The Ring: A Leitmotif in Plasmonics

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ABSTRACT An interesting paper in this issue describes an experiment that is an optical analogue of the "quantum corral" on metal surfaces constructed and observed using scanning tunneling microscopy more than a decade ago. In this Perspective, the mechanism underlying the confinement and manipulation of light in metallic nanorings and related structures are discussed, with an emphasis on recent results.

See the accompanying Article by Babayan *et al.* on p 615.

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Ring structures, with their inherent high degree of symmetry, continue to fascinate scientists in a wide range of disciplines. On page 615 in this issue, Babayan *et al.* present a beautiful application of metallic ring structures fabricated on a dielectric surface as a tool for confining and manipulating light in small volumes.[1] The authors show that light waves excited on the surface of a dielectric material inside the ring will be reflected from the corral walls and can form standing waves with an interference pattern related directly to the structure of the surrounding ring. By changing the wavelength of incident light, the interference pattern can be varied and the intensity of light controlled at a specific spot in this manner. The phenomenon is qualitatively similar to the confinement and interference of surface electron waves generated by a scanning tunneling microscope (STM) tip and first realized in the famous "quantum corral" experiment.[2]

The use of metallic structures to manipulate and to confine light on surfaces or in the junction between closely spaced nanoparticles is a major concept in the field of plasmonics.[3]. The optical properties of metallic nanostructures are determined by their plasmon resonances. The wavelengths of plasmon resonances are determined by the shape and composition of the nanostructure and can be tuned across the visible and infrared region of the optical spectrum simply by changing the geometric shape of the nanostructure. This paradigm has given rise to a large number of optical applications ranging from waveguiding to chemical and biological sensing, and to medical applications such as photothermal ablation of cancer cells and tumors.[3]

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Metallic Ring Structures. Metallic ring structures have played an important role in stimulating the rapid growth of the field of plasmonics. In an early experiment, highly monodisperse substrates of thin gold rings with outer diameters of nominally 100 nm (Figure 1A) were fabricated using colloidal lithography. The optical properties of these substrates were characterized using optical extinction measurements and analyzed using numerical electromagnetic modeling techniques.[4] The authors found that the plasmon resonances of a ring depend significantly on the ratio of the ring thickness to overall ring diameter; this is similar to the observed dependence of the plasmon resonances of nanoshells (*i.e.*, particles possessing a dielectric core and metallic shell) on the ratio of the inner and outer diameters of the metallic shell. The authors also showed that significant electric field enhancements were induced inside the ring for resonant excitation of its dominant dipole-active plasmon resonance and, in particular, that the field enhancements were relatively uniformly distributed in the cavity inside the ring (Figure 1B). This finding suggested that metallic rings could serve as effective substrates for surface-enhanced spectroscopies such as surface-enhanced Raman scattering (SERS) or surface-enhanced infrared absorption (SEIRA) and localized surface plasmon resonance (LSPR) sensing. This idea was subsequently realized in several later studies,[5,6] where the large open cavity of the ring was functionalized to allow a significant volume of the analyte to be incorporated, such that a measurable shift of the ring plasmon resonance could be observed (Figure 1C,D).

