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Gradual Growth of Gold Nanoseeds on Silica for Silica@Gold Core-Shell Nanoparticles and Investigation of Optical Properties

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ABSTRACT

Metal nanoshells consists of a dielectric core surrounded by a thin noble metal shell, possess unique optical properties that render nanoshells attractive for use in different technologies. This paper reports a facile method for growth of small gold nanoparticles on the functionalized surface of larger silica nanoparticles. Mono-dispersed silica particles and gold nanoparticles were prepared by the chemical reduction method. The size of the shell nanoseeds could be altered by repeating the stage of reducing $HAuCl_4$ on Au/APTES/silica particles, and the time for which they react. The nanocore-shell particles prepared were studied using scanning electron microscopy (TEM), UV–Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR) and PL spectrophotometer. The TEM images indicated that by growing gold nano-seeds over the silica cores a red shift in the maximum absorbance of UV-Visible spectroscopy is observed. Furthermore, a remarkable intensification happens in the PL spectra of silica@Au NPs in comparison with that of bare silica NPs. But, the existence of gold nanoseeds on the silica particles surfaces does not change the PL spectra peaks of these nanoparticles.

Keyword: Core-shell; Silica; Gold; Nanoparticle; Surface functionalized; Initial growth.

1. INTRODUCTION

Much recent research has focused on the fabrication of new types of nanoparticles, particularly those with optical and electrical properties that can be controlled with precision. There is increasing interest in the design and synthesis of topological structures composed of monocrystals of various size and shape. Such materials may have unusual optical properties as a result of increasing topological complexity. Core-

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shell structur are of central interest in this context. As noble metals have received particular attention,because of the stability and the ease of preparation of Nanoparticles derived from, Hal and co-workers have recently reported a new hybrid nanoparticle system that consists of a dielectric core surrounded by a thin noble-metal shell [1-3]. These nanoparticles, termed “nanoshells”, possess unique optical properties, including a strong optical absorbance and a large third-order nonlinear optical susceptibility [4]. More importantly, the absorbance can be selectively tuned to any wavelength across the visible and infrared regions of the spectrum simply by adjusting the ratio of the dielectric core to the thickness of the metal overlayer. These features render nanoshells attractive for use in technologies ranging from conducting polymer devices to biosensing and drug delivery [5-7].

At present, the most versatile nanoshell system is bed on the coating of silica nanoparticles with a thin layer of gold. We chose silica nanoparticles as the dielectric cores not only because methods for the functionalization of the surface of silica are well-known, but also because colloidal silica particles can be prepared with reproducibly spherical shapes and narrow size distributions [8].

To prepare these gold nanoshells,a silica nanoparticle core is first treated with an amine-terminated surface silanizing agent (e.g., 3-aminopropyltriethoxysilane, APTES). As the gold metal has very little affinity for silica, a silane coupling agent is used as the surface primer. The interaction between the amines and the negatively charged THPC gold nanoparticles might be electrostatic rather than coordinative in nature [8]. Therefore, the resultant terminal amine groups act attachment points for small colloidal gold particles, which then serve nucleation sites for the coalescence of the thin gold overlayer [9].

Of all possible strategies [10], the reduction of chloroauric acid with tetrakis (hydroxyl methyl) phosphoniumchloride (THPC) affords relatively small gold particles (e.g., 2 nm) with a net negative interfacial charge [8]. While these small colloidal particles can attach to APTMS-functionalized silica cores by coordinating to the lone pairs of the terminal amine groups, the attachment can be enhanced perhaps several fold by electrostatic effects, where in the negatively charged THPC gold nanoparticles are attracted to the amine groups, which are positively charged at the pH used for the attachment process. This strategy leads to silica nanoparticles in which 25% of the surface is covered by colloidal gold particles that can be used to nucleate the growth of the gold overlayer.

In this work, we describe the preparation of gold nanoshellsby the chemical reduction method and characterize the nanoshells by using transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, ultraviolet visible (UV-Vis) spectroscopy and photo luminescence (PL) spectroscopy.

2. EXPERIMENTAL

2.1. Materials

All reagents were purchased from the indicated suppliers and used without further purification: tetraethylorthosilicate, tetrakis(hydroxymethyl) phosphonium chloride, 3-aminopropyltriethoxysilane, sodium hydroxide, ammonium hydroxide, and formaldehyde; hydrogen tetrachloroaurate (III) (all from Merch Co.). Similarly, all solvents were received from the indicated suppliers: HPLC grade water, and absolute ethanol (Merch Co.).

