

STRUCTURAL AND TAILORED OPTICAL PROPERTIES OF GOLD COATED SILICA ($SiO_2@Au$) NANOPARTICLES

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ABSTRACT-In the present work the optical properties of gold coated silica nanoparticles ($SiO_2@Au$) were discussed. Monodispersed silica nanoparticles were synthesized by Stober process and gold nanoparticles were synthesized by citrate reduction method. The evolution of gold-coverage over the surface of functionalized silica particles were demonstrated via tunneling electron microscopy (TEM), FTIR and UV-Visible spectroscopy for morphological and optical study. The study suggested that surface plasmon resonance absorption spectra from 350 nm to 600 nm of the core-shell nanoparticles can be effectively controlled and tuned by the surface gold coverage or by the size of $SiO_2@Au$ core-shell nanoparticles.

Keywords-Core-Shell nanoparticles, Silica nanoparticles, Gold nanoparticles, UV-Vis spectroscopy.

INTRODUCTION

Diverse behaviour of nanomaterials is due to surface effects and quantum confinement effect. The chemical reactivity and mechanical, dielectric, optical, electric, magnetic properties are affected by these factors. Gold nanoparticles are used to tune the properties of metal nanoparticles widely in the last few years. Gold nanoparticles (Au Nanoparticles) can be synthesized by the reduction of chloroaurate ions ($AuCl_4^-$) using different chemicals (using sodium borohydrate, citrate and other reducing agents) and physical (UV radiation, ultrasonication, radiolysis and thermal treatments) processes. Stabilizing agents such as thiols, amines, phosphines, phosphine oxides and carboxylates are used to control the shape and size of the particles [1-8]. When a dielectric core is coated with metal, the plasmon resonance mechanism shows a proper change in spectrum. The wavelength of appearing in the spectrum depends on the ratio of coating thickness to core size. The application of gold nanoshells are of great interest in the biomedical field, as diagnostic and therapy research studies that include optical labeling for tumor cell imaging, controlled drug delivery, and plasmonic photothermal therapy [9-10].

In the present study we have investigated the growth and attachment of small metal gold nanoparticles to the functionalized surface of larger silica nanoparticles. Nearly monodispersed silica particles and gold nanoparticles were prepared by sol-gel method. The size of the particle could be altered by changing the concentration of reactants, temperature and the reaction time. The nano core-shell particles prepared by the above method were studied for their optical properties using UV-Vis spectroscopy and the morphological study was done by transmission electron microscopy (TEM) and FTIR.

Materials and Methods

Pure and analytical grade chemicals were used in all experiments including synthesis of gold, silica and gold coated silica nanoparticles. Silica nanoparticles were synthesized by using the Stöber method [11]. In brief, ethanol, distilled water, and ammonium hydroxide (NH_4OH) were mixed in a round-bottom flask and stirred at room temperature for ~30 min. To this solution, tetraethylorthosilicate (TEOS) was added and the solution was further stirred for 3 h. A white precipitate was obtained which was thoroughly washed with ethanol and then dried. By varying the concentration of NH_4OH and TEOS, we can vary the size of the monodispersed silica nanoparticles. Functionalization of silica nanoparticles was done by using APTES in C_2H_5OH/H_2O (3:1 volume ratio) and adding silica particles to it with APTES/silica ratio as 2.3:1 (w%). The resulting solution was vigorously stirred at $80^\circ C$ for 12 h. The solution was centrifuged, and the precipitate was washed with water to get functionalized silica particles. Gold nanoparticles were synthesized by the citrate reduction of $HAuCl_4 \cdot 3H_2O$. In brief, 10 ml of $HAuCl_4$ (0.002 M) was boiled at $80^\circ C$ for 30 min. A freshly prepared trisodium citrate (10 ml, 0.01 M) was added drop wise to the mixture with constant stirring. The solution changed from colourless to a deep wine red colour. For the synthesis of gold coated silica nanoparticles, 0.2 gm functionalized silica powder was transferred into a round bottom flask, 50 ml C_2H_5OH and 0.5 ml gold particle solution was added drop wise into the flask. Then the mixture was vigorously stirred and heated for 30 minutes. After this, the solution was allowed to settle down and the supernatant solution was then discarded carefully. The remaining solution was centrifuged at 12,000 rpm for 10 min and the supernatant was discarded. The prepared gold nucleated nanoparticles were washed and dried to get gold nucleated light red coloured particles. The prepared nanoparticles were washed and centrifuged three times using distilled water. The coating process was carried out several times for full coating of silica core by gold nanoparticles shell.