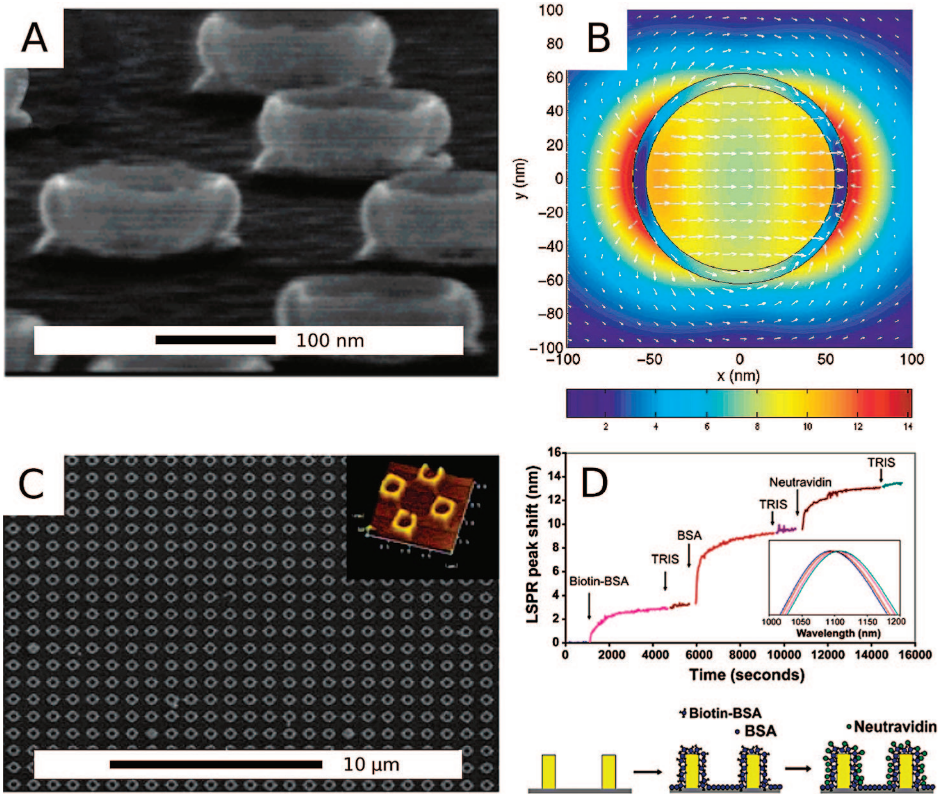

Figure 1. (A) Gold nanoring structure fabricated using colloidal lithography. (B) Calculated electromagnetic field enhancements in a gold nanoring of radius 60 nm and wall thickness 10 nm at a wavelength of 1000 nm. (C) Gold nanorings of diameters 400 nm and thickness 120 nm fabricated using imprint lithography. (D) Local surface plasmon resonance peak shift as a function of uptake time for a gold nanoring of diameter 75 nm. Panel A reproduced from ref 6. Copyright 2007 American Chemical Society. Panel B reproduced with permission from ref 4. Copyright 2003 American Physical Society. Panel C is reproduced from ref 5. Copyright 2006 American Chemical Society. Panel D is reproduced from ref 6. Copyright 2007 American Chemical Society.

Applications. These initial studies of the optical properties of metallic ring structures and their large tunability range have stimulated a vast number of subsequent studies. The unique tunability of the plasmon resonances in metallic rings, combined with the relative ease by which they can be fabricated using lithographic techniques, has led to several interesting proposed applications of these structures beyond chemical and biological sensing. Since the plasmon resonances can be tuned to wavelengths beyond the onset for interband transitions where intrinsic losses are small, metallic ring chains could function as plasmonic waveguides in the optical telecommunications band.[7] Metallic nanorings may also serve as recording marks to achieve super resolution in optical data storage.[8] In another very recent application, Gong *et al.* demonstrate that silver nanorings fabricated using chemical synthesis can be used as highly efficient antennas to focus light onto CdSe/ZnS semiconductor quantum dots positioned inside the ring cavity to achieve significant enhancement of the photoluminescence signal.[9] This application is similar to the "corral" application discussed by Babayan *et al.* in this issue of *ACS Nano*[1] but exploits the unique excitation and scattering properties of higher multipolar dark plasmon resonances in rings, excited at oblique incidence, to manipulate the light inside the ring cavity.

Fabrication Methods. The most commonly used methods for fabricating metallic rings are colloidal lithography,[4] chemical synthesis,[5] nanoimprint lithography,[9] and electron beam lithography.[10] Recently, it has been demonstrated that colloidal nanoparticles can be self-assembled into large circular ring superstructures.[11] This approach provides a low-cost alternative to the more elaborate lithographic methods and a possibility for mass production of metallic ring structures. Although the resulting metallic ring is not continuous, the relative separations between the individual nanoparticles can be controlled very accurately using chemical functionalization. The optical properties of these ring superstructures are found to be strongly dependent on interparticle spacing.[11] It is very likely that such bottom-up self-assembly approaches will ultimately enable the fabrication of rings with collective plasmon modes determined by ring geometry rather than the geometry of the individual particles.

