

Observation and Characterization of the Surface Plasmon Resonances of Platinum Nanoshells[†]

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The controlled fabrication, characterization, and application of nanometer-sized materials with functional properties have been studied widely.¹⁻³ Metal nanostructures attract considerable attention scientifically as well as industrially owing to their intriguing chemico-physical properties that can be tailored as functions of nanoparticle sizes, shapes, and mutual interactions.^{4,5} In particular, noble-metal nanostructures have attracted enormous attention in various fields of study because of their novel properties, including large optical-field enhancements resulting in the strong scattering and absorption of light. They have possible uses in diverse applications such as devices, transistors, optoelectronics, information storages, and energy converters.^{1,6} Among various noble-metal nanostructures, platinum-based nanostructures especially have attracted widespread interest as platinum plays an outstanding role in multifunctional catalysts for many industrial reactions. However, because there are some crucial obstacles such as low platinum-utilization efficiency and high cost, some ways must be found to reduce the amount of platinum used in a specific application by increasing its catalytic activity in order to lower the overall cost.^{1,7} Hollow nanospheres possess structurally tunable features such as shell thickness, interior cavity size, and chemical composition, leading to relatively high surface areas, low densities, and reduced costs compared with their solid counterparts. Thus, hollow-structured noble-metal nanoparticles can be applied to nanometer-sized chemical reactors, efficient catalysts, energy-storage media, and small containers to encapsulate multi-functional active materials.⁸⁻¹⁰

Metal nanoparticles exhibit strong visible absorption bands that differ from the color of the bulk metals.¹¹ These absorption bands appear when the incident photon frequency is resonant with the collective oscillation of the conduction free electrons, which is known as the localized surface-plasmon resonance (SPR). SPR spectra are dependent on the shape, size, interparticle distance, and dielectric property of a nanoparticle material, and, most importantly, on the dielectric properties of surrounding media.^{12,13} For example, solid gold nanospheres have strong optical absorption at 520 nm, and silver nanoparticles have an intense SPR band at 390 nm.¹³ The SPRs can be understood with the Mie theory,

which describes the extinction (absorption and scattering) of spherical particles of arbitrary sizes.¹⁴⁻¹⁶ Although the general Mie solutions for spherical particles have been known for decades, it was only recently theoretically established that a configuration consisting of a metallic shell and a dielectric core should result in plasmon-derived optical resonances variable over large regions of the electromagnetic spectrum.^{17,18} To determine the extinction spectrum of a nanoparticle using the Mie theory, the electromagnetic fields of the incident wave, the scattered wave, and the wave inside the particle are expressed as the sum of a series of vector spherical harmonic basis functions. The electromagnetic fields must then satisfy the Maxwell's boundary conditions of continuity at the junction between the nanoparticle and the embedding medium. The Mie scattering theory is exact and accounts for field-retardation effect that becomes significant for particles whose sizes are comparable to the wavelength of light.^{19,20}

In this paper, we report that hollow platinum nanospheres having an average outer diameter of 148 nm with a shell thickness of 11 nm have been synthesized *via* a hard-template method.²¹ Then, the SPRs of platinum nanoshells are to be reported for the first time to our knowledge and characterized by being compared with extinction spectra calculated using the extended Mie theory.

Because SiO₂@Pt core-shell nanospheres are agglomerated, their spherical structures cannot be observed apparently in their transmission electron microscopy (TEM) image of Figure 1(a). However, their spherical morphologies can be confirmed in their scanning electron microscopy (SEM) image of Figure 1(c). The TEM image of Figure 1(b), as well as the SEM image of 1(d), indicates that hollow platinum nanospheres have empty interiors indeed; the central regions are brighter in Figure 1(b) and darker in Figure 1(d) than the edge regions. A close examination with high-resolution TEM images and energy-dispersive X-ray elemental profiles has shown that well-defined platinum nanoshells in both SiO₂@Pt core-shell nanospheres and hollow platinum nanospheres have an average outer diameter of 148 nm and a typical shell thickness of 11 nm.¹

