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ARTICLE *in* ACS NANO · AUGUST 2011

Impact Factor: 12.88 · DOI: 10.1021/nn203142k · Source: PubMed

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Semishells: Versatile Plasmonic Nanoparticles

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ABSTRACT Localized surface plasmon excitations in metal nanostructures have a strong impact on light scattering, absorption, and local field intensities at the nanoscale. Tweaking the nanoparticle shape, size, and material enables researchers to engineer the resonance wavelength position, the nanoparticles' local field enhancement, and their scattering properties. In particular, by breaking the symmetry of originally symmetric nanostructures, additional degrees of freedom can be explored. One particular example of a highly investigated nanostructure is the so-called semishell (or nanocup or nanocrescent moon). In this issue of *ACS Nano*, King *et al.* report on the angular and spectral scattering properties of plasmonic semishells and the effect of a high-index substrate on these properties.

Noble metal (*e.g.*, gold or silver) nanostructures have interesting optical properties based on localized surface plasmon resonances that originate from the collective oscillation of the conduction electrons excited by incident radiation.[1] It is well-known that the resonance spectra of the metallic nanostructures strongly depend on the details of their geometry. Synthesizing differently shaped nanostructures, such as nanospheres, nanocubes, nanorods, nanoshells, and nanorings, enables tuning the resonance wavelength from the ultraviolet to the near-infrared region. The excited plasmon resonances induce strongly enhanced local fields, large absorption, and scattering cross sections and are very sensitive to the local dielectric environment. Because of these highly tunable optical properties, metallic nanostructures have a wide range of potential applications in the fields of sensing, energy harvesting, photocatalysis, nonlinear optics, *etc.*[2−4]

Initially, most of the work focused on symmetric nanoparticles such as metallic spheres, which can be described well by Mie theory. An interesting development was the introduction of nanoshells, consisting of a dielectric core and a thin metallic shell, which exhibit highly tunable properties because the resonance wavelength position as well as the relative scatter and absorption cross sections are highly dependent on both the total diameter and the shell thickness.[5] These shells could be analytically described by the so-called "plasmon hybridization model", which treats interactions between plasmonic resonances as bonding and antibonding hybridized states.[6] For symmetric particles, plasmonic modes can only mix with other plasmonic modes that have the same angular momentum index. Breaking the symmetry lifts this restriction, and dipolar modes can hybridize with multipolar modes.[7] Breaking the symmetry also results in anisotropy of the angular optical response. Symmetry breaking has been observed thoroughly for the nanoshell system, looking at nanorice (ellipsoidal nanoshells),[8] nanoeggs,[9] and the so-called Fano shells.[10] In parallel, noncontinuous shells have been investigated and, more specifically, the "semishell" particle. A semishell consists of a dielectric core that is only partially covered with metal (see Figure 1).

The term semishell refers to an incomplete nanoshell and is a general denomination in contrast to the nanoshell (Figure 1). Semishells can be described by their inner radius (r), outer radius (R), and height (H). When H is varied, semishell family members may include nanocaps ($H < R$), half-shells ($H = R$), and nanocups ($R < H < 2R$) (see Figure 1). Tuning the core and metal thickness and the height H allows broad tuning of the semishell optical properties, including strongly enhanced local fields and an anisotropic optical response.

Semishell Fabrication. The fabrication of metallic semishells is typically analogous to that of nanoshells, in which a metal layer is chemically or physically deposited onto a template of a dielectric core in a controllable way. To date, there are a number of different techniques reported to prepare semishells. In general, they may be classified into two approaches: dry etching of chemically synthesized nanoshells and template deposition. These approaches are schematically shown in Figure 2, where the top

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Published online August 25, 2011
10.1021/nn203142k

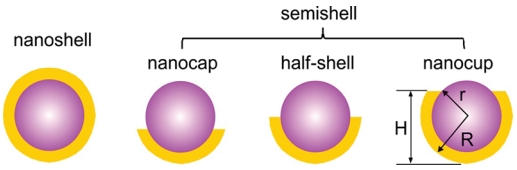

Figure 1. Overview of different shell types: (left) a fully covered nanoshell with a dielectric core; (right) semishells. Depending on the fractional height of the metal, the names nanocap or nanocup are sometimes used.

route (red arrows) corresponds to anisotropic etching of chemically synthesized nanoshells, and the bottom routes (blue arrows) correspond to templated deposition techniques.

