

Modification Method for Preparation Gold Nanoshells

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Abstract

Nanoshells are a novel class of optically tunable nanoparticles that consist of a dielectric core surrounded by a thin gold shell. Nanoshells are fabricated the silica cores were made by reducing tetraethylorthosilicate, the gold colloid adsorbs onto the aminated surface and the gold shell was then grown by reacting sodium tetra chloraurate (gold salt) with the gold –seeded aminated particles in the presence of formaldehyde. The absorbance characteristics of nanoshell were monitored using UV-Vis spectrophotometer (at 528 nm) and the average size of the silica core nanoparticles were then determined by scanning probe microscopy (349 nm). But size of gold nanoparticles (25 nm), Fourier transform infra-red spectroscopy (FTIR) SiO₂-Au particles peak 1098, 80 cm⁻¹ can be assigned to Si–O–Si bond and peak 947 cm⁻¹ can be attributed to Si–OH bond and for functionalized silica particles peaks at 3215 cm⁻¹ is assigned to NH bond. The present method, the combination of citrate and borohydride method, gives much better results and it works at room temperature. The presence of gold coating was confirmed by FTIR spectroscopy.

Keywords: Gold nanoshells, Silicon dioxide nanoparticles, Nanoparticles.

1. Introduction

Nanoshells are composed of a dielectric silica core covered by a thin metal shell which is typically gold [1]. Nanoshells can be designed and fabricated with Plasmon resonances from the visible to infrared regions of the spectrum [2] Although optical properties of gold nanoshells have already been well documented, the reflectance characteristics are not well understood and have not yet been elucidated by experimental measurements. Yet, in order to use gold nanoshells as an optical contrast agent for scattering-based optical methods such as reflectance spectroscopy, it is critical to characterize the reflectance behavior [3]. Surface plasmon resonance (SPR) is the term given to the collective oscillations of free electrons at the metallic interface surface. These oscillations can give rise to the intense colors of nanoparticle solutions because of their strong plasmon-derived absorption bands. A gold nanoshell is a layered nanoparticle consisting of a dielectric core surrounded by a gold metallic shell; these particles exhibit a plasmon-derived optical resonance typically shifted to much longer wavelength than the corresponding plasmon resonance of gold nanoparticles [4]. Experimentally, the first metal nanoshell, developed by Zhou et al. [5], consisted of an Au₂S dielectric core surrounded by a gold shell. Oldenburg et al. developed a new nanoparticle, a silica gold core – shell nanoshell, which overcame many of the limitations of the Au-Au₂S particles [6]. To synthesize these particles in a dielectric silica core grown by the Stober method [7], where tetraethyl orthosilicate is reduced in ethanol under basic conditions resulting in the nucleation and growth of highly monodisperse and spherical silica colloid. Particle diameters ranging from 50 to 500 nm can be synthesized by this method. The surfaces of the silica core particles are then functionalized with amine groups by reaction with aminopropyltriethoxysilane (APTES) [8]. Gold colloid adsorbs to the amine groups on the silica surface, resulting in a silica particle covered with gold colloid as a nucleating site [9]. The wavelength at which the resonance occurs depends on the core and shell size, allowing nanoshells to be tailored for particular applications [10]. The ability to control both wavelength-dependent scattering and absorption of nanoshells offers the opportunity to design nanoshells which provide, in a single nanoparticle, both diagnostic and therapeutic capabilities [11].

2. Materials and Methods

2.1. Materials Preparation;

2.1.1. Silica Sphere Synthesis:

Tetraethyl orthosilicate (TEOS, 99%, Sigma-Aldrich), ammonium hydroxide (NH₄OH, 14.2 M,), and ethanol (EtOH, 99.9%) were used as reagents. Following the Stöber method [12] a solution of TEOS:EtOH:H₂O:NH₄OH (2:23:6:1 mL) was stirred vigorously for 3 h to obtain a white turbid suspension. The monosized spheres,

separated from the mother liquor by centrifugation (6000 rpm/15 min), were washed repeatedly with deionized water, and finally with ethanol prior to redispersion in ethanol in a weight ratio of 1:4 (silica:EtOH).