Results and Discussion

Ammonia-catalyzed reactions of TEOS with water in alcohols (Stöber synthesis) were used for the preparation of monodispersed, spherical silica nanoparticles. White silica nanoparticles were functionalized to attach the gold nanoparticles on it by using the bi-functional organic solvent 3-aminopropyltriethoxysilane (APTES). The gold metal has very little affinity for silica, and it does not form the passivating oxide film in solution, hence silane coupling agent was used as surface primer. The

strong chemical affinity of primary amines for gold drives chemisorptions of the colloids in the case of APTES. Gold prepared by reducing 0.002 M HAuCl_4 solution by 0.01 M trisodium citrate $\text{Na}_3(\text{C}_6\text{H}_5\text{O}_7)$ for coating was used. Brownish red coloured silica-gold core-shell nanoparticles ($\text{SiO}_2@Au$) were obtained after several coating with gold nanoparticles.

Figure 1 shows a typical TEM micrograph of the silica sample sintered at 20°C . TEM observations revealed that the particles obtained by Stober process showed a homogeneous spherical shape, and they were well dispersed without an appreciable clustering. The average particle size of SiO_2 was observed ~ 200 nm. On variation the concentration of reagents used, size of SiO_2 particle decreases to ~ 140 nm.

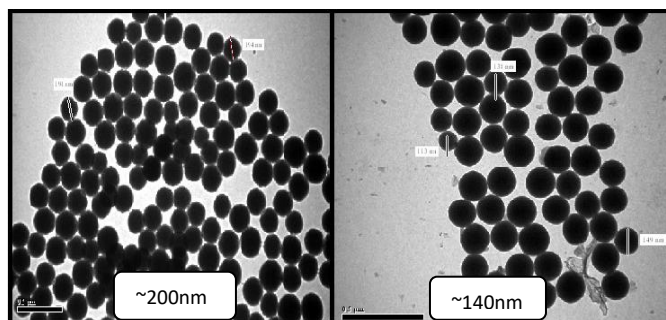


Figure 1: TEM image of silica nanoparticles with different concentration of reagents

The prepared silica particles were spherical and there was no wide distribution in the particle size. The particle size increases on increasing the concentrations of TEOS, ammonia and water. UV-Vis spectroscopy confirmed the formation of gold nanoparticles in a colloidal solution.

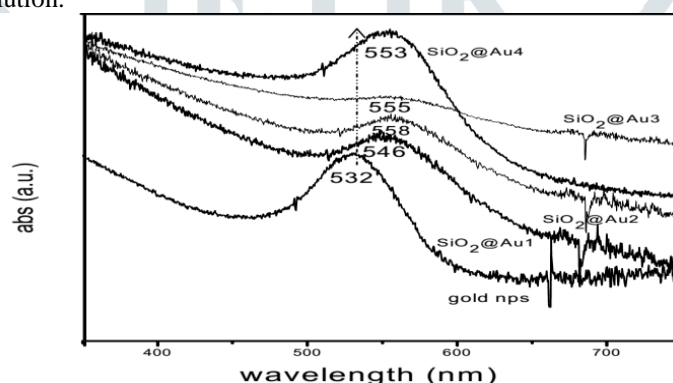


Figure 2: Absorption spectra of $\text{SiO}_2@Au$ nanoparticles

The gold nanoparticles prepared by citrate method were red in color and to examine the optical properties of pure gold and $\text{SiO}_2@Au$, absorption spectra of these nanoparticles were observed. Figure 2 shows UV-Visible absorption spectra in the range of 350-700 nm in the absorbance modes in which the maximum absorbance peak at 532 nm corresponds to pure gold nanoparticles which predicts the average size of the gold nanoparticles to be ~ 40 nm. With an increase in surface gold coverage on the silica nanoparticles, with a specific core size, a red shift from 532 to 558 nm was observed. The red shift was no longer apparent when surface coverage was complete. After the fourth coating the peak was blue shifted to 553 nm [12-14].