Template Fabrication. An elegant way to fabricate semishells is to start with a submonolayer of polystyrene beads on a surface and subsequently to coat it with metal. Depending on the deposition method chosen, either nanocaps, half-shells, or nanocups are generated. This has been demonstrated using chemical deposition techniques (chemical plating) or top-down techniques such as evaporation or magnetron sputtering. For instance, evaporation at a certain angle on a rotating substrate yields nanocups with sharp edges (also called nanocrescent moons).[11] Due to the shadow effect, an incomplete metallic shell can be formed on the template core to produce the asymmetric semishells. In the chemical plating technique, functionalized dielectric cores are immobilized on a substrate and subsequently covered with small Au nanoparticles that grow to an (incomplete) shell by electroless plating.[12] Partially covering the dielectric beads with a polydimethylsiloxane (PDMS) layer prior to nanoparticle deposition allows tuning of the height *H* of the semishell. Both the chemical and top-down deposition methods result in semishells with the opening facing down. The chemical technique has the advantage that only the particles are metal-coated, whereas vacuum deposition techniques cover the entire substrate as well and substrate transfer has to be applied to avoid this.

For most sensing applications, it is more desirable to have the opening facing up, and thus far, a few techniques have been employed to do this. One method is to release the particles from the substrate using acetone or sonication. This results in dispersed semishells, which is interesting for applications used to increase mixing and accelerate binding to target molecules.[11,12] A second method that has been explored for particle transfer is the use of polymer (PDMS) casting and subsequent peeling of the PDMS film off the substrate. In the case of vacuum-deposited metal films, all dielectric particles are entirely covered by a continuous metal film except the parts that contact the substrate. This local discontinuity of the metal film makes it possible to separate the metal layer on the dielectric particles from the interparticle metal layer by the peeling process.[13] This process can be taken one step further, to include not only peeling off the particles but also transferring them to another substrate. This is called orientation-preserving transfer, and it has been reported to transfer the Au semishells from their growth substrate to an application substrate, chosen so that the orientation of the semishells is preserved. The new transfer method mainly includes the lifting of semishells *via* an elastomer film by van der Waals forces and the covalent binding between the semishells and the receiver substrate. This technique offers the possibility of studying the optical properties of semishells at the individual nanoparticle level.[14,15]

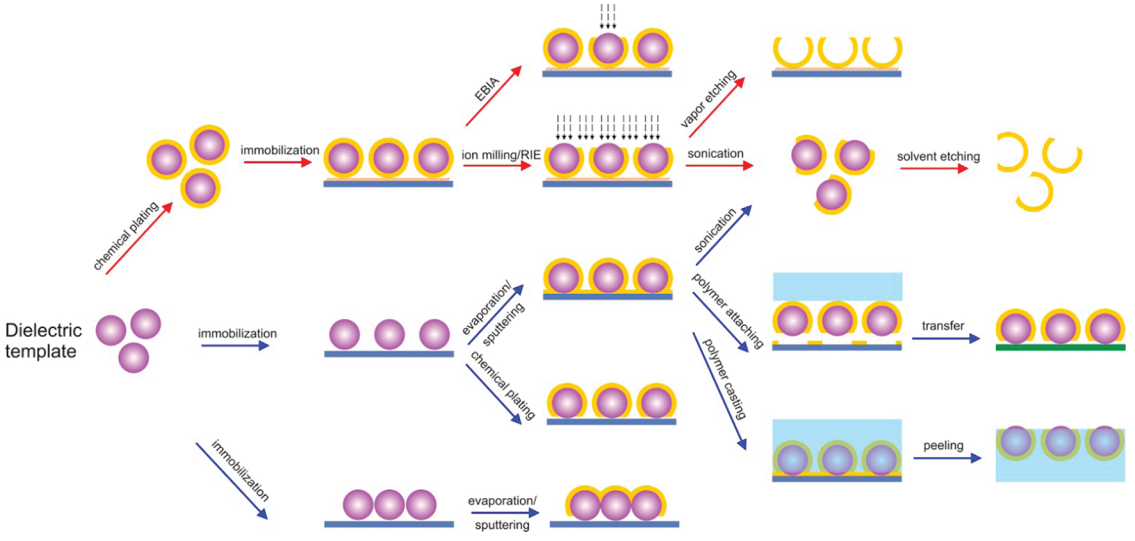

Figure 2. Different reported fabrication procedures for semishells. The top route (red arrows) is based on chemical synthesis of nanoshells, followed by an anisotropic etch procedure; the bottom two procedures (blue arrows) deal with templated deposition processes on top of immobilized dielectric beads.

A particular advantage of this class of fabrication techniques is its versatility. There is great freedom to choose the metal (Au, Al, Cu, Fe, *etc.*). Even multilayers of magnetic and nonmagnetic materials are possible, resulting in new degrees of freedom. Also, the substrate and orientation of the opening of the semishell can be chosen at will.

