Fabrication of SERS substrates using self-assembled nanostructures

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Introduction

Major disadvantage of Raman spectroscopy, very small cross section of Raman scattering, can be overcome by considerable enhancement of the local electromagnetic field due to excitation of localized surface plasmon resonances in metal colloidal particles or structured metal surfaces. This effect, surface-enhanced Raman scattering (SERS), has great potential for applications in biology, medicine and diagnostics but commercial fabrication of the so-called SERS substrates remains a challenge.

Large enhancement factors and reproducibility are two main requirements for high-quality SERS substrates. Unfortunately, they are often complementary. We believe that reproducibility is the key factor for future commercialization of SERS-active surfaces as well as for designing experiments enabling deeper understanding of SERS principles.

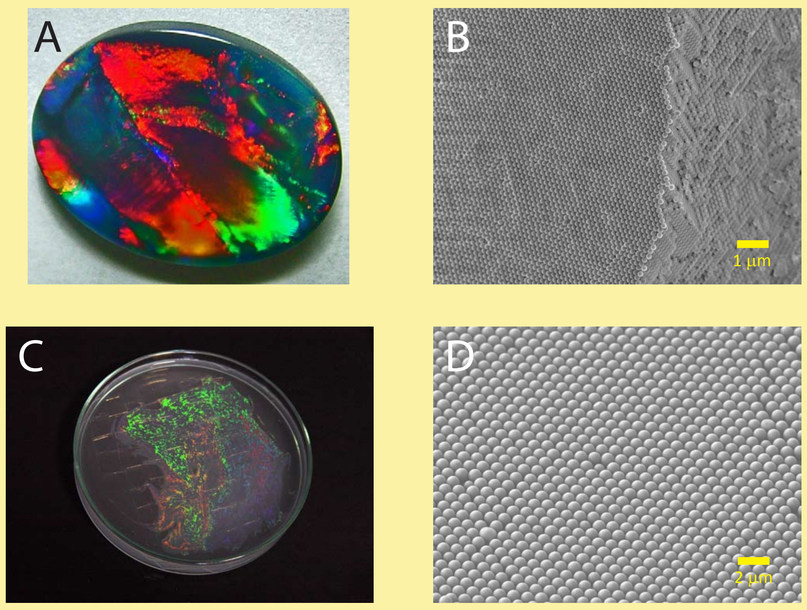
We have designed and fabricated highly reproducible metal nanostructures using self-assembled submicrometer polystyrene spheres. This technique is advantageous thanks to its low cost and the possibility to create large surfaces (i.e. compared to lithographic methods).

Self-assembly

Self-assembly is a spontaneous process commonly encountered in nature, by which objects autonomously assemble into complexes. These structures often have regular patterns because they are formed as systems with a minimum of free energy.

A striking example of these systems are natural opals which are created by self-assembly of silica spherical particles into a close-packed structure. Artificial opals can be fabricated from water dispersions of submicron polymer spheres using the same principle. By restricting the assembly to two dimensions only, hexagonal close-packed monolayer of spheres is formed.

In our experiments, we create this structure by depositing polystyrene (PS) spheres on water surface.



(A) Natural opal [downloaded from *static.opalauctions.com*]. (B) Self-assembled PS spheres of diameter 173 nm forming a synthetic opal (SEM micrograph). (C) Monolayer of self-assembled PS spheres of diameter 535 nm on water surface in a Petri dish. (D) Monolayer of self-assembled PS spheres of diameter 920 nm (SEM micrograph).

