**THE EUROPEAN
PHYSICAL JOURNAL D**

Regular Article

Optimizing surface-enhanced Raman scattering by template guided assembling of closely spaced silver nanocluster arrays

C.H. Xu, B. Xie, Y.J. Liu, L.B. He, and M. Han[a]

National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering,
Nanjing University, 210093 Nanjing, P.R. China

Abstract. We present an easy approach to synthesize closely spaced regular arrays of silver nanoclusters, which are self-assembled by depositing gas-phase synthesized metal nanoclusters onto pre-patterned triblock copolymer templates. The array has a high particle density of about 2×10^3 particles per μm^2, and an average interparticle space of about 20 nm. The surface plasmon resonance wavelength of the array is tuned due to the interparticle plasmon coupling. High SERS sensitivity for less than one layer trans-1,2-bi-(4-pyridyl) ethylene (BPE) molecule detection, with an enhancement factor of 2.6×10^6, has been demonstrated for a substrate with this array. The enhanced Raman signal was found to be 5 times higher than that measured from the substrate with randomly distributed silver nanoparticles.

PACS. 81.16.Dn Self-assembly – 78.30.-j Infrared and Raman spectra

1 Introduction

Plasmonic nanostructures have recently attracted much interest because of their unique optical properties and novel applications [1]. Many efforts are aimed at applying surface enhanced Raman scattering (SERS) with specially prepared noble metal substrates for organic molecules sensing [2–5]. Optimization of the Raman amplification is of paramount importance for applying the SERS technique for single molecule detection, as well as for optical sensors in nanoscale integrated devices. For such optimization, it is a great challenge to find out the connection existing between the local surface plasmon (LSP) resonance and the Raman enhancement factor.

Closely spaced regular nanoparticle arrays composed of metal particles with nanoscale sizes and interparticle gaps appear to be more suitable substrates for improving our understanding of the mechanisms involved in the SERS effect than colloid-based system and randomly roughed surface. Thanks to their very narrow particle size and shape distribution, these arrays exhibit very sharp LSP resonances leading us to demonstrate experimentally the required condition for the optimization. They have been found to be the most efficient SERS substrates owing to junction plasmons created in the nanometer interparticle gaps (hot spots). Maximum LSP enhancement can be achieved under resonant excitation conditions, by tuning the plasmon resonance of the substrate to near the excitation-laser wavelength. Furthermore, closely spaced regular nanoparticle arrays can give rise to more homogeneous and reproducible SERS results due to their spatial uniformity of high density hot spots. As has been pointed out [6], the average enhancement factors have greater relevance for rational design of optimized SERS substrates.

In this paper, we introduce a simple way to prepare SERS substrates by hierarchical self-assembly of silver nanocluster arrays on triblock copolymer templates. The shift of the surface plasmon resonance wavelength of the array due to interparticle near-field coupling was observed. The advantages of using these regular closely spaced nanoparticle arrays in SERS experiments compared to randomly distributed nanoparticles films were investigated. The Raman enhancement factor for BPE molecule detection was found to be 5 times improved.

2 Experimental procedures

Triblock copolymer poly(styrene-b-butadiene-b-styrene) (SBS) (Aldrich Chemical Inc.), with a molecular weight of 140 000 Da, a polydispersity index of 1.2, and a PS weight fraction of 30%, was used for fabricating nanoscale patterned templates through microphase separation process. The copolymer was dissolved in toluene to produce a 4 wt% solution. A small amount of the solution ($\sim$20 μL) was spin-coated onto the fused quartz substrates at about 2500 rpm for 30 s to form a film. Then the as-cast films were placed inside a glass vessel with some drops of volatile toluene added as annealing solvent. The vessel was carefully sealed to generate a very slow evaporation

a e-mail: sjhanmin@nju.edu.cn

rate ($\sim$0.001 mL/h) of toluene. The solvent annealing time was usually 3 days followed by 1 day of slow drying by exposing the polymer film in air. The surface morphology of the SBS copolymer films was characterized with an atomic force microscope (AFM) (NTEGRA Probe NanoLaboratory, NT-MDT Co.) working on semi-contact mode.

Silver nanoclusters were then deposited onto the prepatterned SBS copolymer film surface. The clusters were generated with a magnetron plasma aggregation cluster source. The experimental setup and operation parameters for cluster beam generation have been described in detail elsewhere [7,8]. In our experiment, the clusters were perpendicularly deposited onto the SBS copolymer templates in a high vacuum chamber (10^{-7} torr), with a low cluster coverage of $< 100\%$. The deposition was carried on at room temperature, and the deposition rate was controlled to be about 2 Å/s. Transmission electron microscopy (TEM) was used to characterize the morphologies of silver nanocluster deposits.