2.2.Characterization methods

To collect the TEM images, we used a LEO 912 AB electron microscope operating at a bi voltage of 200 kV. Sample preparation involved deposition of the nanoparticles dispersed in water onto a 200 mesh copper grid. The grid was then set aside to allow for evaporation of any residual water before analysis. The FTIR data were collected using an AVA-TAR-370-FTIR THERMONICOLET spectrometer using two separate procedures. The sample was impacted into a tablet shape and put onto a polished silicon wafer before analysis. UV-Vis spectra were collected using a UVD-2950. LABOMED UV-Visible spectrometer over the range from 400 to 1100 nm. All samples were dispersed in water into a quartz cell for analysis.

2.3. Preparation of silica nanoparticles

An aliquot (3.0 mL) of ammonia (30% NH_3 NH_4OH say) was added to 50.0 mL of absolute ethanol. The mixture was stirred vigorously, and a subsequent aliquot (1.5 mL, 6.7 mmol) of $Si(OC_2H_5)_4$ (tetraethyl orthosilicate, TEOS) was added dropwise. Previous studies have shown that there is usually a concentrationdependent induction period required to form the SiO_2 nucleus from the TEOS monomer. For the concentrations employed here, the induction period was approximately 1.5 hour judged by the change of the solution from clear to opaque white. On the basis of previous work from our laboratories, the concentration of the resultant silica nanoparticles was 7×10^{12} particles / mL. Analysis by TEM indicated that the silica nanoparticles were spherical in shape with 115 nm diameters.

2.4. Functionalization ofsilica nanoparticlesurfaces with APTES

The silica nanoparticles were then surface functionalized by grafting them with 12 mM APTES in volume ratio of 3:7 under constant heating and vigorous stirring at 77°C for 3 h to give a terminal amine group on their surface. Under this condition, the APTES used was in molar excess to achieve a complete surface functionalization. The amine grafted silica particles were then cooled to room temperature and washed with at least 2 cycles of centrifugation and redispersion in absolute ethanol and distilled water at 10,000 rpm for 15 min each to remove residual reactants before resuspending them in 1 mL of water for every 0.3 g of silica used for surface functionalization with amine.

2.5. Preparation of colloidal gold nanoparticles

To a 45 mL aliquot of HPLC grade water was added 0.5 mL of 1 M NaOH and 1 mL of THPC solution (prepared by adding 12 µL (0.067 mmol) of 80% THPC in water to 1 mL of HPLC grade water). The reaction mixture was stirred for 5 min with a strong vortex in the reaction flask. After the allotted time, 1.0 mL (27 mmol) of $HAuCl_4$ 1% in water was added quickly to the stirred solution, which was stirred further for 30 min. The color of the solution changed very quickly from colorless to dark reddish yellow (Figure 1), which we call "THPC gold nanoparticles". Although the size of the THPC gold nanoparticles can be varied, our gold seeds were consistently 2-3 nm in diameter. The solution of THPC gold seeds was stored in the refrigerator for at least 3 days before further use. Dried samples of the gold nanoparticles were dark brown in color. The particles were near the detection limit of our TEM.

Figure 1: *THPC gold nanoparticles solution*

2.6. Attachment of colloidal gold nanoparticles to APTMS functionalized silica cores

An aliquot of APTES-functionalized silica nanoparticles dispersed in ethanol (6.7 mL, 2.4×10^{13} particles/mL) was placed in a centrifuge tube along with an excess of gold nanoparticles (5 mL of gold colloid solution, 3.5×10^{14} particles/mL). The centrifuge tube was shaken gently for a couple of minutes and then allowed to sit for 3 h. The mixture was then centrifuged at 2000 revolutions/min, and a red-colored pellet was observed to settle to the bottom of the tube. After drying, a red-colored pellet was left, which was redispersed and sonicated in HPLC grade water. The purified Au/APTES/silica nanoparticles were then redispersed in 5 mL of HPLC grade water and used described in the following subsection (Figure 2 b).

2.7. Growth of gold nanoshells

To grow the gold overlayer on the Au/APTES/silica nanoparticles, we first had to prepare a suitable solution containing a reducible gold salt. In a reaction flask, we dissolved 25 mg (0.18 mmol) of potassium carbonate (K_2CO_3) in 100 mL of HPLC grade water. After 10 min of stirring, 1.5 mL (20 mmol) of a solution of 1% $HAuCl_4$ in water was added. The solution initially appeared transparent yellow and slowly became colorless over the course of 30 min. To a vigorously stirred 4 mL aliquot of the colorless solution, we injected 200 µL of the solution containing the Au/APTES/silica nanoparticles.