2.1.2. APTES-Grafted Silica Sphere Synthesis:

A stock solution of 12 mM aminopropyl triethoxysilane (APTES, Sigma -Aldrich) was prepared in an EtOH:H₂O (3:1 volume ratio) solvent, to which the silica spheres were added at a 3:1 weight ratio of APTES:silica under vigorous stirring at 70 °C for 2 h. After being cooled to room temperature, the product was collected by centrifugation (8000 rpm/10 min), and then washed three times with deionized water. The APTES-grafted silica was redispersed in deionized water (1:3 = silica:H₂O weight ratio).

2.1.3. Gold Seeding on APTES-Grafted Silica:

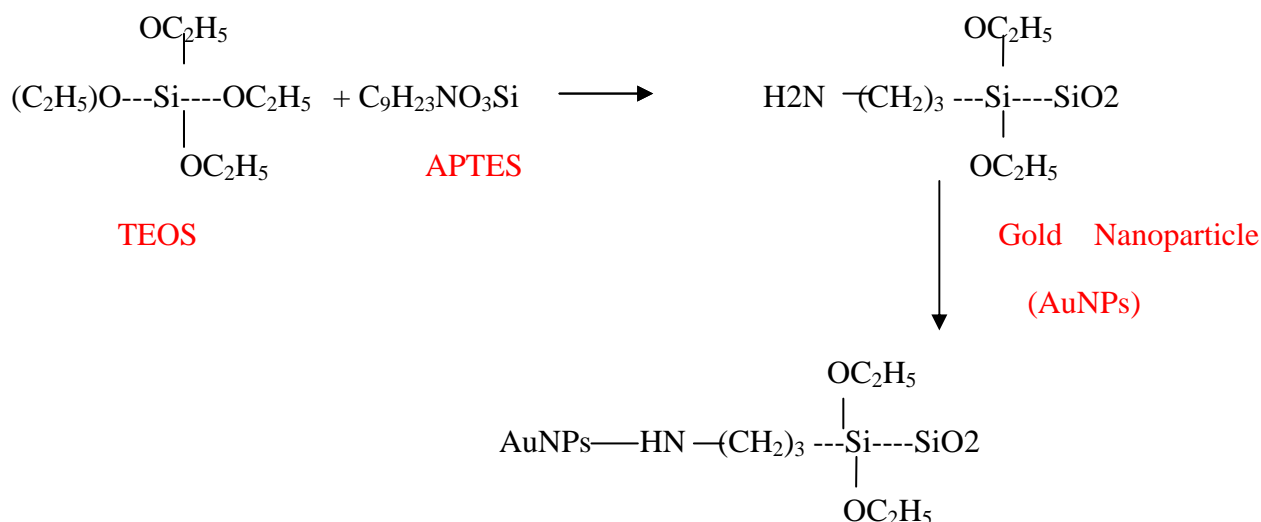
Hydrogen tetrachloroaurate(III) (HAuCl₄·3H₂O, 99.99%, Riedel-DeHaenAG), sodium hydroxide (NaOH, Fluka), potassium carbonate (K₂CO₃, Fluka), and sodium borohydride (NaBH₄, Sigma-Aldrich) were employed as received. A 6.0 mM gold stock solution was prepared by dissolving 0.259 g of HAuCl₄·3H₂O in 100 mL of deionized water (pH 5.0). The APTES-grafted silica spheres were seeded with gold at pH 7 by adding 4.5 mL of 0.1 M NaOH in 20 mL of the gold stock solution to 1 mL of dispersed silica. The suspension was stirred vigorously and heated to 70 °C for 10 min to initiate gold nucleation. Gold-seeded silica was separated by centrifugation and washed twice with deionized water, and finally ultrasonically redispersed in 40 mL of deionized water.

2.1.4. Gold Seeding on Silica Spheres:

The optimum condition for achieving high dispersion of gold nanoparticles on silica spheres has been described previously. In brief, the pH of the gold solution was adjusted by adding 0.1 M NaOH (pH 7) to 20 mL of a 6.0 mM HAuCl₄ solution, into which 1 mL of the uncalcined silica sphere suspension was dispersed with vigorous stirring and warmed to 70 °C for 15 min. The gold-seeded particles were collected using a centrifuge (8000 rpm), washed five times with deionized water, and then redispersed ultrasonically in 40 mL of deionized water.

3. Results and Discussion

To preparation of gold nano shells by this method as following:



The size of silica nanoparticles prepared by stober method was studied using scanning probe microscopy (SPM). The SPM picture of silica particles is shown in figure (1). Size 340 nm while size silica particles in Deepika Kandpal et al. [13] research is 350 nm as shown figure (2) to comparison .

