Fabrication of double nano-cup assemblies and their anomalous plasmon absorption

Jingquan Liu[†,‡], Burak Cankurtaran[†], Richard Wuhrer[†] and Michael Cortie[†]
[†]Institute for Nanoscale Technology
University of Technology Sydney, Australia
Email: michael.cortie@uts.edu.au
[‡]now at University of New South Wales, Sydney Australia

***Abstract*—Double-cup assemblies of nanoscale gold semi-shells have been synthesized using a combination of thermal evaporation and chemical etching. The optical extinction of these structures peaked at 740 nm, but there was also evidence of additional extinction maxima at 560, 940 and 1110 nm. Numerical simulations of the optical properties revealed that the extinction was due mainly to scattering rather than to absorption In contrast, the extinction in simple single-shell nanocups was strongly absorptive in nature. Multiple plasmon resonances were identified in the double-cup structures, including an interesting quadrupole resonance in which oscillations of the inner and outer shells should operate 180º out-of-phase.**

Keywords- plasmon resonance, nanostructure, semi-shell, quadrupole, multipole

I. INTRODUCTION

A variety of precious metal nanoparticle shapes such as shells [1, 2], semi-shells [3], rods [4], caps [5, 6], cups [7, 8], rings [9, 10], rattles [11], triangles [12] and disks[13] have been synthesized. Potential applications of these particles include fields as disparate as medical treatment [14], functional glass windows [15, 16] and the sensing of analytes [17]. Some interesting structures formed by self-assembly of the individual particles have also been reported, for example gold platelets have been induced to form 3D structures [18, 19], gold shells can form asymmetrical dimers [20], spheres can assemble into close-packed solids [21, 22], and nanorods can form long chains [23-25].

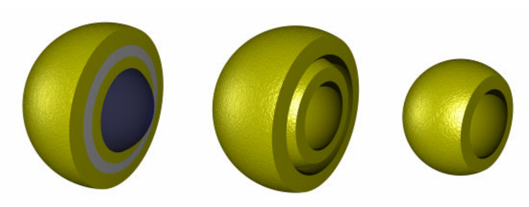

Figure 1. Schematic illustrations of structures examined in this paper, (left) composite particle showing polystyrene core, two layers of Au, and intermediate layer of Al, (centre) same particle after removal of Al and core, (right) single-shell nanocup.

The idea of nanoscale shapes comprised of concentric spherical surfaces has also been mooted [2, 26-32] with the optical properties of such composite shapes being especially interesting. Here we describe a method to produce concentric double-cup, semi-shell, assemblies (Figure 1). The optical properties of these structures are investigated both experimentally and theoretically.

II. EXPERIMENTAL

A. Fabrication of double cup assemblies

Single shell nano-cups have been produced previously using wet chemistry [8] or physical vapor deposition (PVD) [17]. Here we have used a hybrid PVD/wet chemical method to produce the double-cup assemblies. First a template of polystyrene microspheres was spun-cast onto a glass slide. Next a layer each of gold, aluminum and then gold was sequentially thermally deposited at an angle of 50º onto the substrate, which was simultaneously rotated. Each layer of metal was nominally 20 nm thick. Next the polymer cores were removed by CH_2Cl_2 and the intermediate aluminum layer by 2M HCl. The mouth of the cup, which is adjustable in size, can be varied by changing the angle of the metal source relative to the plane of the glass slide. Single cap particles were also produced, for comparison. The particles were then immobilized on a glass slide coated with aminopropyltrimethylsilane (APTMS) which forms a tether between glass and gold [33, 34] for measurement of their optical properties. The optical extinction of the nano-cup assemblies was measured experimentally after they were self-assembled on a glass substrate pre-coated with the APTMS. Scanning electron microscope images were taken in a Zeiss Supra 55VP using an in-lens secondary electron detector. Images were collected in high vacuum mode at 20kV.

B. Simulation of optical properties

The optical properties of the structure were simulated with the discrete dipole approximation (DDA) using the DDSCAT code of Draine and Flatau [35, 36]. The target structures were generated with custom-written software. The dipoles were of the order of 5 nm in size, sufficient in our experience to give peak positions and an approximation of peak shape, but not small enough to give an accurate value of extinction efficiencies.