We then added a 10 µL (0.36 mmol) aliquot of formaldehyde. Over the course of 2-4 min, the solution changed from colorless to blue, which is characteristic of nanoshell formation. The nanoshells were centrifuged and re-dispersed in HPLC grade water until use.

3. RESULTS AND DISCUSSION

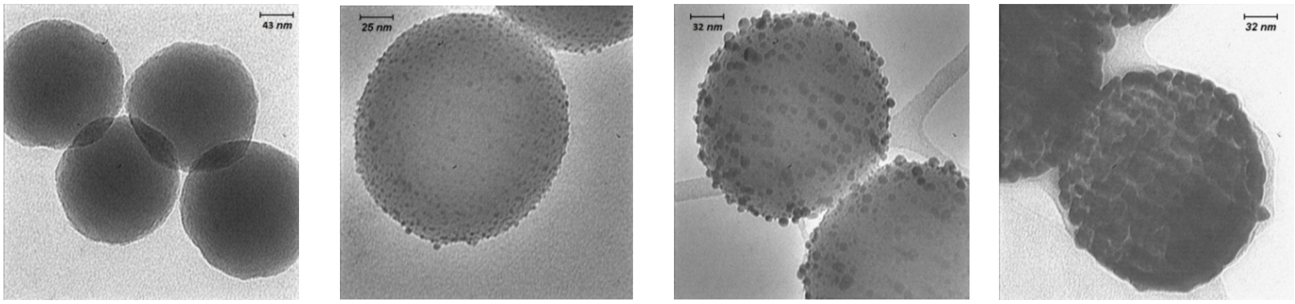
3.1. Imaging by TEM

As described above, we first prepared monodisperse spherical silica nanoparticleswith a size of about 120 nm, and then attached small colloidal particles of gold to APTES-functionalized silica nanoparticles cores and then used the attached gold particles to template the growth of a gold overlayer. NH_3 is the most effective parameter in thespherical shape of silica nanoparticles [11].

By increasing theconcentration of TEOS and H_2O, the size of the nanoparticles increases. It could be due to their influence in increasing therate of condensation and hydrolysis reactions [12]. Figure 2 shows TEM images of the different stages of our synthesis of gold nanoshells produced using this strategy. Figure 2(a) displays single silica nanoparticles. Figure 2(b) shows the desirable arrangement of the small THPC gold nanoparticles with a narrow size of <3 on functionalized silica cores. This improves our success in properly functionalizing silica particles with a layer of bifunctional APTES molecules, and also in preparing THPC gold nanoparticles in narrow size of <3 nm and good aged. Figure 2(c) demonstrates growth of monodispersed gold seedsto a narrow size of <10 nm and thus, a homogeneous shell would be obtained by repeating the last process of reducing $HAuCl_4$ on SiO_2@Au nanoparticles as seen in Figure 2(a-c). Therefore, we also did this last part of coating for one time more on the nanoparticles of Figure 2(c), whichhas shown as the resultant shell growth in Figure 2(d). Thus as it is seen, the used method in this paper for the fabrication of SiO_2@Au core/shell nanoparticles has some benefits such as facile route, the same and spherical size for silica nanoparticles and also uniform attachment of colloidal gold nanoparticles to APTES-functionalized silica cores.

3.2. XRD analysis

In order to indicate identity of the particles, X-ray diffraction (XRD) analysis was performed. The XRD pattern of the resultant nanoparticles (corresponding to Figure 2(d)) showed in Figure 3 exhibited characteristic reflections of fcc gold (JCPDS No.04-0784). The diffraction features appearing at 2θ = 38.20°, 44.41°, and 64.54° which respectively corresponds to the (111), (200) and (220) planes of the standard cubic phase of Au.



