Porous Three Dimensional Arrays of Plasmonic Nanoparticles

Haobijam Johnson Singh* † and Ambarish Ghosh* † ‡

†Department of Physics, Indian Institute of Science, Bangalore, India 560012
‡Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore, India 560012

Supporting Information

ABSTRACT: Plasmonic interactions in a well-defined array of metallic nanoparticles (NPs) can lead to interesting optical effects, such as local electric field enhancement and shifts in the extinction spectra, which are of interest in diverse technological applications, including those pertaining to biochemical sensing and photonic circuitry. Here, we report on a single-step wafer scale fabrication of a three-dimensional array of metallic nanoparticles whose sizes and separations can be easily controlled to be anywhere between fifty to a few hundred nanometers, allowing the optical response of the system to be tailored with great control in the visible region of the spectrum. The substrates, apart from having a large surface area, are inherently porous and therefore suitable for optical sensing applications, such as surface enhanced Raman scattering, containing a high density of spots with enhanced local electric fields arising from plasmonic couplings.

I. INTRODUCTION

Optically excited coherent electron oscillations in metallic nanoparticles (NPs) can have strong resonances1–2 in specific regions of the electromagnetic spectrum, which is affected by a variety of factors, such as the frequency-dependent dielectric constants of the metal and the surrounding medium, the size and shape of the nanoparticles, as well as the coupling of plasmon resonances between neighboring particles. For nanoparticles (NPs) in close proximity, plasmonic coupling can give rise to largely enhanced electromagnetic fields in the small gap between the NPs, which may lead to strong Raman signals3–5 from molecules present in these nanogaps. The effects of plasmonic interactions also cause modifications in the spectral response of the NP assembly, which is observed even at large separations between the particles (far field coupling6–8). Previous theoretical and experimental investigations8–13 with interacting plasmonic nanostructures have been mostly restricted to arrays of metal NPs in one and two dimensions, although there have been recent efforts toward the development of a 3D NP array,14 which due to its large surface area is particularly suited in sensing applications. Examples include self-assembled NP arrays on colloidal crystals5,15 and the walls of small pores, such as those made of alumina templates16 and hollow photonic crystal fibers,17,18 which have been used as substrates for surface-enhanced Raman scattering (SERS) measurements. Here, we report on a new type of porous plasmonic 3D array, which could be fabricated in a single-step wafer scale process, and whose geometrical and material properties could be tailored with good control. Interestingly, there was a large local electromagnetic field associated with individual NPs, as obtained from the high enhancement factor (∼107) obtained by SERS measurements. When the number of NPs in the 3D array was increased, apart from a large change in the visual characteristics, the surface area of the structures could also be increased in a well-designed manner. This, in combination with the enhanced local EM fields, has been used to develop a robust 3D substrate for SERS measurements, which can have important practical applications.

II. EXPERIMENTAL SECTION

A. Fabrication. The 3D arrays of plasmonic NPs were fabricated using an oblique angle evaporation scheme, also referred to as GLAD19 (glancing angle deposition) in the literature. A rotating substrate was kept at an extreme tilt angle (∼84°) with respect to incoming atoms from the source in a physical vapor deposition system, which due to shadowing effects, resulted in the formation of vertical pillars (see the Supporting Information). By alternating the evaporation source between a metal (e.g., Ag) and a dielectric (e.g., SiO2), it was possible to fabricate a porous 3D array of silver NPs, held in place by SiO2 pillars. A schematic of such a structure is shown in Figure 1A. As a first step, typically a long (approximately a few hundred nanometers) pillar was fabricated in the dielectric material, referred to as the “base pillar” in the schematic, which resulted in more well-defined 3D structures. For evaporation onto an “unseeded” substrate, i.e., a substrate without any predefined patterns; the resultant array was random along the substrate plane but showed well-defined positions for the Ag NPs along the vertical direction. Scanning electron microscopy (SEM) images of a typical 3D structure fabricated on an

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unseeded substrate are shown in parts B and C of Figure 1, where the three and six layers of Ag NPs could be easily observed as black stripes, respectively. The height of the base pillar in this particular structure was ∼500 nm, above which six alternating layers of Ag and SiO₂ were evaporated, of thicknesses of 25 and 45 nm respectively. As is evident from the SEM image, the pillars were separated from each other by about 50–70 nm implying a high degree of porosity in the structure.