The main interest of the study was to understand the effect of gold shell thickness on the change in surface plasmon band during particle aggregation. The surface of the core particles is often modified with bi-functional molecules to enhance coverage of shell material on their surfaces. Surface of core particles such as silica can be modified using bi functional organic molecules such as APTES. This molecule has an ethoxy group at one end, and $-\text{NH}$ group at the other end. APTES forms a covalent bond with silica particles through the $-\text{OH}$ group and their surface becomes NH -terminated. The FTIR spectra of SiO_2 , functionalized SiO_2 with APTES and gold coated silica nanoparticles is shown in figure 3.

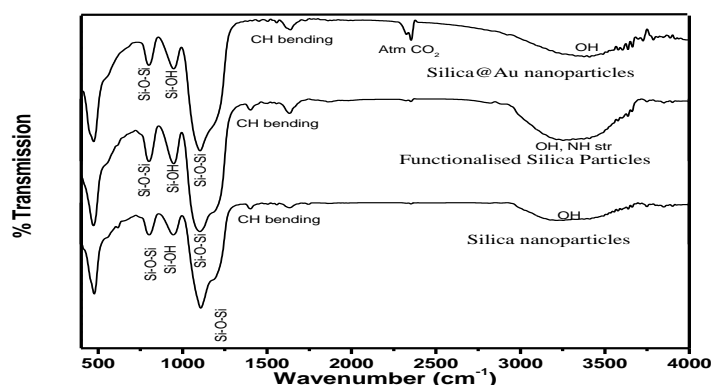


Figure 3: FTIR spectra of $\text{SiO}_2@Au$ nanoparticles

The main peaks were observed at 3431 cm^{-1} (NH_2 asymmetric stretch) which corresponds to functionalized silica particles and 1634 cm^{-1} (C-H bending). The spectrum showed Si–O–Si symmetric stretching at 801 cm^{-1} and characteristic Si–O–Si asymmetric stretching at around 1100 cm^{-1} respectively. After coating silica particles with gold, the intensity of Si–O–Si and Si–OH peaks was reduced significantly. This indicated the presence of gold shell in silica nanoparticles.

Conclusion

Nearly monodispersed spherical core-shell $\text{SiO}_2\text{@Au}$ nanoparticles were synthesized successfully, using citrate reduction method to coat gold nanoparticles. TEM images confirmed the formation of nearly monodisperse spherical silica nanoparticles with different concentration of chemical used. The prepared silica nanoparticles were first grafted with amine functionalities, which were essential for the subsequent surface attachment of gold nanoparticles, in a citrate buffer medium. The presence of citrate ions in solution helped to achieve uniform gold coverage. The surface-attached gold nanoparticles on the amino-functionalized silica core nanoparticles served as seeds for the growth of continuous gold shells. By varying the amount of gold decorated APTES-functionalized silica nanoparticles, to tune the final surface of the gold coverage on the silica nanoparticles, the surface plasmon resonance of the nanoshells could be adjusted to any wavelength from the visible to the NIR region of the electromagnetic spectrum, making them ideal for biomedical and optical applications. The absorption band in UV–Visible spectrum of colloid confirmed the presence of gold nanoparticles in the non-aqueous system. It was observed that the plasmon resonance peak position of gold depends upon the shell thickness. The FTIR results indicated that gold molecules get adsorbed on the surface of silica nanoparticles to form the tunable silica coated gold core shell nanoparticles.

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