Optical extinction spectra of the silver nanocluster films were measured with a UV-Visible spectrophotometer. The silver cluster covered SBS films were used as plasmonic substrates for surface enhanced Raman scattering measurements of trans-1,2-bi-(4-pyridyl) ethylene (BPE). The BPE used in this research was provided by Aldrich Co. SERS spectra were recorded on a confocal Raman spectroscope (NT-MDT NTEGRA Spectra) using a 473 nm laser excitation, which is close to the surface plasmon resonant wavelength of silver nanocluster arrays [9]. The laser beam was focused with an objective to give an illuminated area with 350 nm in diameter on the sample surface. To check the sensitivity of SERS on SBS molecular probe and reduce the damage to samples, the initial laser power (about 10 mW) was attenuated, by the order of 10^{-1} or 10^{-2}, with a circular variable neutral density (ND) filters.

3 Results and discussion

Block copolymers tend to self-assemble into a variety of well-ordered nanostructures from several to hundreds of nanometers because of the chemical immiscibility of the covalently linked segmental chains [10]. In our study, the microphase separation of SBS films were controlled to form parallel cylindrical periodic domains, the space between the adjacent in-plane PS domain cylinders is around 38 nm (Fig. 1). The long range ordering stripe-like domains can serve as a preformed scaffold for silver nanoclusters. Regular arrays of silver nanoclusters can be obtained by decorating silver clusters to the PB domains [11].

Gas-phase synthesized silver clusters were deposited onto the cylindrical SBS copolymer templates perpendicularly at room temperature, with a low coverage of about 10%. As shown in Figure 2a, the silver nanoclusters form chain-like arrays with nearly equal inter-chain spaces, approximately 38 nm, corresponding to the period of the in-plane PS domain cylinders in the SBS copolymer substrate. The mean diameter of the silver nanoparticle is about 10 nm, and the average particle-particle distance
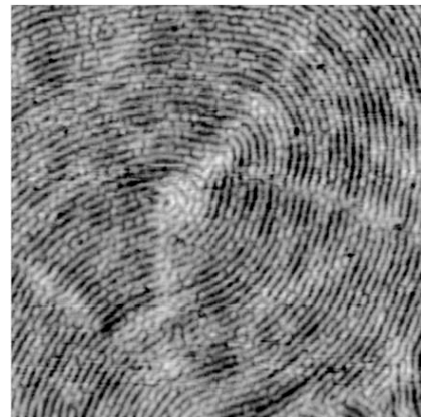

Fig. 1. Typical 2×2 μm phase image of the SBS template by tapping mode AFM.
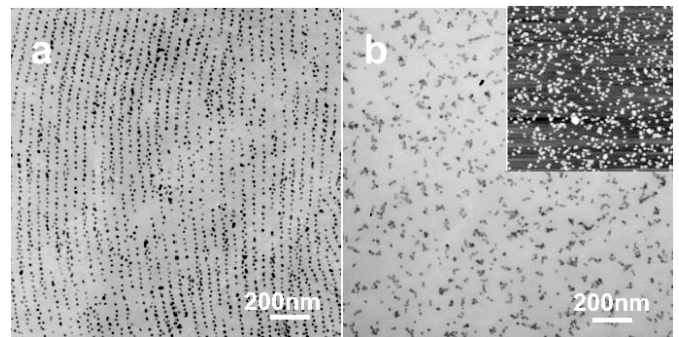

Fig. 2. TEM images of silver nanoclusters deposited on (a) SBS pre-patterned template; (b) amorphous carbon surface. The inset shows typical 3×3 μm height image of Ag nanoclusters on silica glass measured by tapping mode AFM.

within the chain is about 20 nm. A high particle number density about 2×10^3 particles per μm^2, could be calculated for this ordered arrays. For comparison, silver nanoclusters were also deposited onto amorphous carbon films supported with copper grid, or on silica glass. From the TEM image shown in Figure 2b and the corresponding AFM image shown in the inset, these two deposits have similar morphologies. Silver nanoclusters are randomly distributed and short-range aggregated due to limited diffusion on the substrate surface, and the particle sizes are significantly uniform in comparing with the case of patterned SBS copolymer substrate.