Microscopic Nature of Ring Plasmon Modes. The optical spectra of metallic rings have been found to be relatively independent of the geometric cross section of the ring.[12] A comparison of the spectra of circular rings of

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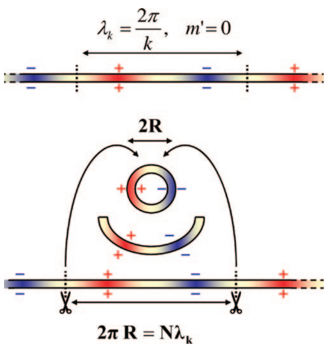

Figure 2. Schematic illustrating how the plasmon resonances in a thin metallic torus can be described as standing waves formed by plasmon resonances of an infinite metallic wire of cylindrical cross section. The plasmons of an infinite cylindrical wire depend on the propagation wavevector *k*, the wire radius *r*, and the azimuthal symmetry *m*′ and can be calculated analytically. The circumference of a torus of radius *R* is 2π*R*, and its plasmon modes can be described as infinite wire plasmons of wavevectors such that an integer number *N* of their wavelengths is equal to the circumference of the torus.

cylindrical and rectangular cross sections of similar cross sectional area revealed only minor shifts of the wavelengths of the plasmon resonances.[12] For cylindrical cross sections (*e.g.*, a torus), the plasmon resonances can be determined analytically using the plasmon hybridization approach.[13] This analysis reveals that the plasmon resonances of a torus of arbitrary dimensions results from the hybridization of simpler (primitive) plasmons that can be described as toroidal harmonics. The resulting hybridized torus modes can be classified according to their multipolar symmetry along the rotation axis of the ring. Most importantly, this analysis showed that, for a thin torus, the plasmon modes can be described analytically as standing waves formed by cylindrical wire plasmons of wavevectors such that an integer number of wavelengths is equal to the circumference of the ring (Figure 2). This analogy provides a very simple description of the plasmonic properties of a torus since the plasmon dispersion of a thin wire can be easily calculated analytically.

Multi-Ring Structures. Several variations of the simple ring structure have been proposed. Concentric multi-ring structures have been fabricated using electron beam lithography and show an increased tunability compared to single-ring structures because of their higher degrees of freedom. The hybridized plasmon resonances of these structures depend sensitively on the geometries and separations between the individual rings. Such concentric multi-ring structures show promise as thermal emitters.[14] Helical and stacked multi-ring structures have been fabricated using a glancing angle deposition method and show potential as optically active devices.[15] A variation of the concentric multi-ring structure is the metallic concentric ring-disk cavity (CRDC).[10] This structure consists of a solid cylindrical disk surrounded by a thin ring. The plasmonic structure of this system can be understood very simply using the plasmon hybridization concept. The hybridized dipolar modes are bonding and antibonding combinations of the dipolar ring and disk plasmons. The bonding mode has an opposite alignment of the disk and ring dipoles and is therefore subradiant; that is, its radiative damping is greatly reduced, resulting in a much narrower line width than its parent ring or disk modes. The antibonding mode, with its parallel alignment of ring and disk dipoles, is superradiant, that is, strongly radiative, resulting in a very broad resonance. Compared to the individual ring, the CRDC exhibits much larger electric field enhancements and a higher degree of tunability, suggesting that the CRDC can serve as an efficient substrate for surface-enhanced spectroscopies such as SERS or SEIRA.[16].

Symmetry Breaking. As with any nanostructure of high symmetry, it is of interest to explore the effects of symmetry breaking on the optical properties of a ring. Quite generally, the effect of symmetry breaking results in lifting the degeneracy of some of the plasmon modes. In plasmonic applications, a more important result is that symmetry breaking can result in the introduction of dipole moments into dark modes. This hybridization occurs because symmetry breaking can introduce coupling between bright dipolar and dark modes. Such symmetry breaking has been used in metamaterials applications to render dark magnetic modes excitable to achieve negative magnetic permeability at optical wavelengths.[17] In a recent paper, an extensive theoretical investigation of the effect of small gaps in the ring on its optical properties was presented.[18] This investigation shows that such broken-symmetry rings exhibit a multitude of normally dark multipolar plasmon resonances and result in significantly increased electromagnetic field enhancements.