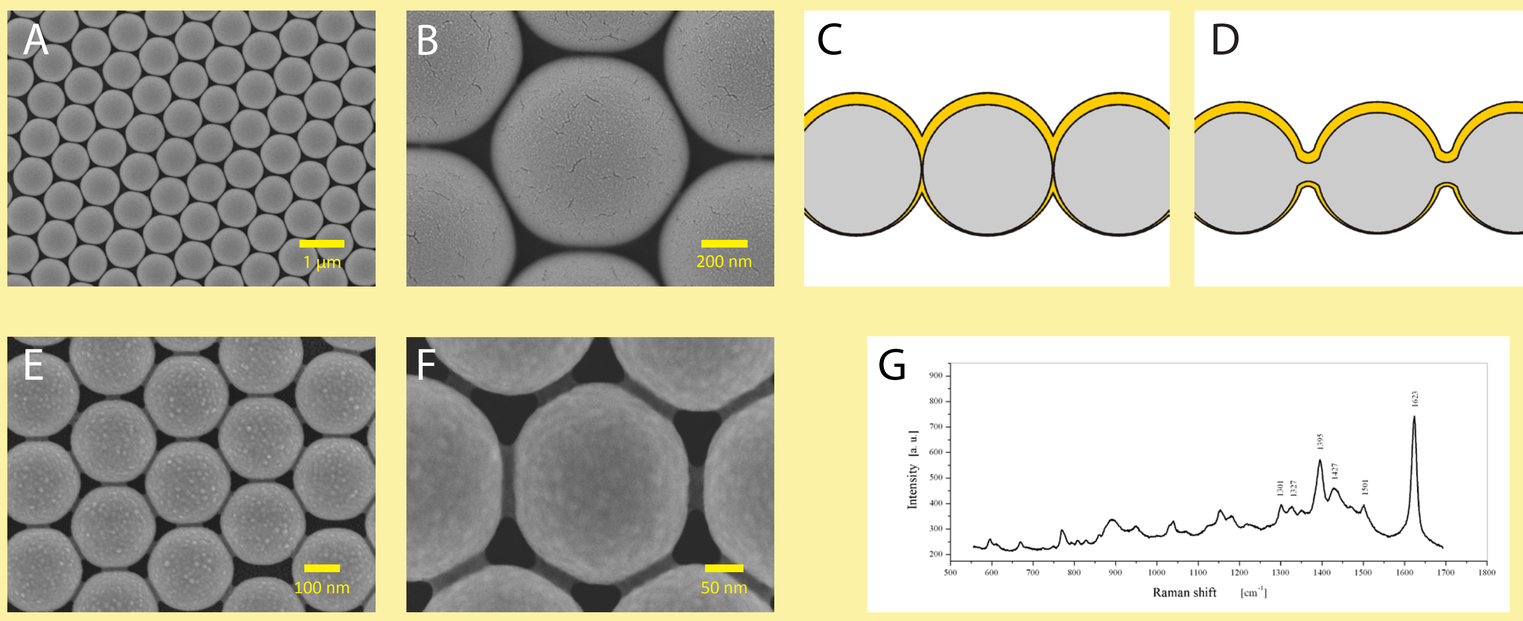
Fabrication of metallic nanoshells

Sputtering of metal onto the surface of self-assembled monolayer of PS spheres is a simple way to fabricate hexagonally ordered nanoshells - metallic shells around a dielectric core which are intensively studied because of their interesting plasmonic properties. Their localized surface plasmon resonances are shifted to NIR spectral region compared to purely metallic spheres which makes them more suitable substrates for biomedical applications. Moreover, the spectral position of the resonances can be easily controlled by diameter of the spheres and shell thickness.

Using the self-assembly technique, the highest possible density of nanoshells, and so the highest number of spots with local electromagnetic field enhancement, is achieved. More importantly, the enhancement is reproducible and homogenous over the whole surface.

Sintering (heating below melting point) of the assembled PS particles prior to sputtering creates small bridges between the spheres which improve the stability of the structure and could also serve as an aditional source of enhancement.

SERS activity of gold-sputtered spheres was verified by measuring SERS spectra of methylene blue (MB). The substrates were dipped in solution of MB for 72 hours and rinsed with deionized water. We obtained SERS spectra of high quality down to concentration 10^{-6} M.