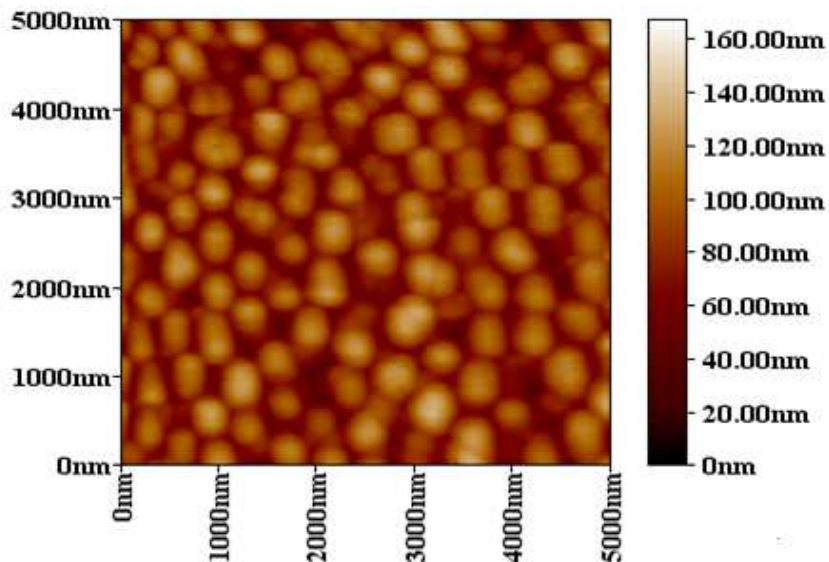


Figure (1): SPM picture of silica nanoparticle (349 nm)

Optical absorption was recorded at various stages of addition of gold nanoparticles in each method using UV-Vis absorption spectroscopy. Optical absorption of pure gold solution was found at 528 nm as shown in figure (2).

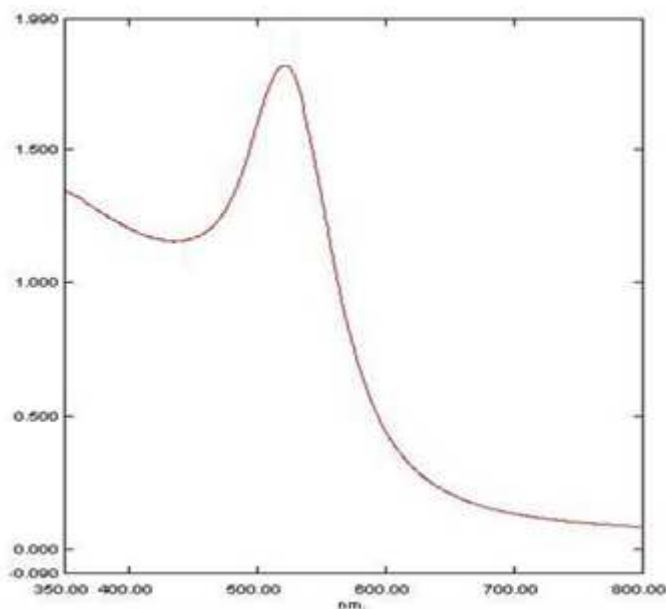


Figure (2): UV-Vis Spectrum of pure gold nanoparticles at 528 nm(Absorption =1.817)

UV-Vis absorption for gold nano shells is shown in figure (2). Gold nano shells picture is shown in figure (3) by AFM(size = 25 nm)

