A versatile method to fabricate particle-in-cavity plasmonic nanostructures

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We have developed a versatile method to fabricate gold particle-in-ring and magnetic particle-in-nanobowl plasmonic nano-structures, which are of great potential for the investigation of the surface enhanced Raman scattering spectroscopy and the magneto-optical effect, respectively.

Noble metal-based plasmonic nanostructures manipulate and concentrate light in nanoscale regions that are much smaller than conventional optic components. When such nanostructures are illuminated with light, a collective oscillation of the quasi-free electrons called surface plasmons generates a strong optical resonance, consequently producing enhanced near fields in deep subwavelength scales that enable interesting applications, such as waveguides, biochemical sensors, and surface enhanced Raman scattering (SERS) spectroscopy. 1–3

Plasmon resonances of nanostructures strongly depend on their geometries and can be tailored throughout the visible and near-infrared part of the spectrum with structures of different shapes, such as nanoshells, nanocubes, nanorings, and nanorods. 4–9 A number of publications about the particle-in-cavity plasmonic nanostructures have been recently reported. 10–14 Hao and co-workers have presented a concentric disk-in-ring cavity with a particularly high tunability. 15 This structure sustains both subradiant and superradiant modes set up via hybridization of individual disk and ring plasmons, resulting in a strong field enhancement. The field enhancement is further increased when the symmetry of the structure is broken, which is of significant potential as a substrate for surface enhanced spectroscopies. 11,12 Such a non-concentric disk-in-ring cavity additionally exhibits a highly tunable Fano resonance, which can be used for localized surface plasmon resonance (LSPR) sensing with a large sensitivity. However, most of these structures were fabricated by electron beam lithography. Recently, magnet–metal hybrid plasmonic nanostructures have attracted much interest due to the observation of a plasmon enhanced magneto-optical (MO) Faraday rotation effect. 13–16 In particular, the composite shape has been found to exhibit a strong influence on the MO effect. Although varied shapes including core–shell, ellipsoid, and sandwich have been developed, 16–18 simple methods to achieve the magnetic core–metal cavity asymmetric structure are still needed.

We have previously described a method to fabricate geometry controllable nanobowl and gold (Au) particle-in-nanobowl cavity structures using ion milling and vapor HF etching. 19 This symmetry-broken Au particle-in-nanobowl structure exhibits strong near-field enhancements at the top edge and the particle–bowl junction, which we experimentally proved via the location dependent SERS spectroscopy. 20 In this communication, we modify the previous method to fabricate Au particle-in-ring and magnetic particle-in-bowl plasmonic nanostructures. This particular approach comprises an ensemble of techniques including bottom-up methods (e.g. wet-chemical synthesis) and top-down methods (e.g. metal sputtering, ion milling, and vapor HF etching). The combination of bottom-up and top-down methods offers a number of advantages: (i) simple and low cost; (ii) core particle composition and shape changeable and (iii) cavity geometry controllable. The optical and/or magnetic properties of the particle-in-cavity structure are mainly determined by the interaction between the core particle and the cavity. A variation of the core particle composition (e.g. magnetic materials or noble metals), the shape (e.g. sphere or rod), or the cavity geometry (e.g. ring or bowl) may lead to different plasmon–plasmon or magneto-plasmon coupling effects. In addition, finite difference time domain (FDTD) simulations show that the offset particle-in-ring cavity produces a much stronger near-field enhancement than the concentric one under optimal conditions, indicating its promising potential as SERS substrates for single molecule detection.

Experiment and simulation

Au particles were synthesized by adding 0.8 mL of 1% (m/v) sodium citrate (Acros Organics) into a 100 mL boiling aqueous solution containing 0.01% (m/v) hydrogen tetrachloroaurate trihydrate (Acros Organics). Fe 2 O 3 particles were prepared by boiling 20 mM aqueous solution of ferric chloride (Aldrich) for 2 days. The SiO 2 coating on the Au and Fe 2 O 3 particles was performed using a Stöber process. 21 The SiO 2 -coated Au particles were drop-cast on a Si substrate or deposited on a polydiallyl-dimethylammonium (Aldrich) functionalized Si substrate, followed by sputtering a 30 nm thick Au on the top. Then a 60 s Xe ion milling and a 45 min vapor HF etching were applied to produce Au particle-in-ring cavities. A complete outer Au shell was formed on the SiO 2 -coated Fe 2 O 3 particles by a chemical plating procedure as we described before 29 and the obtained particles were deposited on the Si substrate. Particle-in-nanobowl cavities were created by further employing a 40–120 s Xe ion milling and a 45 min...
vapor HF etching process. All SEM images were obtained by using a Philips XL30 FEG instrument.

Electric field distribution profiles were obtained from the FDTD simulations (Lumerical Solutions, Inc.). We have used the dispersion model for Au derived from the experimental data provided by Johnson and Christy.22 The particle-in-ring cavity was illuminated with light from the top with a polarization parallel to the ring. In the simulation model, the Au particle locates in the centre of the ring or offset from the centre touching the ring.

