced by more than 12 orders of magnitude.[7,8] In order to fabricate noble nanoparticle arrays with high SERS activity and improve the uniformity, lithographic techniques have been employed.[3,9–11] Although these efforts illustrate the potential of using SERS as a sensitive molecular sensing tool, precise control of the gaps between the nanostructures on a SERS active substrate in the sub-10 nm regime (necessary for intense SERS enhancement) is still extremely difficult to obtain by current lithographic techniques and other nanofabrication methods.[12,13]

We have recently reported a relatively simple strategy to fabricate uniform silver nanocrystal superlattices in bulk quantities via a conventional hydrothermal method. This nanotechnique can be used to conveniently assemble noble metals with precise gap control in the sub-10 nm regime (~3 nm).[14] Here, we report the SERS measurements of molecules adsorbed on silver nanocrystal superlattices deposited on several kinds of substrates including Si, Al, and polyacrylate. A reliable, stable, and uniform SERS signal spanning a wide range has been recorded. Our results not only suggest a simple strategy to obtain a universal, ultrasensitive SERS active coating but also enable a better understanding of the fundamental SERS phenomena.

Silver nanocrystals were fabricated via a conventional hydrothermal method based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid, and solution phases. The detailed sample fabrication procedures can be found in Ref. 14. To determine the morphology and size distribution of the silver nanocrystals, we deposited droplets of the ethanol solution with the Ag nanocrystals onto carbon films supported by Cu grids. Since particle diffusion is much faster than the rate of arrival during the drying process, the particles self-assemble into highly ordered two-dimensional arrays on the surface of the grid as verified by transmission electron microscopy (TEM, Philips CM20, 200 kV). We also used high resolution transmission electron microscopy (HRTEM, JEOL JEM-4000EX) to probe the structure of the silver nanocrystals (inset in Fig. 1). The typical particle consists of many small twinned nano-

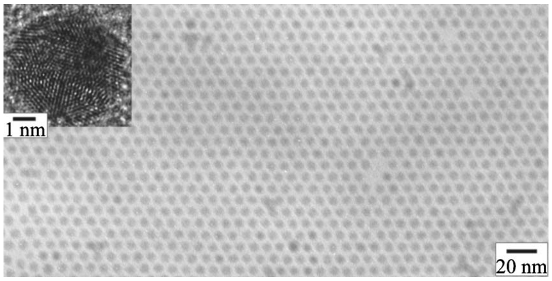

FIG. 1. Bright-field TEM image of a self-assembled monolayer of silver nanocrystal superlattice. The inset shows the HRTEM image of a typical silver nanocrystal.

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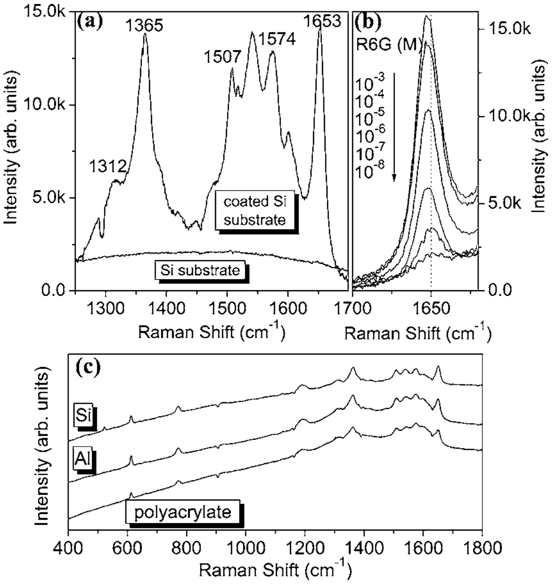

FIG. 2. (a) SERS spectrum of R6G adsorbed on the silver superlattice coated on Si substrate (top) and that directly adsorbed on a Si substrate for reference (bottom). (b) SERS spectra of R6G adsorbed coatings with different molecular concentrations, demonstrating the intensity variation of the SERS signal at 1653 cm^{-1}. (c) SERS spectra of R6G adsorbed coatings on different substrates (Si, Al, and polyacrylate).

crystals with lattice fringes corresponding to the {220} plane of silver. The near-complete monolayer silver nanocrystals have a relatively narrow particle size distribution (~5.0 nm) and the gaps (~3.0 nm) can be precisely controlled due to *in situ* generated passivation (alkyl chains).[14]

In order to evaluate the Raman-enhancing capability of the silver nanocrystal superlattice coating, aqueous solutions containing $10^{-8}-10^{-3}M$ Rhodamine 6G (R6G) were prepared. Using the TEM sample fabrication method, droplets of the ethanol solution with the nanocrystals were deposited on different substrates. After drying, the substrates were kept for 30 min in the R6G solution before they were taken out and rinsed thoroughly to facilitate molecule adsorption. Raman measurements were performed on a Jobin-Yvon T64000 triple Raman system with the 514.5 nm laser line at room temperature. The probed area was 1–2 μm in diameter and the incident power was 5 mW. SERS spectra were recorded from multiple sites on the substrate surface to check reproducibility. Similar SERS spectral characteristics, such as enhancement, position, and relative intensity of the bands, were obtained at various locations suggesting good reproducibility.