(a) (b) (c) (d)

Figure 2: *TEM images of different stages of preparing gold shell, (a) bare silica nanoparticles, (b) small colloidal THPC gold nanoparticles on APTES/silica nanoparticles, (c) first stage of growth of gold seeds on the cores, and d) second stage of (the resultant) shell growth.*

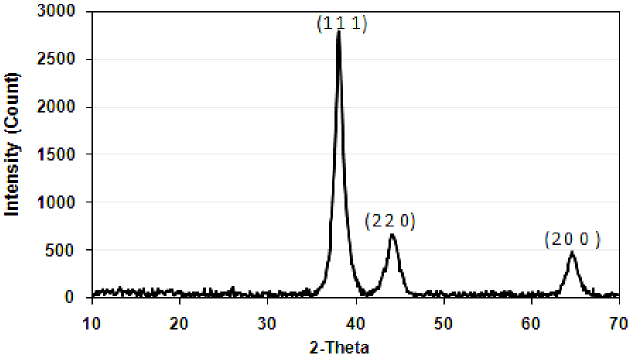


Figure 3: *XRD spectra of the resultant silica-gold nanoparticles.*

3.3. FTIR analysis

The structure study, i.e.bonding of these core-shell particles was also done using Fourier transform infrared spectroscopy (FTIR). The results are shown in Figure 4. The Figure shows the FTIR spectrum of silica, functionalized silica and silica-gold core-shell particles. It indicates an intense characteristic absorption band between 3300 and 3500 cm^{-1} assigned to O–H stretching in H-bonded water. Also this band can be cross checked through the 1635 cm^{-1} band due to the scissor bending vibration of molecular water. For SiO_2 and SiO_2@Au particles peak 1105 cm^{-1} can be signed to asymmetric vibration of Si–O bond, peak 954 cm^{-1} can be attributed to Si–OH bond and peak 795 cm^{-1} relates to symmetric vibration of Si–O. For functionalized silica particles peaks at 3215 cm^{-1} is signed to NH bond.

The absorption bands between 800 and 1260 cm^{-1} have been described as a superimposition of various SiO_2 peaks, Si–OH bonding and peaks due to the residual organic group's one. After coating these particles with gold, the intensity of Si–O–Si and Si–OH peaks have been reduced significantly. This indicates the presence of gold seeds on silica particles.

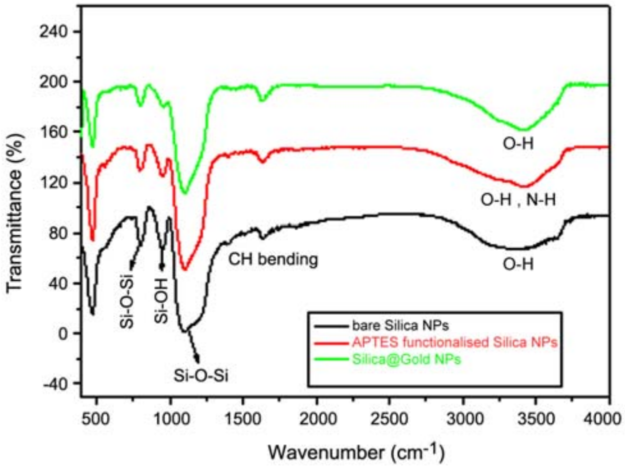
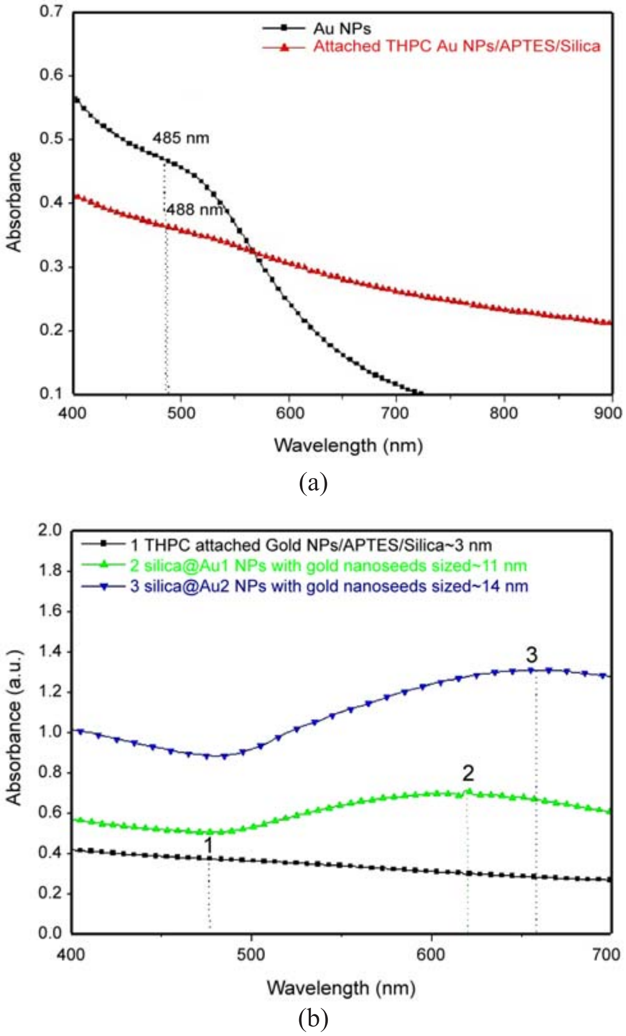