The optical extinction spectra of the SBS copolymer substrate templated siliver nanocluster arrays manifest an intriguing shift on the surface plasmon resonance (SPR) wavelength, as illustrated in Figure 3. For silver nanoclusters deposited on silica glass, the maximum extinction is at 395 nm. However, the SPR peak appears at 424 nm with a narrower width when silver nanoclusters are deposited on the SBS template. The SPR properties of metal nanoclusters are mainly determined by the size and shape of particles, the nanostructure of particle assembly and the surrounding medium dielectric function [12]. From Figure 2, we can find that there is no significant difference on the size and shape of the silver nanoclusters between
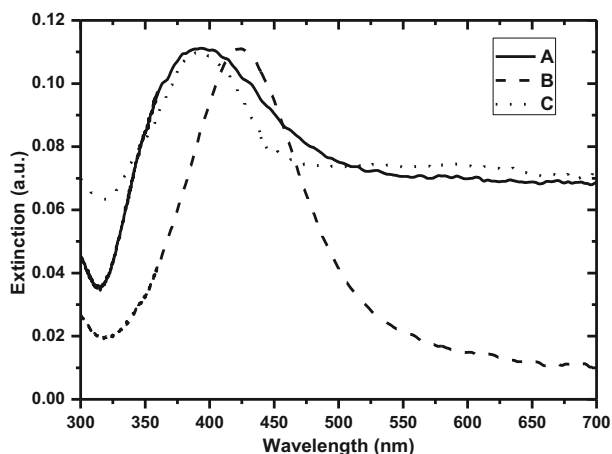
Fig. 3. Optical extinction spectra of silver nanocluster assemblies. (A) Randomly distributed nanoclusters deposited on silica glass substrate; (B) silver nanocluster linear arrays on SBS template; (C) randomly deposited silver nanoclusters embedded in SBS film.

Fig. 4. Raman spectra of trans-1,2-bi-(4-pyridyl) ethylene (BPE) molecules. (A) On substrate with silver nanoclusters deposited onto SBS template. (B) On substrate with silver nanoclusters deposited onto silica glass. (C) On pure silica glass. For spectra (A, B, C), 2×10^{-6} M BPE concentration and $100\ \mu$W laser power was used. Spectrum D was measured from of BPE molecules on pure silica glass with a 4×10^{-2} M BPE concentration and 1 mW laser power. The spectrum D was magnified 150 times for clarity. Both spectrum A and B has an increased baseline, which come from the luminescence background that always accompanies SERS spectra.

the two kinds of substrates. Furthermore, the SPR peak of silver nanoclusters exhibits little difference when they were embedded in SBS film (see Fig. 3), which excludes the influence from the dielectric functions of different surrounding mediums. On the other hand, the SPR property change of SBS copolymer templated siliver nanocluster arrays can be explained if we take into account the near field electromagnetic coupling of adjacent nanoclusters in closely spaced nanoparticle arrays. It has been manifested that the SPR peak of noble metal nanocluster assembly is red-shifted with the decreasing of interclusters distance [13]. Therefore, we attribute the 29 nm shift on the SPR wavelength observed for the regular arrays of closely spaced nanoclusters on SBS template to the interparticle near-field coupling.

For SERS measurements, about 10 μL of 2×10^{-6} M BPE methanol solution was dropped onto the substrates covered with silver nanoclusters and dried in air to hold a BPE molecule surface density as low as 2×10^{-13} mol/mm^2. The laser beam was attenuated to about 100 μW before focusing onto the surfaces of samples. Within the laser illumination spot, about 350 nm in diameter, there's estimated to be about 1.2×10^4 BPE molecules. That means the coverage of BPE molecules is much less than one monolayer if we assume the approximate area of a single BPE molecule is 30 Å^2. With such low BPE concentration, no Raman signal is detectable under the above laser illumination condition if only pure BPE specimen is used. However, strong Raman lines can be observed at about 1010, 1200, 1340, 1610, and 1640 cm^{-1}, corresponding to the Raman of BPE molecule, when the BPE molecules are attached to the silver nanoclusters covered substrates, as shown in Figure 4. Obviously, Raman scattering of BPE molecules is significantly enhanced by the SPR local field near the silver nanoparticle surface generated by 473 nm laser.