Figure 2 shows the UV-vis extinction spectra of the platinum nanostructures dispersed in water. Although both spectra are somewhat featureless, we can see a discernable SPR peak at ~520 nm for SiO₂@Pt core-shell nanospheres. Furthermore, we can note that the SPR spectrum of SiO₂@Pt

[†]This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

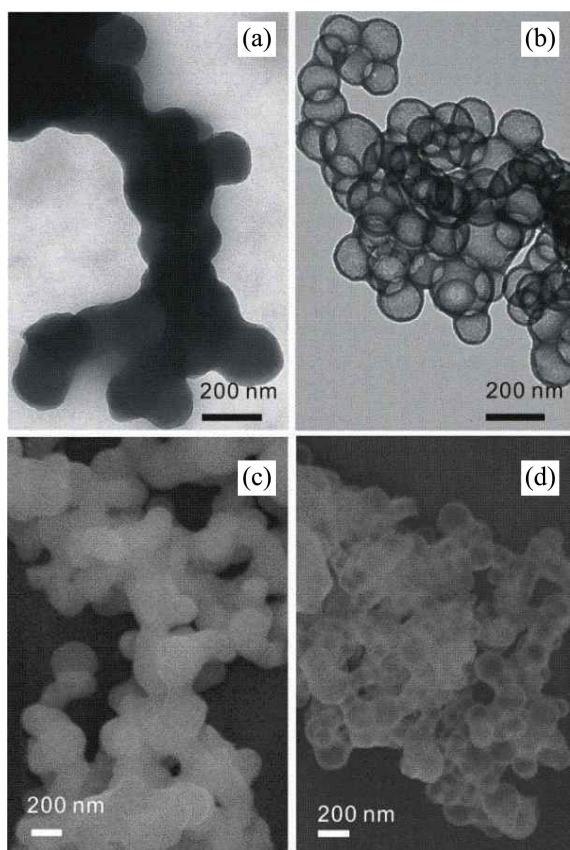


Figure 1. TEM (a,b) and SEM images (c,d) of SiO₂@Pt core-shell nanospheres (a,c) and hollow platinum nanospheres (b,d).

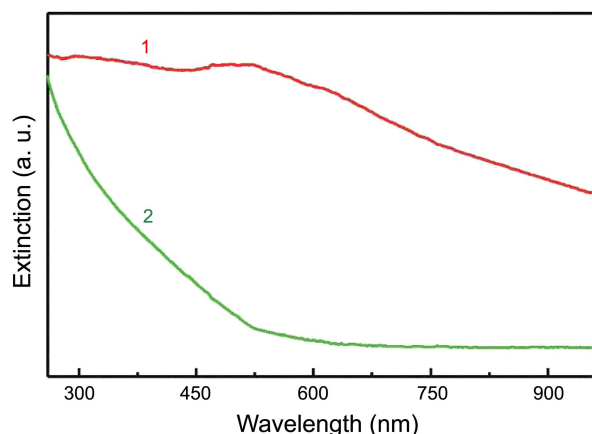


Figure 2. Experimentally observed extinction spectra of SiO₂@Pt core-shell nanospheres (curve 1) and hollow platinum nanospheres (curve 2) dispersed in water.

core-shell nanospheres is largely shifted to the red compared with that of hollow platinum nanospheres. This suggests that the SPR spectrum of platinum nanoshells are dependent greatly on the dielectric constant of the core medium. The SPRs of platinum spherical nanoshells have been characterized in the following for the first time to our knowledge by employing the extended Mie theory.

