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A route to increase the enhancement factor of surface enhanced Raman scattering (SERS) via a high density Ag flower-like pattern

from

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Introduction:

- Very localized plasmon modes, created by strong electromagnetic (EM) coupling between two adjacent metallic objects, dominate the SERS response in an array of nanostructures.
- Different preparation techniques focus on the organization of nanoparticle arrays with controllable inter-particle gaps of SERS substrate such as porous anodic aluminum oxide nanochannels, Langmuir–Blodgett technique, nanoparticle assembling by solvent evaporation.
- Hot-spots induced in interstitial gaps between the nanoparticles, have major contribution to the Raman enhancement.
- From theoretical point of view finite difference time domain (FDTD) method allows to assess the relative contributions of different geometries to the experimentally observed SERS intensities.

Experimental section:

- The electrochemical depositions of different silver geometries were carried out within a two-electrode system on a Si (100) substrate.
- The Si (100) plate was mounted as a cathode with a graphite rod as the anode. The applied potential E was controlled at ~ 100 V with the constant potential mode by a dc voltage-stabilized power supply. Following deposition, the samples were rinsed with ethanol.
- FDTD calculation has been done to calculate local EM fields at the excitation wavelength 514 nm. The Ag dielectric function was represented using a Drude model, with parameters chosen to match experiments for wavelengths in the 350–600 nm range. The enhancement factor is $EF = (E_{loc}/E_0)^4$, where E_0 is incident electric field enhancement.

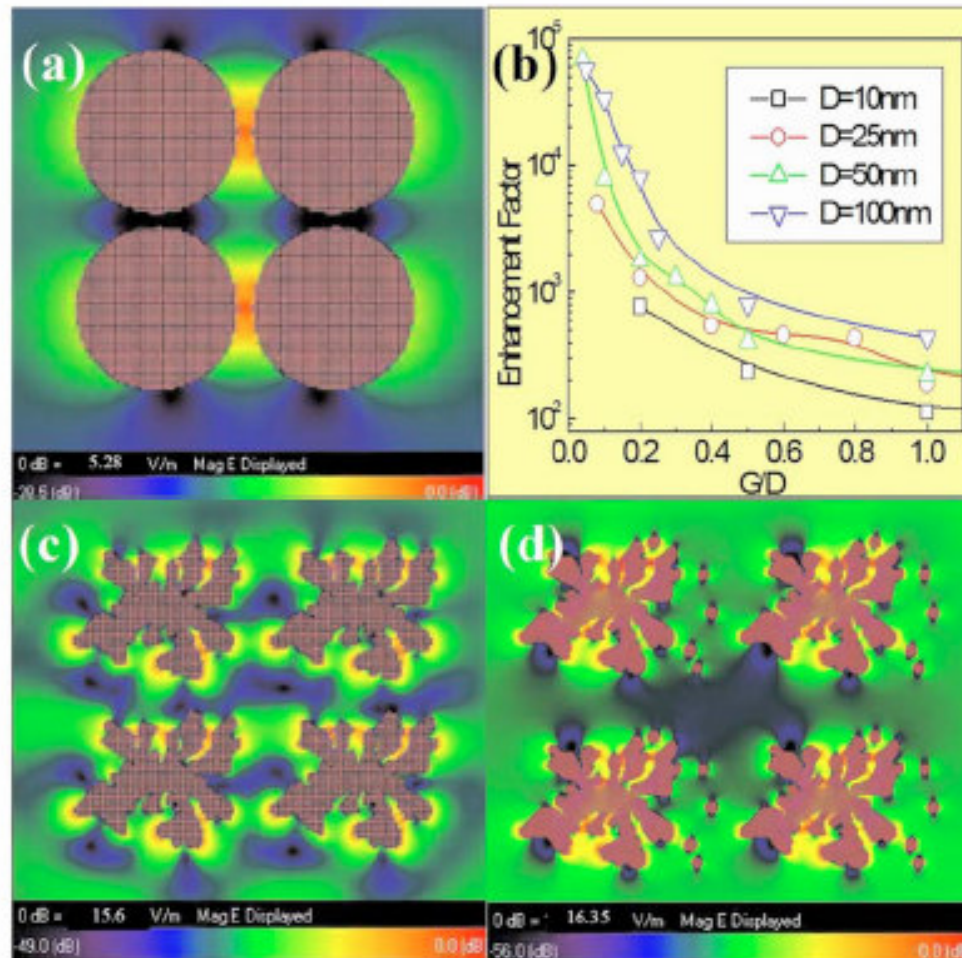


FIG. 1. (Color online) (a) A color contour plot of the near-field distribution for a (10,2) nm Ag nanoparticle arrays. (b) Enhancement factor vs G/D for the nanoparticle arrays of different diameters. (c) A color contour plot of the near-field distribution for a (392 \times 341 \times 40) nm flowerlike pattern. (d) Same size of flower as (c) with additional nanoparticles (40 nm).