Anisotropic Etching. Another method to fabricate semishells is based on the original nanoshells with a full shell. These shells are usually fabricated using a chemical synthesis technique originally developed by researchers at Rice University.[16] They can be easily immobilized on a substrate, forming a submonolayer of nanoshells. Subsequently, an anisotropic etching process can remove the metal on the top of the nanoshell, resulting in upward facing semishells. This process has been demonstrated using a Xe-based ion milling process[17] and an Ar-ion plasma etch for monolayers of nanoshells[18] and even for single semishells using localized electron-beam-induced ablation (EBIA).[19]

Combinations of templated deposition and anisotropic etching have also been employed recently to obtain "perforated" semishells, that is, semishells featuring additional holes.[20] Moreover, the dielectric core can also be removed without problems by etching it away using either HF (for silica) or an oxygen plasma (for polystyrene), resulting in nanobowls.[21]

Optical Properties and Applications of Semishells. The optical properties of semishells have been investigated in detail by different groups, both experimentally and numerically. These findings usually point toward the importance of symmetry breaking in these nanostructures. In particular, instead of one bonding dipole resonance in a symmetric nanoshell, there are two distinct bonding dipole resonances in an asymmetric nanoshell, one of them parallel to the axis of symmetry (usually called the axial mode) and one of them perpendicular to the axis of symmetry (usually called the transverse mode) (see Figure 3). For the transverse plasmon mode, the electric field component of the light excites a current loop in the metallic semishell, leading to a strong magnetic component of the plasmon resonance, similar to the magnetic resonance in a split-ring resonator.

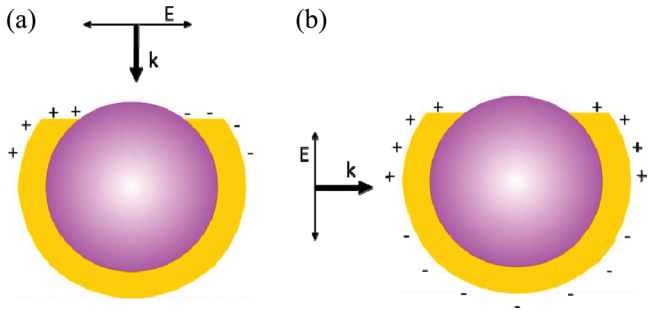

Figure 3. Two dipolar plasmon modes in semishells: (a) the transverse mode and (b) the axial mode.

> Instead of one bonding dipole resonance in a symmetric nanoshell, there are two distinct bonding dipole resonances in a nonsymmetric nanoshell, one of them parallel to the axis of symmetry (usually called the axial mode) and one of them perpendicular to the axis of symmetry (usually called the transverse mode).

This resonance has been described in the framework of the hybridization model as the hybridization of the dipole resonance of the rim of the semishell with the bonding dipole of the nanoshell. It coincides with a large charge accumulation at the edge of the rim and a correspondingly large field enhancement.[17,22] The hybridization and the large field confinement near the edge of the rim lead to strong red shifts of the semishell transverse plasmon resonance. The resonance wavelength position can be tuned significantly by tuning the height of the semishell.[17] Changing the metal itself also allows researchers to tune the optical properties. It has been shown that Au, Ag, Al, and Cu semishells all show similar optical properties but at different parts of the optical spectrum. The transverse resonance in Al semishells, for example, is blue-shifted compared to their Ag, Au, or Cu counterparts.[15]

Interestingly, the two distinct dipolar plasmon modes exhibit different scattering properties. The group of Prof. Naomi Halas at Rice University has thoroughly investigated this process both numerically and experimentally in a series of papers, where they have exploited almost all of the fabrication procedures described above to obtain a clear picture of the physical processes involved.

In their first paper, Mirin and Halas showed numerically that the two known dipolar resonances of the semishell exhibit very different scattering properties and that the scattering direction is dominated by the angle of incidence for the axial mode and by the nanoparticle geometry for the transverse mode, which always scatters light in a direction parallel to the symmetry axis.[20] In order to examine this, they fabricated semishells using the templated fabrication procedure and changed the orientation by the

angle of evaporation. In so doing, they showed that depending on the polarization of the incident light either both modes (for p-polarized light) or the transverse mode alone (for s-polarized light) could be excited. Interestingly, as the particles were distributed rather densely on the substrate, the peak was red-shifted, which could be ascribed to particle−particle coupling. Changing the orientation of the semishells proved to be an elegant way to tune this coupling.

In a second paper, the same group experimentally investigated individually oriented semishells using a method that allowed transferring the particles to another substrate without changing their three-dimensional orientation.[14] Halas and co-workers employed a modified dark-field scattering approach to investigate the scattering behavior of both the axial and transverse plasmon modes. This enabled them to look at the scattered field directly, and indeed, they found that they could "switch" between exciting one or the other mode by tailoring the angle of incidence, the orientation of the semishell, and the direction of polarization.