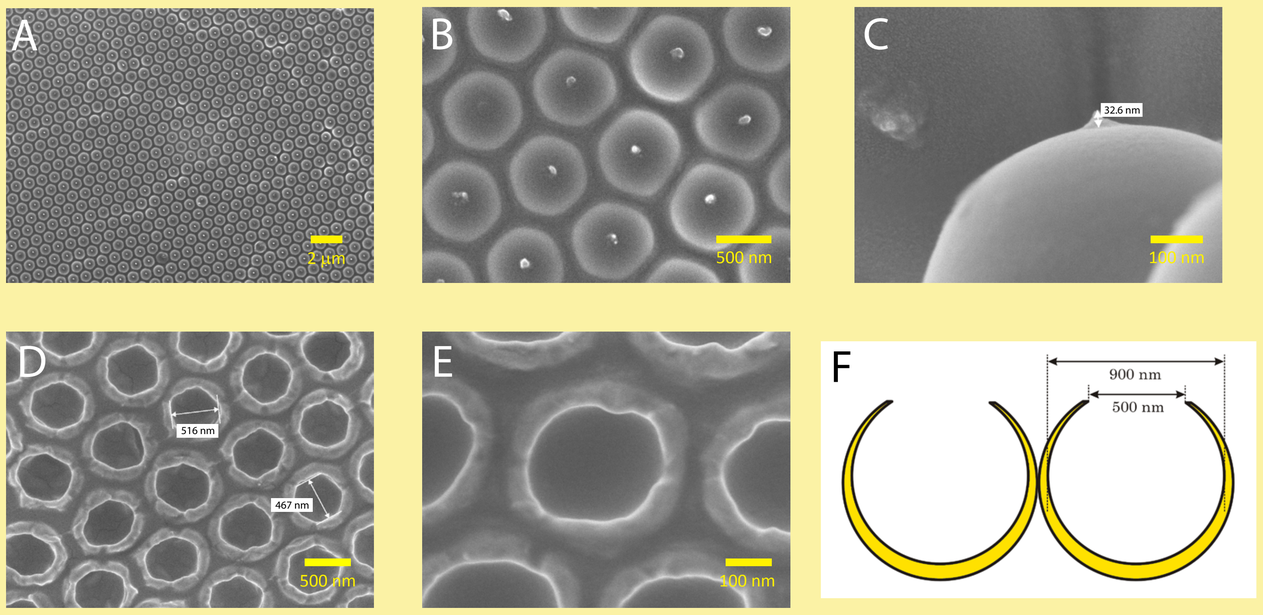
(A) Self-assembled PS spheres of diameter 920 nm sputtered with 20 nm of Au. (B) Detail of the connections between the spheres. (C) Schematic diagram of PS spheres sputtered with a thin layer of metal. (D) Schematic diagram of sintered PS spheres sputtered with a thin layer of metal. (E) Sintered self-assembled PS spheres of diameter 266 nm sputtered with 20 nm of Au. (F) Detail of the connections between sintered spheres sputtered with 20 nm of Ag. (G) SERS spectrum of methylene blue (MB) on PS spheres of diameter 173 nm sputtered with 20 nm of Au (Raman microspectrometer *LabRam HR800* HORIBA Jobin Yvon, power 0.2 mW, excitation wavelength 633 nm, accumulation time 60 s, MB concentration 10^{-5} M).
(A), (B), (E), (F) are SEM micrographs.

Fabrication of metallic nanocups

Further modification of metal sputtered monolayers of hexagonally assembled PS spheres can lead to SERS substrates with even more interesting plasmonic properties. Signal enhancement originating from an array of close-packed metallic nanocups should be very high because of sharp edges on the cups facing the incident light.

This structure can be fabricated from metal nanoshells in two steps - turning the metal-coated monolayer upside down and dissolving the PS spheres. In the first step, we pressed the coated monolayer on a glass substrate into polydimethylsiloxane (PDMS) and removed the glass (lift-off technique). The spheres left in polymer remained ordered (see Figure A, B). Small metal particles which rest upon the top of PS microspheres (detail in Figure C) originate probably from metal sputtered on the glass-sphere interface. We assume that they could serve as another source of signal enhancement. The PS spheres were then dissolved in acetone and toluene.

From SEM micrographs we could measure the size of holes and estimate the shape of obtained gold nanocups (Figure F).



SEM micrographs: (A) Unperturbed ordering of PS spheres of diameter 920 nm sputtered with 40 nm of Au after pressing them into PDMS and detaching them from the glass substrate. (B) Detail of the same structure. (C) Detailed side-view of a single gold-coated sphere. (D) Au nanocups obtained by dissolving the PS spheres. (E) Detail of the same structure. (F) Estimated shape of gold nanocups based on measurements of SEM micrographs.

Conclusion

Self-assembly of monodisperse submicrometer polystyrene spheres is a simple technique which can be used for the fabrication of SERS-active surfaces. By sputtering a thin layer of metal over the structure, hexagonal arrays of nanoshells were created. Measured SERS spectra of methylene blue verified SERS activity of this substrate. By simple modification, we obtained metal nanocups with undisturbed ordering in two short steps. Major advantages of this approach are its low cost, the possibility to create relatively large areas and high reproducibility of this type of SERS substrates.

References

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