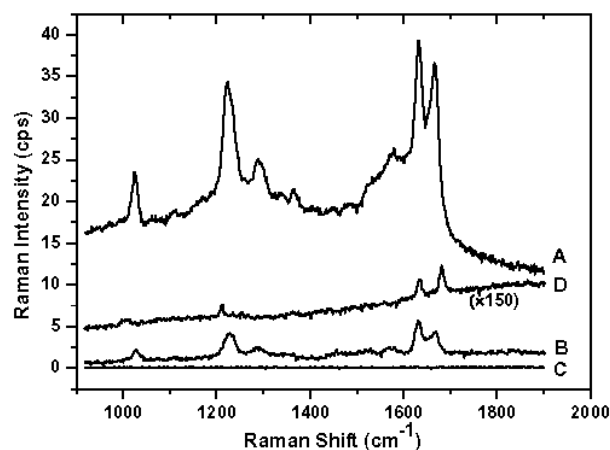From Figure 4, it is apparent that the SERS of BPE molecules measured on the substrate with SBS templated regular silver nanocluster arrays is much stronger than that measured on the substrate with randomly distributed silver nanoclusters. The larger enhancement of the former can arise from two facts: (1) under SBS template guiding, closely spaced regular arrays of silver nanoclusters are formed, which provides homogeneously distributed hot spots with high density. Great local field enhancement are realized by the SPR coupling at the hot spots; (2) the surface plasmon resonance band of the closely spaced regular arrays of silver nanoclusters is shifted to near the excitation-laser wavelength, great LSP enhancement can be achieved under resonant excitation conditions. In fact, the Raman intensity varies significantly with moving the detecting position when a silica glass covered with randomly distributed silver nanoclusters is used as substrate, while stable Raman signals can be detected at various positions on the substrate with closely spaced regular arrays of silver nanoclusters. Obviously, the later one is more efficient for SERS measurement.

To estimate the SERS enhancement factor per molecule for the silver nanocluster assembly, a reference specimen was prepared on silica glass surface by increase the BPE concentration to 2×10^4 times higher. Under 1 mW exciting laser power, which was also 1 order of magnitude higher than that used for SERS measurements, the reference Raman signal of pure BPE molecules was measured and shown in Figure 4. Raman gains were then calculated approximately. For the SBS templated closely spaced regular silver nanocluster arrays, a 2.6×10^6 Raman gain was obtained, which is 5 times of that estimated for the randomly distributed sliver nanocluster assembly (5.1×10^5).

4 Conclusions

We have demonstrated an efficient way for preparing high density regular arrays of metal nanoparticles for SERS measurements by hierarchical self-assembing of gas-phase synthesized metal nanoclusters on block copolymer scaffolds. The surface plasmon resonance was observed to occur at a wavelength that is red-shifted from the single-particle LSPR wavelength, and is ascribed to particle-particle near-field coupling. We have shown efficient SERS detection of BPE molecules by using these arrays as SERS substrate. Typically, a BPE surface density as low as 2×10^{-13} mol/mm^2, less than one layer, has been readily detected. A Raman enhancement factor of 2.6×10^6 is obtained, which was found to be 5 times higher than that measured from the substrate with randomly distributed silver nanoparticles. The improvement can be attributed to the homogeneous spatial distribution and high density of hot spots, as well as the tuning of the plasmon resonance of the substrate to near the excitation-laser wavelength, which gives rise to a resonant excitation condition for LSP enhancement.

References

1. S. Lal, S. Link, N.J. Halas, Nature Photonics **1**, 641 (2007)
2. K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari, M.S. Feld, Chem. Rev. **99**, 2957 (1999)
3. S. Nie, S.R. Emory, Science **275**, 1102 (1997)
4. N.Félidj, J. Aubard, G. Lévi, Phys. Rev. B **65**, 075419 (2002)
5. R.G. Freeman, K.C. Grabar, K.J. Allison, R.M. Bright, J.A. Davis, A.P. Guthrie, M.B. Hommer, M.A. Jackson, P.C. Smith, D.G. Walter, M.J. Natan, Science **267**, 1629 (1995)
6. D.A. Genov, A.K. Sarychev, V.M. Shalaev, A. Wei, Nano Lett. **4**, 153 (2004)
7. M. Han, C. Xu, D. Zhu, L. Yang, J. Zhang, Y. Chen, K. Ding, F. Song, G. Wang, Adv. Matter. **19**, 2979 (2007)
8. J.B. Chen, J.F. Zhou, A. Häfele, C.R. Yin, W. Kronmüller, M. Han, H. Haberland, Eur. Phys. J. D **34**, 251 (2005)
9. N. Félidj, J. Aubard, G. Lévi, J.R. Krenn, A. Hohenau, G. Schider, A. Leitner, F.R. Aussenegg, Appl. Phys. Lett. **82**, 3095 (2003)
10. F.S. Bates, G.H. Fredrickson, Phys. Today **52**, 32 (1999)
11. Z. Shi, M. Han, F. Song, J. Zhou, J. Wan, G. Wang, J. Phys. Chem. B **110**, 18154 (2006)
12. A.J. Haes, R.P. Van Duyne, J. Am. Chem. Soc. **124**, 10596 (2002)
13. L.L. Zhao, K.L. Kelly, G.C. Schatz, J. Phys. Chem. B **107**, 7343 (2003)