In a third paper, published in this issue of *ACS Nano*, King *et al.* perform a thorough analysis of the angular and spectral scattering behavior of plasmonic semishells, where they constructed a setup consisting of a supercontinuous laser and a rotating stage enabling them to get a complete picture of the angular spread of the backscattering of the light from the sample in the plane of incidence.[18] In addition, they compared chemically synthesized nanoshells with semishells with the same core size and metal thickness, as they used the dry-etching technique to form semishells directly from chemically synthesized nanoshells. As expected, the nanoshells showed a single dipolar resonance near 700 nm, while the semishells exhibited a blue-shifted axial resonance and a red-shifted transverse mode. Measuring the angular far-field scattering intensity confirmed the theoretical results both qualitatively and quantitatively for the symmetric nanoshells. In the case of symmetric nanoshells, they behave like a dipolar scatterer and the scattering pattern depends purely on the polarization and angle of incidence. For the semishells, however, the oscillating dipoles are fixed due to the reduced symmetry, and the scattering is maximized in a direction parallel to the symmetry axis for the transverse mode and parallel to the substrate for the axial mode. This theoretically expected behavior follows qualitatively from the measurements, although the transverse mode does not redirect the light completely. King *et al.* attributed this finding to the roughness of the rim, which generates subtle changes to the scattering pattern. In addition, they investigated the effect of a large-index substrate and found strong interactions between the particle and the substrate through the excitation of image charges in the substrate. Moreover, this interaction is highly sensitive to the presence of a low-index dielectric spacing layer. In this geometry, the axial mode dominates and the direction of scattering is governed by the angle of incidence.

For the sake of simplicity, this research has focused on backscattering and its dependence on particle morphology and/or proximity to a substrate. However, for a number of emerging applications, such as plasmonically enhanced solar cells, forward scattering into the substrate is of relevance. It has been shown convincingly now that, when excited properly, semishells do redirect light; however, this redirection depends on details in the particle orientation and the quality and smoothness of the rim of the semishell. Moreover, the presence of a high-index substrate completely changes the picture. For future investigations, it would be beneficial to determine the exact proportions of light that scatter into the substrate and into free space, depending on particle orientation, permittivity of the substrate, or thickness of a spacer layer.

In addition to directional scattering, semishells offer other interesting applications, including surface-enhanced Raman scattering (SERS). In general, Raman scattering of molecules can be strongly enhanced near the surfaces of metal nanostructures due to the excitation of plasmon resonances and the subsequent local field enhancement. Semishells support strong plasmon resonances, and the field is highly confined near the edge of the semishell rim. Surface-enhanced Raman scattering on semishells was first shown by Lu *et al.*, who studied semishells with a sub-10 nm sharp edge, fabricated using the templating method, dispersed in solution, and deposited on a substrate.[11] They investigated the SERS activity of single semishells and were able to measure SERS signals of Rhodamine 6G down to a concentration of 1 μM, corresponding to ~6000 molecules adsorbed on the edge of the semishell surface. These initial SERS results were obtained by looking at individual semishells with uncontrolled orientations and hence large uncertainties on the modes excited at a particular wavelength. The different fabrication procedures described above enable fabrication of a submonolayer of semishells with well-defined orientations, facilitating their use for SERS.

In addition to directional scattering, semishells offer other interesting applications, including surface-enhanced Raman scattering.

The field enhancement of a semishell is strongly confined near the rim, and hence only molecules

present there can be sensed using SERS. This follows from numerical simulations and recently has also been demonstrated experimentally using the electron-beam-induced deposition (EBID) method, which allows precise deposition of a 20−30 nm amorphous carbon nanoparticle (CNP) as a Raman reporter at different locations on an individual Au semishell.[23] Indeed, while looking at the SERS of these (single) carbon particles, only particles located directly at the edge of the rim could be observed in the Raman measurements.

The templated deposition technique is an elegant method for fabricating semishells, where the metal film consists of a multilayer of magnetic and nonmagnetic materials. Liu *et al.* used this property to their advantage and fabricated a SERS-active Au/Fe/Ag/Au multilayered semishell that they could manipulate by applying a magnetic field.[24] By using a fluorescently active dielectric core, they showed that they could move and rotate the particle at will. Moreover, as the optical response is highly anisotropic in nature, the SERS response could be manipulated simply by rotating the magnetic field. This technique could also be used to take advantage of the directional scattering reported by King *et al.* in this issue of *ACS Nano*, for example, for enhanced *in vivo* imaging.

The broken symmetrical geometry of semishells results in directional scattering, large SERS enhancement factors, and the potential for enhancement of other nonlinear processes. Moreover, fabricating multilayered semishells allows researchers to control the semishell motion and orientation magnetically. Combining magnetic, plasmonic, and fluorescent properties in a single particle results in multifunctional particles with a bright future.

Acknowledgment. P.V.D. and J.Y. both acknowledge financial support from the F.W.O. (Flanders).

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