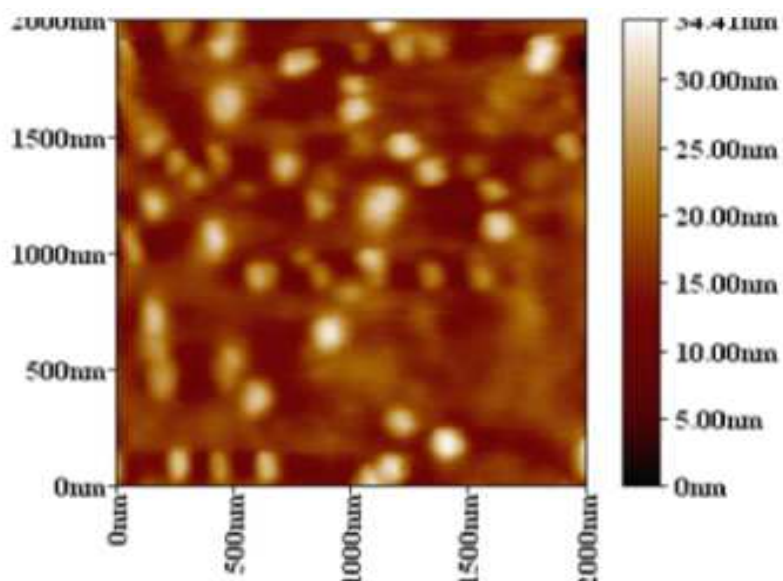
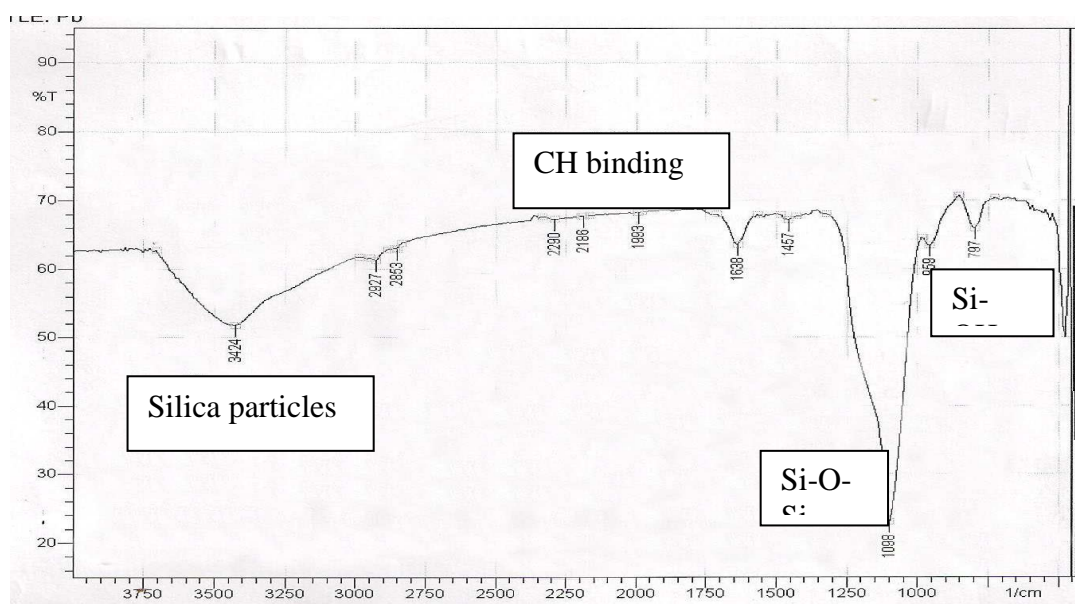


Figure (3):Picture of gold nanoparticles by AFM (size = 25 nm)

The gold particles prepared by citrate method are more stable but its reduction rate is very slow. In nucleation process silica react with separately prepared gold nanoparticles so the gold particles should be stable, but in coating the shell of gold nanoparticles were prepared directly on the surface of functionalized and gold nucleide silica nanoparticles. These gold particles directly attach with silica core and now they behave like stable core-shell particles. So for coating reducing reagent (NaBH_4) is more useful because of its high reduction rate.



Figure(4): FTIR Spectrum of gold nano shells

The structure study, i.e. bonding of these core-shell particles was also done using Fourier transform infra-red spectroscopy (FTIR). The results are shown in figure (4).

This figure shows the FTIR spectrum of silica, functionalized silica and silica-gold core-shell particles. For SiO_2 and SiO_2 -Au particles peak 1098, 80 cm^{-1} can be assigned to Si-O-Si bond and peak 947 cm^{-1} can be attributed to Si-OH bond and for functionalized silica particles peaks at 3215 cm^{-1} is assigned to NH bond. After coating these particles with gold, the intensity of Si-O-Si and Si-OH peaks has been reduced significantly. This indicates the presence of gold shell in silica particles.

4.CONCLUSION:

In this research we can prepared a gold nanoshell in new modification method.The present method, combination of citrate and boro hydride method, gives much better results and it works at room temperature.

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