New Techniques for Generating Core/Shell Nanoparticles

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Abstract:

The outstanding potential of core/shell nanoparticles stems from the ability to obtain structures with combinations of properties that neither individual material possesses. Although spherical gold nanoparticles generally have a surface plasmon resonance at a wavelength of about 520 nm, a spherical silica core with a gold shell offers a very highly tunable plasmon wavelength depending on the thickness of the shell and the core diameter.

While silica core/gold shell nanoparticles have been fabricated previously by chemical reduction of gold ions, our work attempted to generate these structures by photochemical reduction and by nanosphere lithography. These techniques could provide finer control over the properties of the shell. In addition to using gold, the nanosphere lithography method was also attempted with silver. Optical spectroscopy and electron microscopy were used in the characterization of these nanoshells. Although both techniques are able to generate nanoparticles on the silica core, the current experimental conditions fail to provide a smooth shell.

Introduction:

Although the inherent nature of core/shell nanoparticles makes them potentially very useful in many areas, it is the biomedical applications that are getting the most attention. Our research focused on new ways of fabricating nanoparticles with a silica core and a shell of gold or silver, a concept pioneered by Halas et al [1]. The motivation for developing this structure lies with the surface plasmon resonance, which is the collective oscillation of free electrons in an applied electromagnetic field, resulting in intense absorption and scattering. Using a silica core, the plasmon becomes very sensitive to the shell thickness. Using silica/gold nanoshells with an 800 nm plasmon, Halas et al. found that NIR laser light (808 nm) focused on tumors with nanoshell accumulation results in localized heat delivery that selectively kills the tumors cells [2]. However, the considerable surface roughness of typical core/shell structures leaves room for improvement. This research attempted to apply the methods of photochemical reduction and nanosphere lithography to produce the nanoshells.

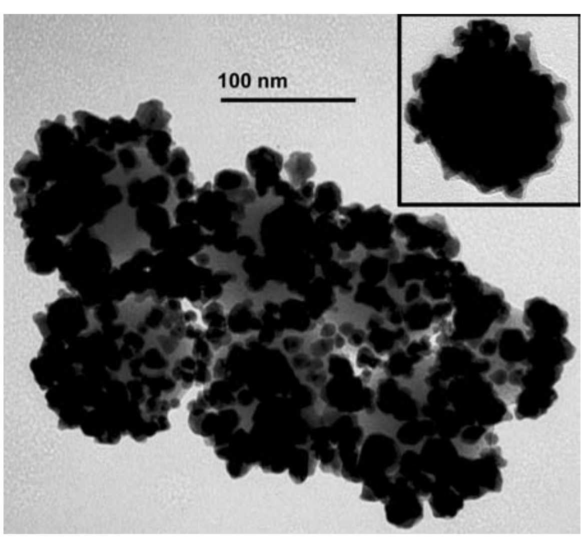

Figure 1: TEM images from photochemical reduction.

Experimental:

The photochemical reduction is a combination of the procedures of Halas et al [1] and Eustis et al [3]. Small gold colloid (1-2 nm) was prepared as described by Duff et al [4]. Silica nanoparticles 110 nm in diameter were suspended in ethanol and functionalized with 3-aminopropyltriethoxysilane (APTES). The APTES-covered silica was purified and the pH was adjusted. The negatively charged gold seeds absorbed onto the positively charged amine groups on the silica surface. A solution was prepared of the gold-modified silica and $HAuCl_4$ in ethylene glycol. Irradiation was performed with a mercury xenon lamp and a band filter selecting wavelengths from 230 nm to 400 nm. Absorbance spectra were measured with a Shimadzu UV-3103-PC spectrophotometer. Nanoshells were analyzed using a JEOL100 transmission electron microscope.

The nanosphere lithography method was performed as described by Van Duyne et al [5]. The unmodified silica nanoparticles mentioned previously were used. A PVD75 Filament Evaporator was used to deposit 5, 10, and 20 nm of gold and silver on the silica. Without removing the silica layer, absorbance spectra were measured with a Beckman DU 650 Spectrophotometer. Samples were further analyzed using a LEO 1530 Scanning Electron Microscope.

Results and Discussion:

Figure 1 shows a sample of the photochemical reduction after irradiation. The vast majority of silica nanoparticles appeared as seen here, characterized by incomplete coverage of the silica surface. Some silica particles were observed with complete gold coverage of the silica, shown in the inset. However, these particles had very rough shells, due to the growth of clusters of gold nanoparticles that encased the silica. The low yield of core/shell structures explains the absence of a plasmon peak near 800 nm, and the absorption peak at 540 nm can be attributed to spherical gold nanoparticles formed in solution and on the silica.