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Symmetry breaking can also lead to interesting plasmonic interference effects such as Fano resonances. In a recent investigation of the plasmonic structure of metallic nonconcentric ring disk cavities (NCRDC), it was shown that, for a nonconcentric alignment of the ring and the disk, a strong narrow Fano resonance can appear (Figure 3A).[19] For nonconcentric alignment, the multipolar resonances of the disk and ring are no longer orthogonal. The Fano resonance is as a result of the interference between a quadru-

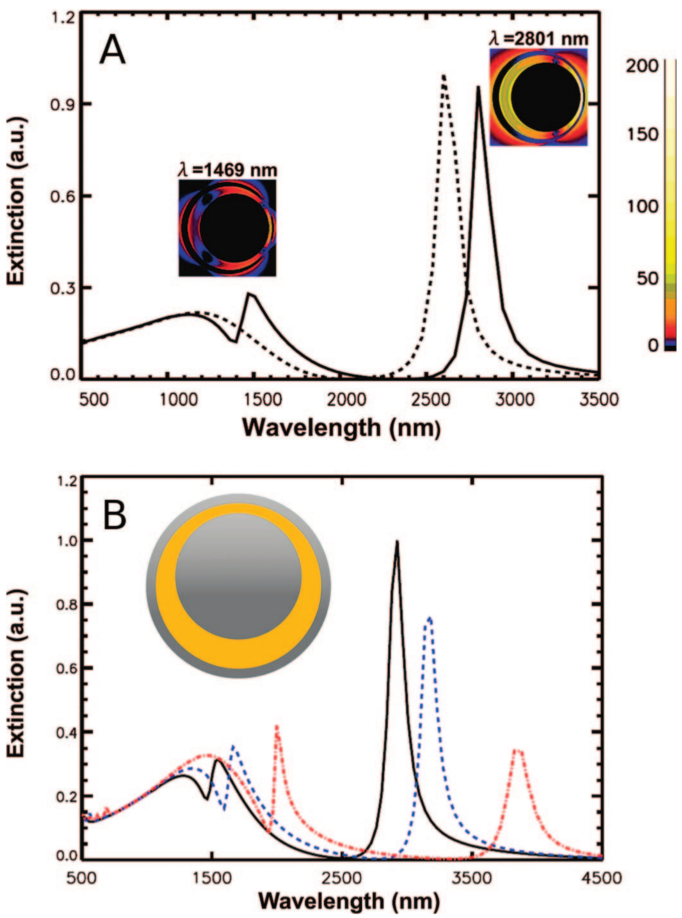

Figure 3. (A) Extinction spectra of a concentric ring-disk cavity (CRDC; dashed) and a symmetry-broken nonconcentric ring-disk cavity (NCRDC; solid) where the center of the disk has been displaced relative to the center of the ring. (B) Effect of filling the space between the ring and the disk of a NCRDC on a glass substrate with a dielectric material of relative permittivity of 1 (solid), 1.5 (blue dashed), and 3 (red dotted).[19] Panels A and B are reproduced from ref 19. Copyright 2008 American Chemical Society.

polar ring plasmon and the broad superradiant continuum formed by the superradiant antibonding hybridized dipolar ring disk mode. The complex interference phenomena underlying the Fano resonance are highly dependent on the electromagnetic interactions between the ring and disk modes. The shape and energy of the Fano resonance is therefore quite sensitive to the presence of dielectric medium in the cavity (Figure 3B). Since the width of the Fano resonance is very narrow, the NCRDC can serve as a highly sensitive LSPR sensor with a high figure of merit.

FUTURE DIRECTIONS AND CHALLENGES

The optical properties of metallic ring structures represent an exciting and vigorous field of research with a significant potential for important applications, such as chemical and biosensing, metamaterials, and the nanoscale manipulation of light. The major challenges to overcome are the development of accurate methods for their controlled fabrication. In particular, plasmonic coherence and interference effects such as subradiance and Fano resonances are highly sensitive to small structural variations.

The article by Babayan *et al.* in this issue is a significant step toward understanding how metallic ring structures can be used to manipulate the properties of light.

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