The core-shell system depicted in Figure 3 has been studied with the Mie scattering theory,²² and expressions for

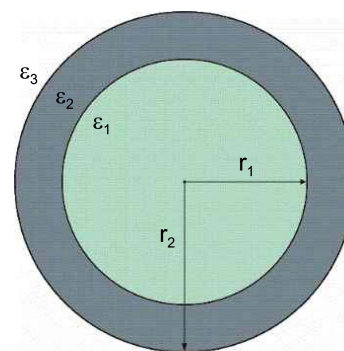


Figure 3. Schematic description of a core-shell nanosphere. ϵ_1 , ϵ_2 , and ϵ_3 are the dielectric constants of the core, the shell, and the surrounding medium, respectively.

the polarizability and the extinction cross section of a core-shell nanoparticle have been derived. The quasi-static equations has also been useful in the calculation of nonlinear optical effects in nanoshells.¹³ The extinction efficiency spectrum has been calculated in the region of the near-ultraviolet to the near-infrared by using the extended Mie theory.²³ The core has a radius of r_1 and a dielectric function of ϵ_1 , the shell has a thickness of $r_2 - r_1$ and a dielectric function of ϵ_2 , and the surrounding medium has a dielectric function of ϵ_3 ($= n_0^2$, where n_0 is the refractive index of the surrounding medium in Figure 3). It is important to note that each dielectric function of ϵ_n ($n = 1, 2, 3$) having real and imaginary frequency-dependent components can be written as $\epsilon(\omega) = \epsilon_r + i\epsilon_i$, where ω is the angular frequency of the light.²⁰ Especially, the optical response of the metal shell region is dominated by two contributions of the conduction electrons to the dielectric function. ϵ_r is associated to intra-band optical processes that can be described in the first approximation by a Drude dielectric function. On the other hand, ϵ_i corresponds to inter-band optical processes which can be described as

$$\begin{aligned} \epsilon(\omega) &= \epsilon_r + i\epsilon_i, \\ &= \epsilon_b(\omega) - A(1 - i/(\omega\tau)) \end{aligned} \quad (1)$$

where $\epsilon_b(\omega)$ is the dielectric function of the bulk metal due to inter-band transitions, A is $(\omega_p/\omega)^2/(1 + 1/(\omega\tau)^2)$, ω_p denotes the plasmon frequency of the bulk metal, τ is the relaxation time, and ω is the frequency of the electromagnetic wave.²² It is noteworthy that, in the study of the optical properties of nanoparticles, the limited mean free path of the electrons is one of the most important factors leading to modifications of relaxation time, plasma frequency, optical constant, and dielectric constant. The size-limited relaxation time is

$$\tau = \frac{\tau_0 d}{2v_F\tau_0 + d} \quad (2)$$

where v_F denotes the Fermi velocity, d is the particle diameter and τ_0 is the relaxation time in the bulk material.²⁰⁻²³ According to the quasi-static theory of nanoshells, the absorption (σ_{abs}) and the scattering cross sections (σ_{sca}) obtained from the Mie theory calculation are given as follows