Results and discussion

Fig. 1 outlines the fabrication steps (1–4) for the particle-in-ring and steps (1, 5–7) for the particle-in-nanobowl cavities. The SiO₂ layer in step (1) plays an important role in both cavity structures because (i) it acts as a template to form the final cavity geometry; (ii) it is removable by vapor HF to create hollow cavities and to make the electromagnetic “hot spots” accessible, which is meaningful for the SERS application; (iii) the coating can be accomplished in a simple Stöber process and the thickness is controllable; and (iv) the coating can be realized on the core particles of different compositions and shapes, such as spheres, rods, stars, and cubes.21,23,24 The sputtering process in step (2) renders us different possibilities to create a nanoring cavity composed of other metals like platinum. However, although the metallic nanoshell coating via chemical plating in step (5) is well established, it has more limitations in terms of the material composition if considering the plating feasibility and the material resistance to HF as well.

Fig. 2A shows the SEM image of the SiO₂-coated Au particles. The size of the Au particles and the thickness of the SiO₂ layer are estimated to be around 60 and 90 nm, respectively, based on the SEM images. Fig. 2B displays the obtained Au particle-in-ring cavity structures with a diameter of about 200 nm. Most of the cavity structures are individually separated from each other. After a closer examination, we found that not only concentric but also offset particle-in-ring cavities exist and the latter account for more than 90% of the total amount. Their high magnification SEM images are shown in Fig. 2C and D. It is clearly observed that in the offset cavity the core particle is offset from the centre and touches the ring. The larger possibility of forming the offset particle-in-ring cavities can most likely be explained by the poor adhesion of the core particles to the substrate.

The Fe₂O₃ particle-in-bowl cavities are another example of the cavity structures prepared using the procedure in Fig. 1. SEM images of the Fe₂O₃ and SiO₂-coated Fe₂O₃ particles are shown in Fig. 3A and B, respectively. The Fe₂O₃ particles are around 70 nm in size and the SiO₂ layer is around 80 nm thick. Fig. 3C shows the Fe₂O₃–SiO₂–Au core-shell particles, synthesized using the sample in Fig. 3B, exhibiting a complete outer Au shell layer. The obtained hollow Fe₂O₃ particle-in-bowl cavities after ion milling and vapor HF etching are shown in Fig. 3D and E. They have a rough bowl edge. Each Fe₂O₃ particle sits inside one bowl with a random location (see the arrows in Fig. 3E). Fig. 3F shows some nanobowl cavities with a smooth bowl edge. More interestingly, a variation of the ion milling time allows us to fabricate the nanobowls with different heights (see Fig. 3F and G) and it may result in different plasmonic behaviors, such as the resonance position and the near field enhancement.25

An obvious advantage of the fabrication method described herein is that it offers us a high tunability for different geometrical particle-in-cavity structures. It supplies the capabilities to change the core particle’s size, shape, and composition, and the cavity’s geometry, diameter and height. Due to a geometrical similarity, previous results of asymmetric disk-in-ring structures11,12 imply that the offset particle-in-ring may also have interesting plasmonic properties. Therefore, we used the FDTD simulation method to investigate the concentric and offset particle-in-ring cavities.
offset particle-in-ring cavities. Fig. 4A and B show the electric field profiles of a concentric and an offset Au particle-in-ring structure (60 nm core size and 200 nm outer diameter of the ring) at their resonance wavelengths of 922 nm, indicating that the latter has a maximum electric field intensity ($|E|^2$) of $2.1 \times 10^5$, 2–3 orders of magnitude larger than the former. The electromagnetic “hot spots” of the offset cavity locate at the gap between the core particle and the ring and they are generated due to the plasmonic coupling effect between the core and the ring as well. This extremely high near-field enhancement is of high importance for the offset particle-in-ring cavity as a substitute for the SERS-based molecule detection and the LSPR sensing. Moreover, recent reports on the enhanced MO effect of the magnetic core–metallic shell nanoparticles\textsuperscript{15,16} imply that the Fe$_2$O$_3$ particle-in-nanobowl hybrid structures may also be a potential candidate to study the magneto-plasmonics interaction phenomenon. More detailed investigation is underway.

Conclusions

In summary, we have presented a general strategy via the combination of chemical synthesis, ion milling and vapor HF etching techniques for producing particle-in-cavity plasmonic nanostructures including Au particle-in-ring and magnetic particle-in-bowl cavities. The extremely high near-field enhancement in the offset particle-in-ring cavity indicates a promising application for SERS and LSPR biosensing. This synthetic strategy offers us a high tunability to vary the core particle and the cavity’s size, shape, and material composition, and the obtained hybrid particle-in-cavity structure may act as a suitable single-plasmonic-nanostructure platform for the study of plasmon hybridization, optical trapping, Fano-like resonance effect, SERS-based biosensing, and MO effect.

Acknowledgements

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References

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Fig. 3 SEM images of structures in the fabrication process of Au nanobowl cavities: (A) Fe$_2$O$_3$ nanoparticles; (B) SiO$_2$-coated Fe$_2$O$_3$ nanoparticles; (C) Fe$_2$O$_3$–SiO$_2$–Au core–shell nanoparticles; (D and E) Au nanobowl cavities with a Fe$_2$O$_3$ core. (F and G) Nanobowl cavities with two different heights. All scale bars are 300 nm.

Fig. 4 On-resonance electric field ($\log |E|^2$) distribution profiles of (A) a concentric and (B) an offset Au particle-in-ring cavity excited by the 922 nm laser line. The maximum electric field intensities are shown at the bottom.