Controlling optical properties of metallic multi-shell nanoparticles through suppressed surface plasmon resonance
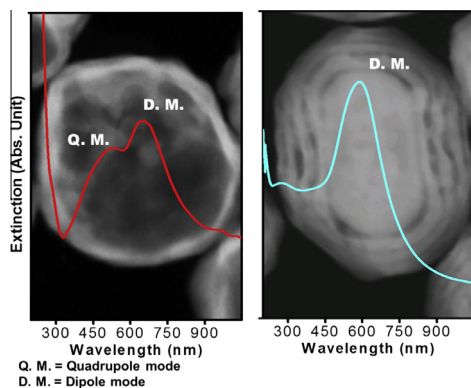
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GRAPHICAL ABSTRACT

Q. M. = Quadrupole mode
D. M. = Dipole mode

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ABSTRACT

Herein, we report the surface plasmon resonance of plasmonic multi-shell nanoparticles compared to bimetallic Ag/Au hollow nanospheres of similar final size, shape, and percent composition. The surface plasmon resonance of solid and hollow nanoparticles exhibited a quadrupole mode that was particularly prominent around the 100 nm size regime, while multi-shell nanoparticles did not show a quadrupole mode at a similar size. In the latter case, the quadrupole mode of the outermost nanoshell was suppressed by the dipole modes of the inner shells, and the suppression of the quadrupole mode was not affected by the shape of the inner nanostructures. Light interaction of the multi-shell nanoparticle was investigated through simulated electromagnetic field distribution obtained by finite-difference time domain (FDTD) calculations which were in a good agreement with the results of surface-enhanced Raman spectroscopy (SERS).

1. Introduction

Studies involving the plasmonic properties of metal nanoparticles have been increasing due to their wide variety of potential applications such as in solar cells [1,2], electronics [3], and sensing devices [4–6]. The root of these applications relies primarily on the localized surface plasmon resonance (LSPR) of the nanoparticle, which is sensitive to the surrounding chemical environment. LSPR takes place when the plasmonic nanoparticle is irradiated with light causing the electrons at the conduction band to oscillate, which is driven by the electric field [7]. In this way, LSPR results in the manipulation of photons to be absorbed and radiated as well

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as enhancement of the electromagnetic (EM) field around the plasmonic nanoparticle [8,9]. The practical metal nanoparticles related to this field of research consist of gold (Au) and silver (Ag), since they exhibit high optical features at visible to near-IR spectral regions. Dipole plasmon resonance mode is only observed when the diameter of nanoparticle is almost equal or less than the wavelength of incident light; however, higher order modes such as quadrupole, octupole, and hexadecapole begin to appear as nanoparticle size increases [10]. Moreover, LSPR is influenced not only by the size, but also the nanoparticle's shape, composition, and dielectric environment, thereby providing researchers an advantage in their ability to fully control and manipulate light [11–13].

Complex nanostructures have started to appear in the field of solution-based synthesis of metal nanoparticles, and thus far have exhibited exceptional LSPR behavior. One such example in this category is the asymmetric core-satellite nanoassemblies reported by Yoon et al. [14], who demonstrated that LSPR coupling between the core and satellite nanoparticle exhibits a quantum tunneling effect. In addition, pure Au nanoshells [15] have been reported to exhibit a wide LSPR tuning range, going as high as the NIR frequency, which is controlled by the radius of the dielectric core and the thickness of the gold nanoshell. Nanocups and nanoshells that are partially opened by an offset core have a unique spectral property of far field scattering that is strongly dependent on the polarization of light [16].

The ability to control the composition and morphology of Au nanocages [17,18] allows the precise tuning of LSPR through galvanic replacement between Ag nanoparticle and Au ions. Such hollow nanostructures have been extensively studied both experimentally and theoretically through their conversion to multilayer nanoshells [19,20], also known as nanomatryushka. Specifically, it has been shown that the dielectric spacer layer between the core and shell determines the coupling of LSPR resulting in next-level tunability of optical responses at a greater spectral coverage than for individual Au nanoshells. Compared to simple nanostructures where the absorption and scattering efficiencies are primarily a function of nanoparticle size, such a clear dependency for multilayered nanostructures becomes more complex and geometry-dependent. Nanomatryushka have been reported to have a greater scattering efficiency under a thick Au shell condition while greater absorption efficiency can be attained when the Au shell is thin, which accounts for the coupling effect of constituent plasmons of the nanoparticle [21]. The theoretical offset conditions for the cores of gold–silica–gold multilayer nanoshells was reported by the Drezek group [20]. Specifically, they demonstrated that as the core nanoparticle moves away from the center but does not touch the nanoshell, the dipolar interaction tends to undergo a red shift due to increased plasmon interaction between the core and shell.