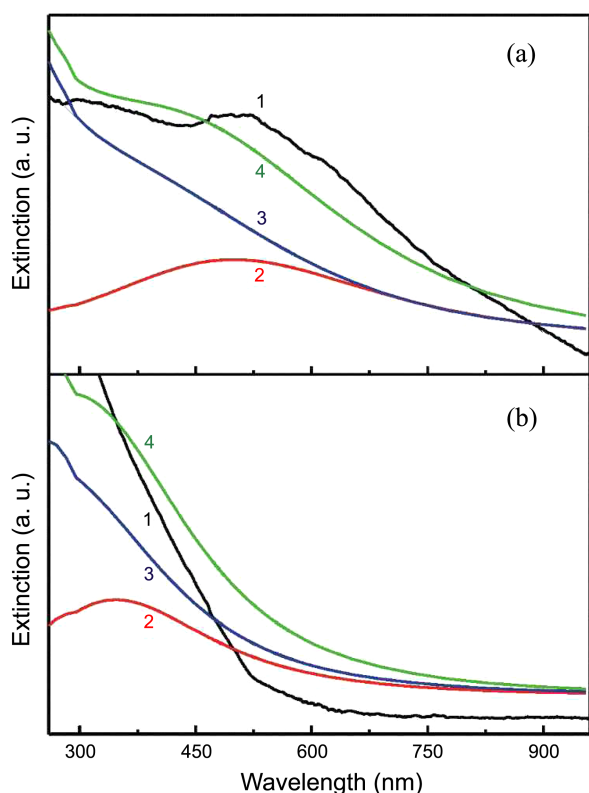


Figure 4. Observed extinction (curve 1) and calculated absorption (curve 2), calculated scattering (curve 3), and calculated extinction spectra (curve 4) of SiO₂@Pt core-shell nanospheres (a) and hollow platinum nanospheres (b) dispersed in water.

$$\sigma_{\text{abs}} = \frac{k}{\epsilon_0} \text{Im}(\alpha) \quad (3)$$

$$\sigma_{\text{sca}} = \frac{1}{6\pi\epsilon_0^2} k^4 |\alpha|^2 \quad (4)$$

$$k = 2\pi\sqrt{\epsilon_3}/\lambda \quad (5)$$

where ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$), and α is the polarizability derived from the Laplace's equation.¹³ α is given by²²

$$\alpha = 4\pi\epsilon_0 r_2^3 \left[\frac{\epsilon_a + \epsilon_b}{\epsilon_c + \epsilon_d} \right] \quad (6)$$

where $\epsilon_a = r_2^3 (\epsilon_2 - \epsilon_3)(\epsilon_1 + 2\epsilon_2)$, $\epsilon_b = r_1^3 (\epsilon_1 - \epsilon_2)(2\epsilon_2 + \epsilon_3)$, $\epsilon_c = 2r_1^3 (\epsilon_1 - \epsilon_2)(\epsilon_2 - \epsilon_3)$, and $\epsilon_d = r_2^3 (\epsilon_1 + 2\epsilon_2)(\epsilon_2 + 2\epsilon_3)$.

The above equations have been used extensively to explain the extinction spectra of small metallic nanostructures qualitatively as well as quantitatively. As a function of size increase, contributions from higher-order multipoles and retardation effects become important.²⁴⁻²⁶

Figure 4 shows the absorption, scattering, and extinction calculated using the extended Mie theory for the platinum nanoshells having an average inner radius of 63 nm and an average outer radius of 74 nm. We have used a dielectric constant of 2.10 for the core material corresponding to silica and a dielectric constant of 1.75 for the surrounding medium to calculate the spectra of Figure 4(a) while we have used

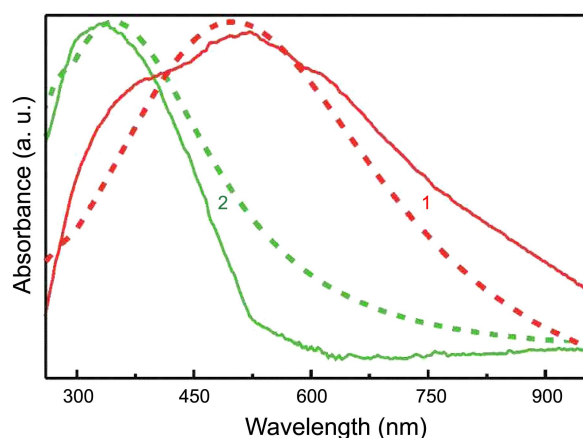


Figure 5. Observed (solid) and calculated (dashed) absorption spectra of SiO₂@Pt core-shell nanospheres (curves 1) and hollow platinum nanospheres (curves 2) dispersed in water.