Though not yet ideal, this result demonstrates that the photochemical reduction is capable of reducing gold onto the surface of silica nanoparticles. In addition, without the gold seed, no gold is reduced onto the surface of the silica.

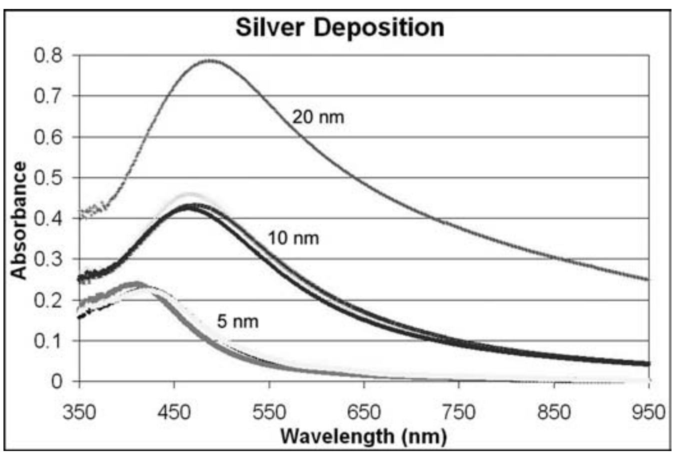

Figure 2: Absorbance spectra for varying deposition thicknesses.

With nanosphere lithography, as the deposition thickness was increased for both gold and silver, the plasmon peak red-shifted and the absorbance increased (silver is shown in Figure 2). Both of these facts are consistent with theoretical calculations for the growth of a shell [2]. As seen in Figure 3 from left to right, at 5 nm thickness, quasi-spherical silver nanoparticles pepper the surface of the silica and at 10 nm, almost completely cover the silica surface. However, the silver particles fail to coalesce to form a shell and at 20 nm thickness, the silica is buried under large, irregularly-shaped silver particles.

Future Work:

To maximize the amount of gold reduced on the surface of the silica rather than in solution during the photochemical reduction, the initial concentration of $HAuCl_4$ might be reduced or $HAuCl_4$ might be added incrementally. The effects of changing lamp power, using a narrow band filter, or otherwise altering the speed of the reaction, should also be explored. The nanosphere lithography technique may require better monodispersity of the silica nanoparticles or modification of the silica surface. For both methods, it will be necessary to encourage the formation of a smooth shell instead of isolated gold particles.

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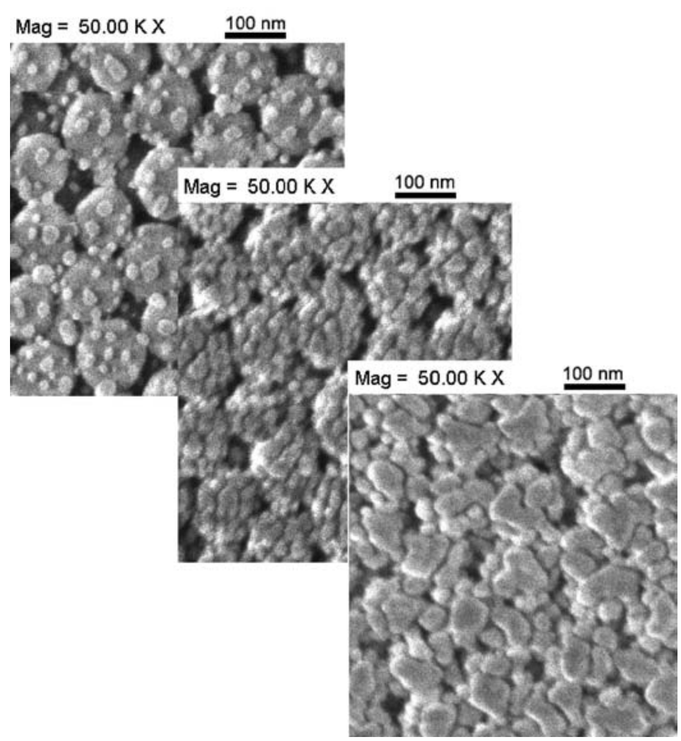

Figure 3: SEM images of silver deposition.