III. RESULTS

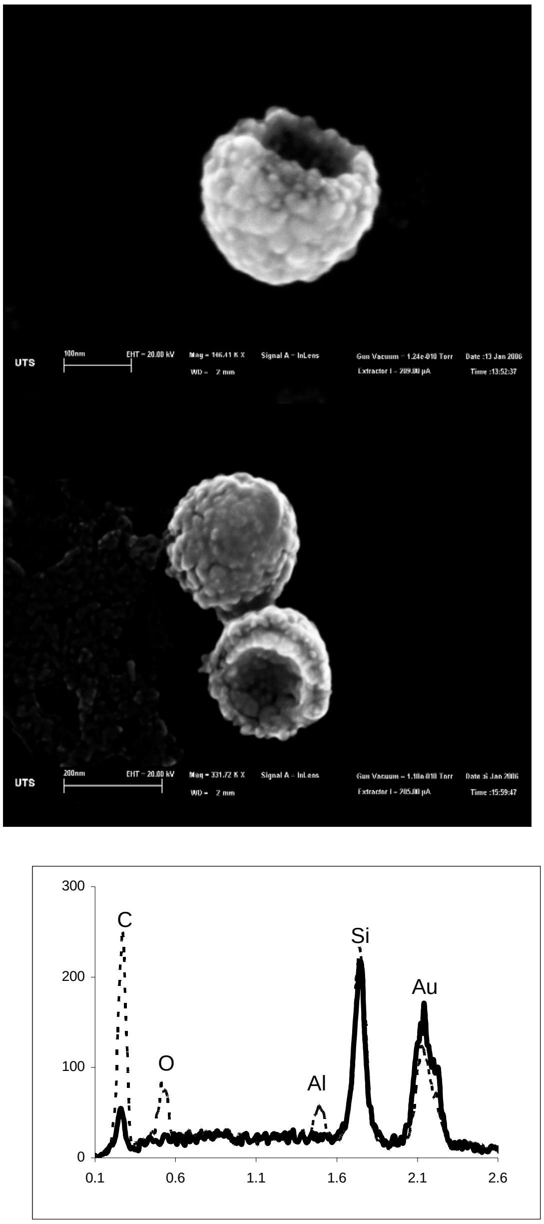

Figure 2. SEM micrograph of a) single nanocup assembly before removal of Al layer, b) pair of particles after removal of Al layer, c) energy dispersive X-ray spectroscopy (EDS) spectrum of cup assembly before (dotted line) and after (solid line) removal of Al layer.

Figures 2a and b show examples of the cup assemblies. In some cases several assemblies were joined together, however the incidence of this was minimized by using a very dilute PSP solution. Such aggregates could also be readily separated out by precipitation. The dark line along the opening of the assembly corresponds to the removed layer of Al. Energy dispersive X-ray spectroscopy (EDS) was carried out in order to find out whether all the aluminum had been etched out. As shown in Figure 2c, the Al peak had indeed disappeared after the etching process. This analysis was performed several times on several particles.