1.75 for both ϵ_1 and ϵ_3 to calculate the spectra of 4(b). Figure 4 displays that calculated extinction spectra are reasonably fitted to their corresponding observed extinction spectra. In particular, Figure 4(a) indicates that the discernable SPR peak of SiO₂@Pt core-shell nanospheres at ~ 520 nm is mostly due to their absorption. However, it is not evident that the extended Mie theory can be applied to characterize the SPRs of platinum nanoshells because the calculated extinction spectra are significantly deviated from the corresponding observed spectra. We attribute the deviation to the aggregation of platinum nanostructures, which affects the scattering spectrum seriously.

An optical extinction spectrum represents the sum of absorption and scattering. Because the scattering spectrum is badly affected by the agglomeration of nanoparticles,¹⁴ we have obtained the scattering-removed absorption spectra of Figure 5 by subtracting c/λ^4 , where c is an arbitrary constant, from the respectively corresponding extinction spectra of Figure 4. Figure 5 reveals that the absorption spectra calculated from Eq. (3) using the experimentally observed radii of the system shown in Figure 3 agree very well with the respectively corresponding observed absorption spectra, suggesting that the SPRs of platinum shells can also be well characterized by the extended Mie theory. The wavelength at the absorption maximum and the bandwidth of each calculated absorption spectrum match well with the respective ones of the corresponding observed absorption spectrum.

In summary, we have synthesized well-defined SiO₂@Pt core-shell nanospheres and hollow platinum nanospheres. Platinum nanoshells of both systems have an average outer diameter of 148 nm with an average shell thickness of 11 nm. The SPR spectra of both platinum nanostructures dispersed in water have been observed and compared with the respectively corresponding extinction spectra calculated using the extended Mie theory with the experimentally observed radii. The good agreement of our observed absorption spectra with the respectively corresponding calculated spectra suggests that the SPRs of platinum nanoshells can be well characterized by the extended Mie theory.

Experimental

For the synthesis of monodisperse SiO₂ nanospheres, 25.0 mL of ethanol(l), 4.5 mL of deionized water (> 17 MΩ cm), 0.4 mL of 25% NH₃(aq), and 1.6 mL of tetraethyl orthosilicate (l, 99%) were mixed and kept under stirring for 1 h. Produced SiO₂ nanospheres were centrifuged with 10,000 rpm for 10 min and redispersed in 31.4 mL of ethanol three times.^{27,28} Platinum seeds were prepared by mixing 10 mg of H₂PtCl₆(s, 99.995%) in 10.0 mL of 35% HCl(aq), 10.0 mL of 0.20 M NaBH₄(aq), and 10.0 mL of 0.30 g L⁻¹ PVP(aq) at once. The products were centrifuged at 10,000 rpm for 10 min and redispersed in 30.0 mL of ethanol three times.²⁹ In order to modify the surfaces of SiO₂ hard templates with amino groups, 10.0 mL of SiO₂ nanospheres-dispersed ethanol and 5.0 mL of 1.0 M (3-aminopropyl)triethoxysilane (l, 98%)-dissolved ethanol were mixed and kept under stirring for 2 h. Then, the reaction mixture was added with 5.0 mL of platinum seeds-dispersed ethanol and stirred for 1 h to attach platinum seeds on SiO₂ nanospheres. For the transformation of platinum seeds into platinum shells, 4.0 mL of 2 days-aged 10 mM H₂PtCl₆(aq) and 2.0 mL of the above mixture were mixed, stirred for 1 h, added with 0.32 mL of 100 mM L-ascorbic acid(aq), and stirred for 1 h.³⁰ Finally, 10.0 mL of HF(aq) and 1.0 mL of the above colloid were mixed and stirred for 2 min.³¹ The produced hollow platinum nanospheres were centrifuged at 10,000 rpm for 10 min and redispersed in 1.0 mL of ethanol three times.

TEM images were measured with a Carl Zeiss LIBRA 120 microscope while SEM images with a JEOL JSM-6700F microscope. Extinction spectra were obtained using a Scinco S-3000 UV/vis spectrophotometer.

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