It was also possible to fabricate similar 3D structures in regular patterns, with better control over the various geometrical parameters. To do so, we used nanoparticle lithography (see the Supporting Information) to fabricate a regular pattern of Ag pyramids (lateral dimensions ∼250 nm, height ∼100 nm) arranged in a Fischer pattern. This resulted in a “seeded” substrate where subsequent growth of the base pillar and the alternating Ag-SiO₂ layers occurred on the Ag pyramids. SEM image of a 3D NP array fabricated on a seeded substrate is shown in Figure 1D. For such thicker structures, the black stripes for the Ag layers could not be imaged, although the presence of the silver could be easily confirmed by comparing the total height of the pillars with the chosen fabrication parameters. The dimensions of the resultant 3D array were determined by the size and spacing of the Ag pyramids, which in turn depended on the size of the polystyrene beads used in the nanoparticle lithography step. The resultant 3D NP arrays, fabricated either on seeded or unseeded substrates, were observed to have large differences in their appearances and depended in a nontrivial manner on the number of Ag-SiO₂ layers, their dimensions, and the directions of observation. Photographs of few such structures have been shown in Figure 1E taken with a digital camera under white light illumination. As evident from the digital images, the samples showed a high degree of spatial uniformity in their appearance across the surface, and their bright colors depended strongly on the direction of observation. In general, as the number, Nlayer, of Ag-SiO₂ layers was increased; the samples became darker, which was probably due to increased absorption from the silver layers. As is evident from the SEM images, each Ag NP can be approximated as a disk, which may have more than one resonant mode. The typical distance between two such Ag nanodiscs within the same pillar was of the order of 40−50 nm (through SiO₂), while the Ag nanodiscs belonging to two neighboring pillars could also interact, determined by a typical distance ∼250 nm (through air) for a seeded substrate. These...

Figure 1. (A) Schematic of a 3D metallic (Ag) NP array separated by dielectric (SiO₂) nanorods. Typically, the base pillar was made of SiO₂ as well. (B and C) SEM images of 3D NP arrays containing three and six layers of Ag-SiO₂ on an unseeded substrate respectively. (D) SEM image of a 3D NP array fabricated in a seeded substrate. (E) Color photographs of various 3D NP arrays under white light illumination. On left are arrays grown on unseeded substrates for Nlayer = 3, 6, 11. On right are arrays grown on seeded substrates for Nlayer = 1, 3, 7, 11.

Figure 2. (A) Intensity at the detector for 3D arrays with varying Nlayer = 1, 3, 7, and 11 dipped in a 1 µM aqueous solution of R6G. The arrays where fabricated on a seeded substrate with typical lateral dimensions 250 nm and heights ranging from 450 nm to 1.2 µm, depending on the number of layers. (B) The Raman signal obtained by calculating the area under the 614-cm⁻¹ peak of the spectrum (after background correction) for various concentrations of R6G and substrates with different Nlayer. Note the available surface area in the focal volume for this particular structure, after considering the dimensions of the base pillars and the Ag-SiO₂ layers, increased in a ratio of 1:1.4:2.1:3 for Nlayer = 1, 3, 7, and 11 (details in the Supporting Information). The molecules in principle can attach either to silver or SiO₂; however, as we show later, we found the molecules to preferentially attach to SiO₂, especially at low molecular concentrations.
dimensions suggest the possibility of a strong far-field coupling in three dimensions between the Ag nanodiscs, which could be the most important factor in determining the spectral response of the 3D arrays. A detailed experimental and computational effort will be necessary to understand this complex behavior, which as far as we know, have never been attempted for three-dimensional NP arrays; although there have been recent efforts toward understanding the effects of radiative coupling in a 3D stack of plasmonic nanowires.

B. Characterization. An important aspect of the 3D substrates presented here was their porosity, which made it suitable for various sensing applications. Interestingly, we found the arrays grown on seeded substrates to be extremely robust, where the nanopillars remained intact even after dropping a liquid sample on the substrate and subsequently drying it. This was possibly due to their higher widths (∼250 nm) compared to unseeded substrates, where the rods did not collapse when the liquid is evaporated. It is important to note that the fabrication process can be adapted to a wide variety of materials, both metals and dielectrics, as it is based on a physical vapor deposition scheme. The surface area of the nanostructured surfaces could be scaled up by increasing the number of layers, which could be useful in loading large number of molecules within some detection volume. Furthermore, the part of the nanopillars made of SiO2 could be useful for functionalizing and attaining different molecules for capturing target analytes through standard silane chemistry. A promising area of application is to use the 3D NP arrays as SERS substrates, where the strength of the Raman signals could be enhanced by having a large number of target analytes, in close vicinity to the metallic NPs, within the laser focal volume. The SERS spectrum of particular concentrations of Rhodamine-6G for different values of Nlayer under the illumination of 514.5 nm laser line is shown in Figure 2A. Typical laser powers used were around 250 μW, with an averaging time of 3 s. The spectra are shown without any background correction. As is observed clearly, strengths of both Raman and fluorescence signals increased with increasing number of Ag-SiO2 layers.

III. RESULTS AND DISCUSSION

It is important to note that the GLAD technique has been used by researchers in the past for developing SERS substrates based on plasmonic materials deposited on nanostructured thin films. The substrates in these earlier studies typically consisted of metallic nanorods or a layer of noble metals deposited at the top of an array of dielectric rods that gave rise to large SERS enhancements. The technique presented in this paper, for the first time, extends the plasmonic NP arrays to multiple layers, which as we show below not only demonstrates a high enhancement factor but also offers a route toward increasing the available surface area. The primary reason behind the observed increase in Raman signal in the present work with increase in the number of Ag-SiO2 layers was due to the larger available surface area available for the molecules inside the laser illumination volume. Exactly how the available surface area increased with Nlayer depended on the geometrical parameters of the particular substrate. A particular example has been discussed in the Supporting Information.