The EF of different dimensions of flower-like Ag nanostructures:

Flower dimension (nm)	Distance of flowers (nm)	Nanoparticles	EF
261 × 227 × 40	200	No	12201.43
261 × 227 × 40	200	40	29540.02
392 × 341 × 40	50	No	59224.09
392 × 341 × 40	50	40	71461.32
785 × 683 × 40	200	40	5734.25
785 × 683 × 40	200	No	1235.3

Experimental section:

- They prepared high density Ag nanoparticle arrays and fractal flowerlike patterns on Si substrate by electrodeposition technique with tuning various parameters.
- With the above prepared Ag nanostructures, the SERS performances are investigated using Rhodamine 6G (R6G) molecule 10^{-4} (M) methanol solution and 514 nm laser excitation.
- Allowing the molecule adsorption, the substrates were maintained for 24 h into R6G solution and then were taken out and rinsed thoroughly with methanol.

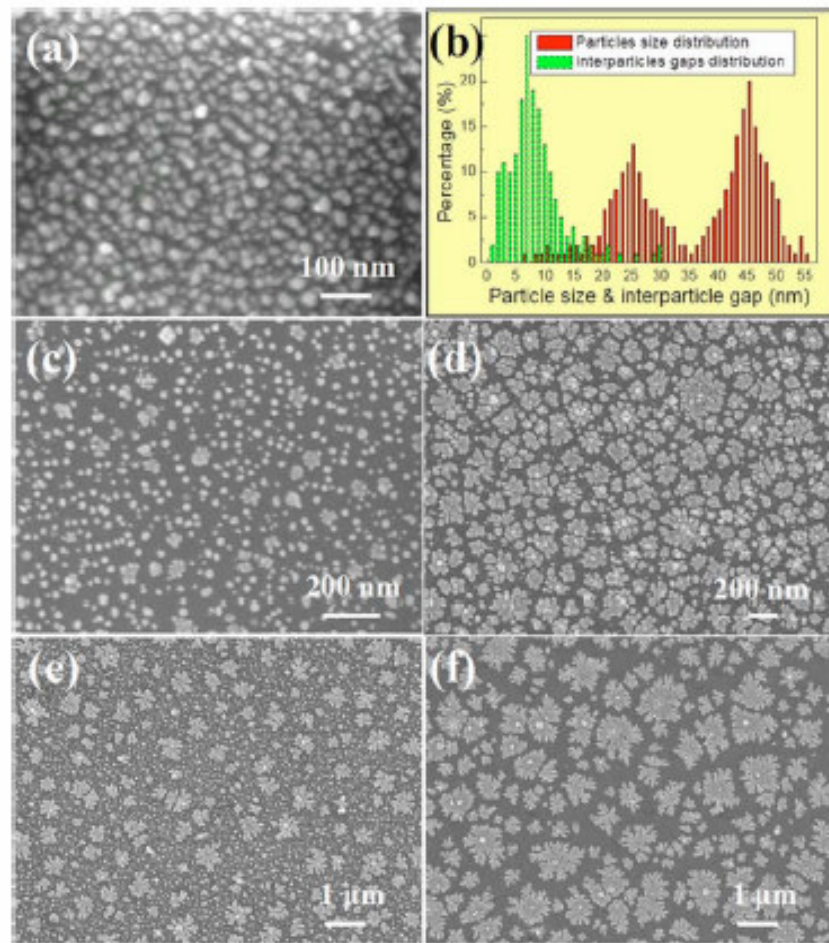


FIG. 2. (Color online) The SEM images for different Ag nanostructures synthesized at applied potential, AgNO_3 (aq) concentration, and reaction time. (a) Nanoparticles arrays, 100 V, 0.001 mM, and 10 min. (b) The particle size and interparticle gap between nanoparticles of (a). (c) Nanoparticle pattern, 15 V, 0.01 mM, and 30 min. (d) High density flowers, 15 V, 0.1 mM, and 20 min. (e) flowers+nanoparticles pattern, 15 V, 0.01 mM, and 60 min. (f) Flower pattern, 5 V, 0.1 mM, and 20 min.