Figure 2 shows a collection of spectra illustrating the efficiency of the SERS coatings. Because R6G fluorescence and Raman spectra overlap in the spectral range of 540–580 nm (Stokes shift, 920–2200 cm^{-1}),[2,4] the Raman spectra exhibit a fluorescence background. The SERS spectrum of the $10^{-4}M$ R6G molecules adsorbed on the coated Si substrate is displayed in Fig. 2(a). Many peaks above the fluorescence background can be clearly observed, and the more pronounced ones at 1312, 1365, 1507, 1574, and 1653 cm^{-1} can be assigned to the totally symmetric modes of in-plane C–C stretching vibrations.[15] For comparison, R6G adsorbed directly on Si exhibits no visible R6G Raman bands [see the bottom of Fig. 2(a)]. It has also been reported that R6G adsorbed on an unstructured flat Ag layer deposited on Si also shows no detectable Raman features.[4]

The SERS surface enhancement factor (EF) can be calculated for R6G on the silver nanocrystal superlattice coating according to the equation $\mathrm{EF}=(I_{\mathrm{surf}}/I_{\mathrm{bulk}})/(N_{\mathrm{surf}}/N_{\mathrm{bulk}})$.[16] In this expression, I_{surf} and I_{bulk} denote the integrated intensities of the 1653 cm^{-1} band of R6G on the SERS substrate and in the bulk sample, respectively, and N_{surf} and N_{bulk} represent the corresponding number of R6G molecules excited by the laser beam. Assuming that in the densely packed R6G monolayer in which a single molecule should not occupy an area of more than 4 nm^2,[17] the number of adsorbed molecules per nanoparticle can be calculated. This number together with the total number of silver nanocrystals in the probed area determines the total number of adsorbed molecules that contribute to the SERS signal (N_{surf}). Due to highly ordered two-dimensional pattern of the silver nanocrystals, an EF of $\sim 1\times 10^5$ can be easily achieved.

Solutions with different concentrations $(10^{-3}-10^{-8}M)$ of R6G are used to study the SERS dynamic range. The variation in the SERS signal intensity at 1653 cm^{-1} is shown in Fig. 2(b). The SERS spectrum obtained from the solution with a high R6G concentration shows a factor of 8 increase in the intensity compared to that with a low concentration.

In order to investigate whether the silver nanocrystal superlattice coating possesses universal SERS activity, three coated substrates (semiconductor-Si, metal-Al, and polymer-polyacrylate) are chosen for the SERS measurements. All the spectra in Fig. 2(c) exhibit enhanced R6G Raman features above the fluorescence background. Thus, high SERS EF, large dynamic range, and universal SERS activity can be accomplished and the coating can potentially be used for the sensing of chemical and biological molecules by SERS.

Previous theoretical studies have described that highly localized electromagnetic (EM) fields at the junction of metal nanostructures affect the incident light.[7,8,18,19] Very localized plasmon modes created by strong EM coupling modify the spectroscopic properties of an adsorbed molecule in a radical manner by changing the laser field on the molecule. The most well known effect is SERS. García-Vidal and Pendry have postulated a model to quantitatively measure the interaction between EM with the neighboring metallic objects.[7] In their model, the distances between the centers of two adjacent particles (d) and the particle diameter ($2R$) are important parameters. In our systems, $d=\sim 8$ nm and $2R=\sim 5$ nm and these values fit well with their calculated enhancements of 10^5-10^6 observed for the Raman signal. It should be noted that the dependence of the EF on d and $2R$ reported by Gunnarsson *et al.* is noticeably different from our results.[4] This difference may originate from the much larger d and $2r$ of their arrays and from the disklike shape of their Ag nanoparticles. These geometric factors can produce distinct local field distributions between nanoparticles and therefore lead to different interparticle interactions.[11]

In summary, we report a simple technique to fabricate a SERS active coating made of silver nanocrystal superlattices. This coating exhibits a high Raman signal EF due to precise gap control between the nanostructures in the sub-10 nm regime. This is necessary for intense SERS enhancement as well as a very high density of both Ag nanoparticles ($\sim 1.8\times 10^{12}$ cm^{-2}) and "hot junctions" ($\sim 5.4\times 10^{12}$ cm^{-2}). The silver nanocrystal superlattice coating shows universal SERS activity and hence, the method will be useful in the development of plasmon-based analytical devices, specifically SERS-based biosensors.

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