Figure 4: *FTIR spectra of silica, silica@THPC attached Au and the resultant silica@Au particles prepared.*

3.4. UV-Vis analysis

Optical absorption was recorded at various stages of addition of gold nanoparticles in every method using UV–Visible absorption spectroscopy. Optical absorption of pure gold solution was found at 485 nm shown in Figure 5(a). The singly attached Au NPs have a similar spectrum shape to that of free gold nanoparticles



(a)

(b)

Figure 5: *(a) UV-Vis spectra of attached THPC gold NPs/APTES/silica has no noticeable plasmon peak shift in comparison with THPC gold pure NPs, (b) By growing gold nanoseeds on the silica cores, in the stage of gold nanoseed growing to obtain a complete gold nanoshell, a red shift in the maximum absorbance is observed.*

(at appropriate concentration), and like that is flat in the plasmon resonance region. In contrast, the absorption spectrum for gold nanoparticles attached in clusters to silica nanoparticles shows an enhanced absorption in the plasmon resonance region. This result is interpreted as a collective effect of the gold nanoparticles in the cluster which would indicate the presence of gold nanoparticle clusters on the silica nanoparticles and the effect of plasmon-plasmon interactions on the absorption of the group of gold nanoclusters on a silica core has appeared [13, 14]. We have seen from the UV–Visible spectra of silica-gold core-shell particles that after two coatings (in SiO_2@Au1 and SiO_2@Au2) the Plasmon peak demonstrated more spreading and red shift from 622 to 662 nm respectively (Figure 5(b)). So it reveals that as more gold chloride has reduced on the attached gold particles and the particles has begun to grow and merge, Their aspect ratio has increased and this has leaded to a red shift of the absorption maximum. The mechanism for the spreading could be related to the extinction cross section and electron mean free path in the metal shell [15].

3.5. PL analysis

Figure 6 shows the PL emission spectra under 540 nm excitation wavelength of the silica NPs and silica@Au NPs. The silica@Au NPs prepared by two methods in water display one strong emission band at 784 nm. As this Figure shows, the existence of gold nanoseeds on silica nanoparticles does not shift the emission peak position.

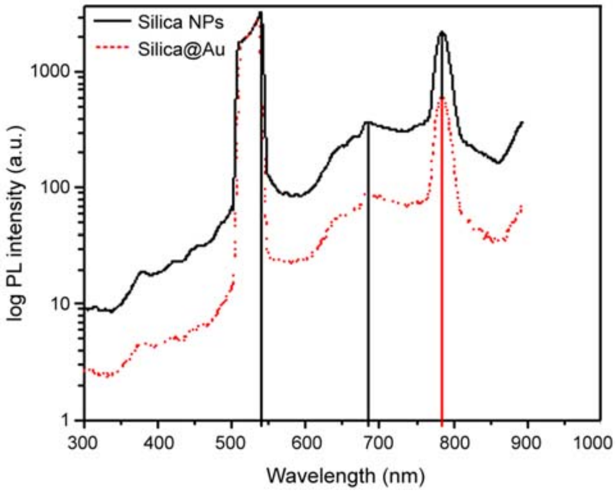


Figure 6: *PL spectra of silica and silia@Au in comparison with each other.*

4. CONCLUSIONS

Silica@gold core-shell particles were synthesized by reducing gold chloride on THPC attached silica nanoparticle cores for several stages. The morphology of these particles was also studied using TEM. TEM images demonstrated the growth of monodispersed gold seeds in narrow sizes up to 10 nm and making a whole shell by their linkage. Therefore, a uniform shell was obtained by repeating the last process of reducing $HAuCl_4$ on these particles on the nanometer scale. UV–Vis absorption spectroscopy shows a red shift from 482 to 574 nm. It indicates that the Plasmon resonance peak position of gold depends upon the sizes of gold shell seeds. Therefore, by changing the sizes of gold seeds on core surfaces and thus by changing shell thicknesses; it is possible to design a material with desired optical properties.The presence of gold coating was confirmed by FTIR spectroscopy.

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