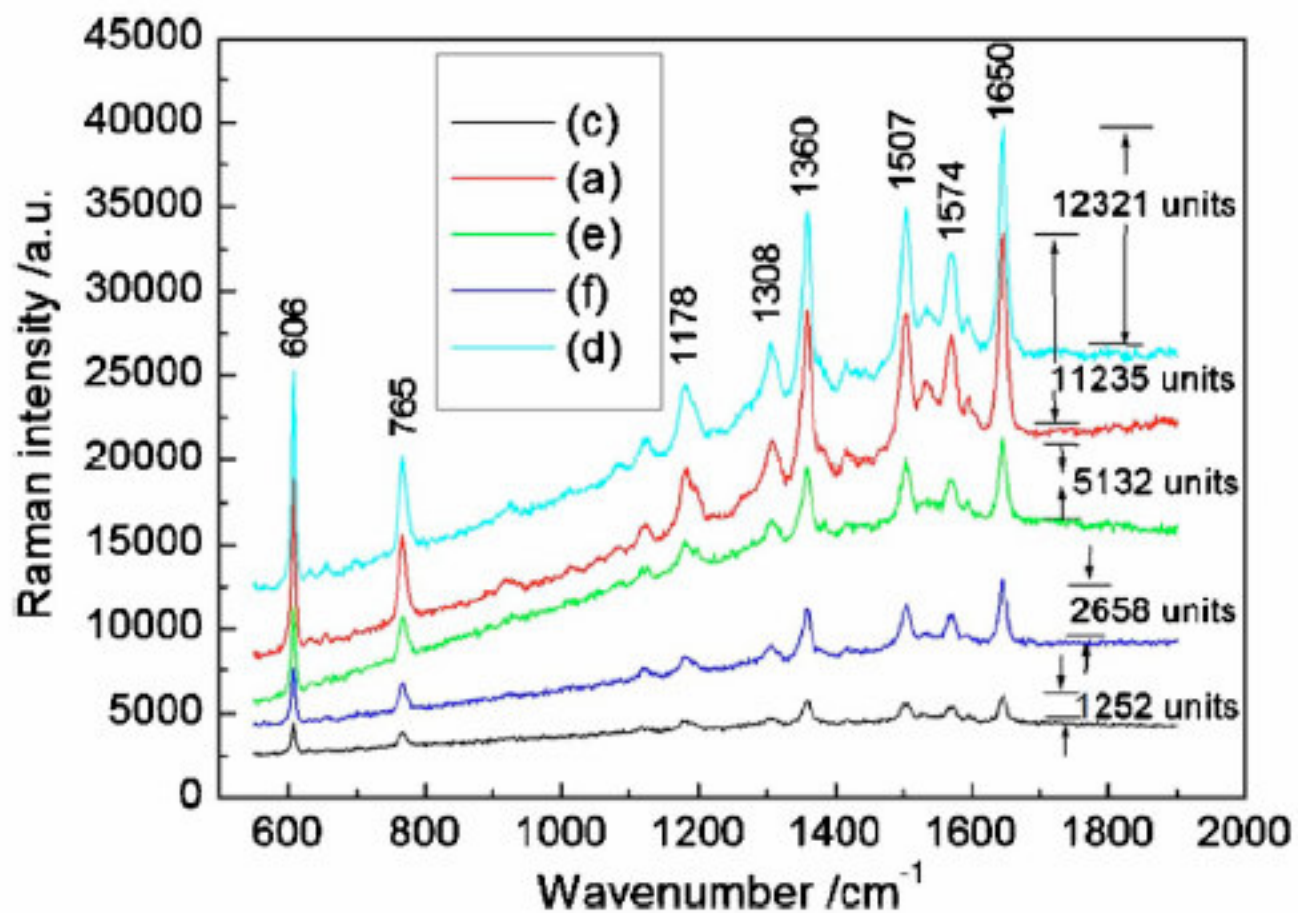


FIG. 3. (Color online) SERS spectral comparison of Ag nanoparticles arrays (sample a in Fig. 2) and flowerlike patterns (samples c, d, e, and f in Fig. 2). A quantitative enhancement comparison is shown as insets. (Excitation power of 20 mW, excitation length of 514 nm, charge-coupled device (CCD) detector, scan time of 30 s.)