Another possible reason for the enhancement in the observed Raman signal could be through electromagnetic coupling between the metal NPs. For a row of NPs of size a and interparticle distance d, the Raman intensity enhancement solely due to interparticle electromagnetic coupling was found to be proportional to \((a/d + 1)^2\), in comparison to the Raman signal from an isolated NP. For a row of Ag NPs (diameter 200 nm) separated by 100 nm, the signal enhancement was found to be around 15, both theoretically and experimentally. The situation is much more complicated with 3D arrays, as in our case, where the coupling could occur either through 250 nm of air or through 45 nm of SiO2, along different directions. Even without any numerical calculations, it is safe to assume some finite and positive contribution to the Raman signal due to interparticle electromagnetic interactions in 3D NP arrays, in addition to the effect due to enhanced surface area arising out of multiple NP layers. It is not possible to estimate the exact magnitude of the SERS signal enhancement, without a detailed numerical calculations of the EM fields and their spatial distribution.

For results shown in Figure 2, the samples were prepared by simply immersing the substrate in a known concentration of R6G in water for a specific time (~12 h). Accordingly, it was not clear how many molecules were actually physisorbed on the nanopillars, and therefore it was difficult to estimate the enhancement factor from this study. However, it is important to note that a particular Raman line at 232 cm⁻¹ was typically not observed at low R6G concentrations, which is a common signature of R6G binding to silver. This suggests that most of the molecules were simply attached to the silica portion of the structures. Furthermore, while fluorescence may be quenched for molecules in direct contact with a metal surface, a layer of a dielectric (silica in our case) in close proximity to a metallic nanostructure typically enhances the fluorescence. A strong fluorescence signal was observed in our studies, suggesting again that most of the R6G was physisorbed on to silica. Following the same protocol, we could detect down to 100 nM R6G concentrations for a single Ag-SiO2 layer. The area under the 614-cm⁻¹ peak of the Raman signal, after correcting for the background, has been shown for various concentrations and values of Nlayer in Figure 2B. The enhancement of the Raman signal with Nlayer for a particular R6G concentration was primarily due to the increase in surface area available for R6G to bind in the focal volume, which had a linear dependence on the number of Ag-SiO2 layers.

The local electromagnetic fields in the vicinity of the silver NPs were enhanced, as is evident from the strong SERS signals. A quantitative measure could be obtained from estimating the SERS enhancement factor (EF), for which it was essential to estimate the number of molecules being bound to the substrate. To do so, we prepared the samples by dropping a known number of rhodamine molecules (~10 μL of a particular concentration) onto a sample of known and definite area and subsequently allowed the substrate to dry over a couple of hours. This provided us with an accurate estimate on the number of molecules per unit area in the focal volume. The results for the strength of the Raman signal at 614 and 1186 cm⁻¹ are shown in Figure 3. For molecules down to few thousands (~6000) we get an EF > 10⁶ (detailed calculation is given in the Supporting Information) for both the peaks at 614 and 1186 cm⁻¹. Since most rhodamine molecules were attached to silica, chemical enhancement due to the binding of Rhodamine to Ag played a negligible role, implying the high enhancement to be almost entirely electromagnetic in nature. The strength of the signal and therefore the EF remained constant to within 5–10% for a particular substrate, implying uniform distribution of the molecules throughout the surface of the cm sized substrate.
IV. CONCLUSION

We have described a wafer scale method of fabricating porous 3D metallic (Ag) NP arrays that are held in place by dielectric (SiO$_2$) rods. The optical response of these structures showed a complex behavior arising out of plasmonic interactions in 3D and would require detailed theoretical and experimental investigation. The structures are inherently robust and have large shelf lives (>few months), and show excellent spatial uniformity as substrates for SERS measurements. While an extremely large SERS EF, capable of single molecule detection, has been obtained in certain regions ("hot spots") for colloidal NPs, as well as for NP arrays in 1D and 2D, for practically important applications, the enhancement factor, as well as the spatial density of the metallic NPs within the laser illumination volume, arranged in a porous 3D array needs to be large, such that any molecule in the vicinity of the metal NP gives rise to an enhanced Raman signal. Having a large number of metallic NPs within the laser illumination volume increases the probability of a target molecule to come in the vicinity of the metal NPs. This has been achieved in the structures reported here, where high EF in conjunction with large surface area available in a three-dimensional structure, makes the 3D NP arrays attractive candidates as SERS substrates.

ASSOCIATED CONTENT

Supporting Information
Details of the sample preparation along with the experimental methods and the estimation of enhancement factor. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: johnsonthonga196@gmail.com (H.J.S.); ambarish@ece.iisc.ernet.in (A.G.).

Notes
The authors declare no competing financial interest.

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