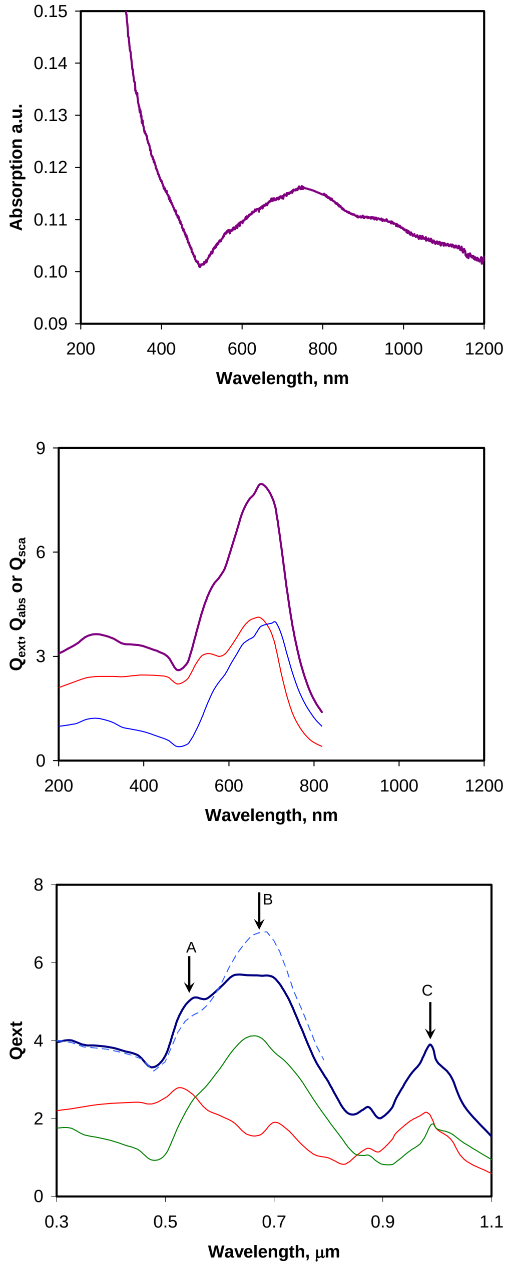

Figure 3. Optical absorption of nanocup assembly, (top) measured transmission spectrum of double semi-shells on a glass slide, (centre) orientationally-averaged extinction coefficients calculated for a simple gold semi-shell and (bottom) calculated extinction coefficients for double gold semi-shell (dashed: averaged over multiple orientation, solid: average of orientations shown in Figure 4). Note the strong absorption of UV by the glass slide in the experimental data, a feature which is necessarily lacking in the spectra calculated for the individual nanoparticles

Figure 3a gives the optical absorption of the double assemblies, as immobilized on the glass slide. The extinction peak was centered at 735 nm. The calculated, orientationally-averaged, extinction efficiencies of a single nano-cup, in vacuum, are shown in Figure 3b, and those for a double-cup in Figure 3c. The extinction of the single cup is substantially due to two dipole resonances at 550 and 660 nm, designated the α and the β resonances and analogous to the transverse and longitudinal modes of other shapes [37]. Unlike the single cup, the double-cup exhibits significant extinction beyond 800 nm, due evidently to at least one additional resonance, at C. The calculated peak extinction of the assembly is at 675 nm, somewhat lower than the measured 735 nm. This discrepancy is most likely due to the red-shifting effect of the glass substrate in the experimental sample. However, it may also be due in part to the tapered nature of the deposits in real structures [38]. The illumination responsible for the extinction of Figure 3c can be broken into various components, Figure 4a, and the effect of each tested individually. When this is done it becomes evident that resonance A is due to component J0=1, and resonances B and C are due to component J0=2.

Furthermore, extinction in the single cup is due, in about equal proportions, to absorption and scattering. However, in these particles insertion of an additional semi-shell within the first has a marked effect on the nature of the optical extinction, with absorption becoming a vastly less significant phenomenon. The dipole resonance at position C of Figure 3c is quadrupole in nature, Figure 4b.

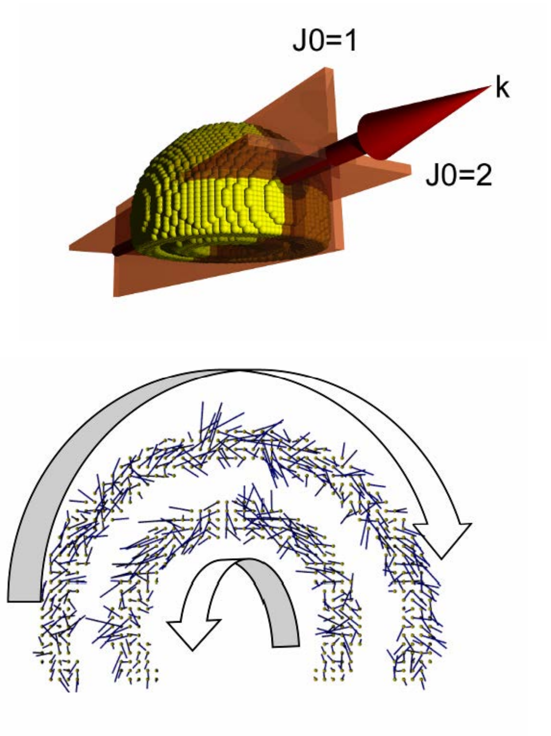

Figure 4. (a) The two distinct polarizations of light possible for this symmetry.(b) Quadrupole β plasmon resonances produced in double-cup assembly at 975 nm by J0=2 polarization.

In conclusion, double-cup semi-shell assemblies can be produced by a templating process and offer some surprising and interesting optical properties. Not only do they exhibit anomalously strong scattering relative to absorption, but they also have a strong quadrupole plasmon resonance.

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