There is little information in the present literature regarding studies of the optical properties of structures with more than two nanoshells, and as a result there is a limited understanding of the LSPR of these complex nanostructures. It has been suggested that multi-shell nanostructures can act as optical condensers to multiplicatively collect and focus light toward the center of the structure causing an exponential increase in near-field enhancement as the number of metal shells increases [21]. For example, a double shell of hollow nanoparticles made from SiO_2/TiO_2 exhibits a unique light scattering effect within the nanoparticle [22], with multiple scattering events occurring between the inner and outer shell affecting the reflectance of light. In addition, changing the geometry of the core nanoparticle, notably those with anisotropic properties, may further contribute to the limited evidence of the effect of resonance frequency. Lastly, compared to nanospheres, nanorods have two distinct dipole LSPR characteristics

consisting of the transverse mode, originating from the shorter axis oscillation of electrons, and the longitudinal mode, which depends on the aspect ratio (long axis length/short axis length) and is usually associated with a more intense band with a longer wavelength.

In this work, we report the surface plasmon resonance behavior of a complex multi-shell nanoparticle utilizing galvanic replacement [23–24] as shown in Fig. 1A and B. The optical properties of the multi-shell nanoparticle were investigated through comparison with hollow nanospheres of similar final dimensions (Fig. 1C). We found that the optical response of plasmonic nanoparticles could be controlled by the presence of multiple nanoshells inside the outer most nanoshell under the conditions of similar final size and percent composition. The controlled optical response was due to the strong interaction of constituent surface plasmon involved on the structure of the multi-shell nanoparticle. The observations were further confirmed by performing simulation of EM field distribution and were supported by SERS spectroscopy.

2. Experimental section

2.1. Materials

Gold chloride ($HAuCl_4 \cdot 3H_2O$) was purchased from KOJIMA. Sodium citrate was purchased from YAKURI. Sodium borohydride ($NaBH_4$) and silver nitrate ($AgNO_3$) were purchased from JUNSEI. Sodium iodide (NaI) and ascorbic acid were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) was purchased from SAMCHUN, and cetyltrimethylammonium bromide (CTAB) was purchased from Fluka. All involved reagents were dissolved and containers were rinsed with distilled water (18.2 MΩ) prepared via a Milli-Q water purification system.

2.2. Synthesis of gold nanorods

Gold nanorods were prepared by following a similar procedure reported by Chon et al. [25]. First, a seed solution of gold was prepared by reducing 20 mmol of $HAuCl_4$ in 10 mL of a 0.1 M CTAB solution with 600 μL of 6.0 mM $NaBH_4$. Second, a growth solution of Au was prepared by slowly adding 0.1 M ascorbic acid into 100 mL of a 0.1 M CTAB solution containing 0.05 mmol $HAuCl_4$ and 6.0 mmol $AgNO_3$. The orange color of the gold salt solution disappeared, indicating that the Au was reduced. Finally, 120 μL of the seed solution was added to the growth solution under mild
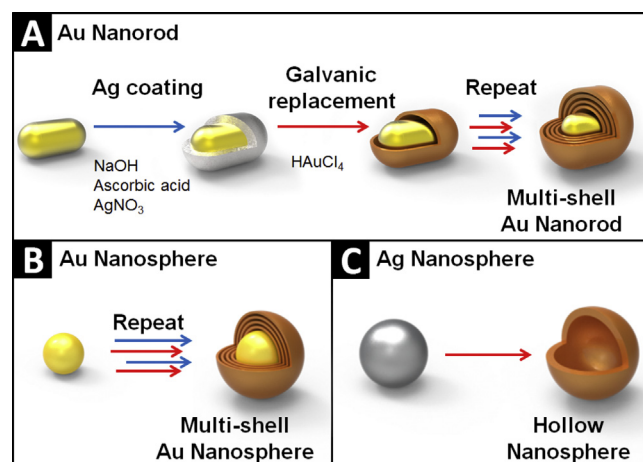

Fig. 1. Schematic illustration for the synthesis of (A) multi-shell Au core nanorod and reference sample of (B) multi-shell Au core nanosphere, and (C) hollow nanosphere.