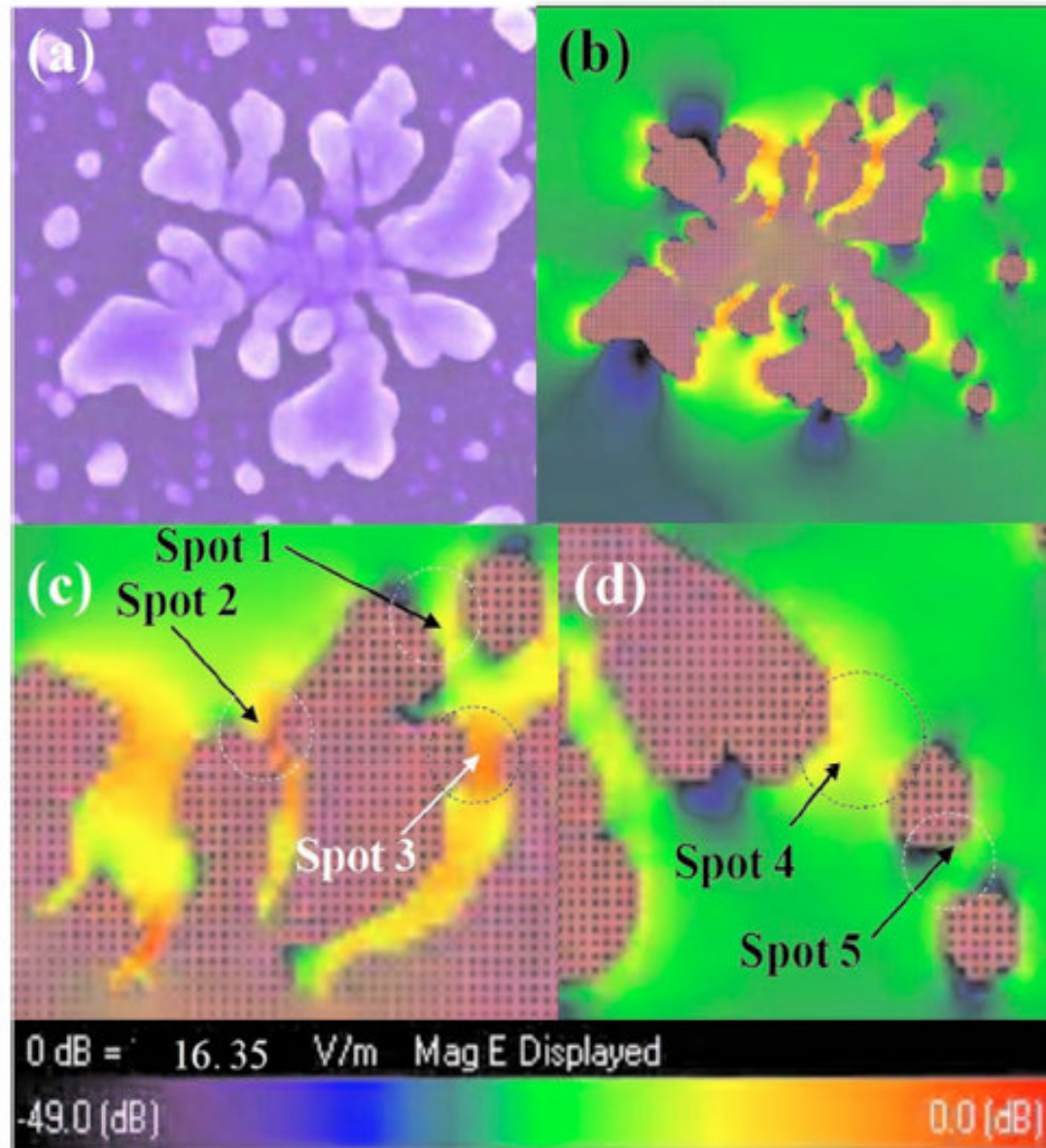


FIG. 4. (Color online) (a) A magnified flower in Fig. 2(d). (b) A magnified model pattern in Fig. 1(d). [(c) and (d)] A magnified leaves area from (b).

- This strong enhancement is due to the fact that the flowers are assembled on the Si substrate with a very high density and with many horns and, therefore, the hot spots are expected to be abundant.
- The interaction between leaves to leaves could contribute stronger local EM field enhancement than those of particles to particles.

Summary:

- A route to prepare a high enhancement factor of SERS substrate via a high density Ag flowerlike pattern has been explored.
- The present investigation opens a possibility of applying such fractal nanostructures as SERS substrate offering excellent properties and further increasing the enhancement factor of the SERS.

Thank you