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Preparation and Characterization of Self Assembled Gold Nanoparticles on Amino Functionalized SiO_2 Dielectric Core

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***Abstract*—**Wet chemistry methods are used to prepare the SiO_2/Au nanoshells. The purpose of this research was to synthesize gold coated SiO_2 nanoshells for biomedical applications. Tunable nanoshells were prepared by using different colloidal concentrations. The nanoshells are characterized by FTIR, XRD, UV-Vis spectroscopy and atomic force microscopy (AFM). The FTIR results confirmed the functionalization of the surfaces of silica nanoparticles with NH_2 terminal groups. A tunable absorption was observed between 470-600 nm with a maximum range of 530-560 nm. Based on the XRD results three main peaks of Au (111), (200) and (220) were identified. Also AFM results showed that the silica core diameter was about 100 nm and the thickness of gold shell about 10 nm.

***Keywords*—**Gold nanoshells, Synthesis, UV-vis spectroscopy, XRD, AFM

I. Introduction

IN recent years noble nanoparticles and nanoshells have been focus of many research fields including: Biomedical, optoelectronics, chemical sensors and surface – enhanced Raman scattering (SERS) [1]. The optical property of nanoshells is dominated by the response of the metal's conduction electrons, particularly the surface plasmon resonance (SPR)[2]. Excitation of surface plasmons via photons, requires specific condition that are defined by their dispersion relation:

$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (1)$$

Where k_{sp} is the surface plasmon wave vector, ω is the frequency of light and ε_1, ε_2 represent the dielectric of medium 1(here SiO_2) and 2 (Au) respectively. It should be noted that ε_{diel} is the (purely real) dielectric constant, and ε_{met} (Au) = $\varepsilon_r + i\varepsilon_i$ is the complex dielectric constant of the metallic nanoparticles. The real part (ε_r) determines the degree to which the metal polarizes in response to an applied external electric field and the imaginary part, $i\varepsilon_i$, quantifies the relative phase shift of this induced polarization with respect to the external field and it include losses (e.g. ohmic loss as heat). For solid spherical nanoparticles the wavelength at which the plasmon resonance occurs is only weakly dependant on the particle size. For nanoshells, the plasmon resonance wavelengths depends on the relative sizes of the core and shell and can be placed from 600- 2500 nm using silica core and gold shells[3].

Novel optical effects are expected by appropriately arranging metal particles on the surface of insulating cores of spherical shape, so as to compose, on a nanometer scale, core-shell structures. Optical resonances from near-infrared to the visible range may then be tuned by adjusting the core size, shell thickness and type of metal and/or core material [4]. Core-shell structures have been intensively studied very recently, in particular since such structures exhibit peculiar properties which make them attractive for applications in optical and biological sensors and in optoelectronics [5]. For practical reasons, solution methods, such as the deposition of nanoparticles from a colloidal route of synthesis or particle formation directly on the surface by appropriate processes, are preferred. The first route includes electrostatic deposition of colloidal particles by means of adhesives such as poly electrolytes covering the oxide surface [6] and ligand-mediated immobilization of metal colloids on functionalized oxide surfaces [2]. The second route includes controlled chemical reduction or photochemical reduction [7].The aim of producing core-shell structures requires one to achieve a high nucleation but low growth rate, so as to obtain a high number density of metal nanoparticles without the formation of aggregates. Further nanoparticles coating from complementary processes to form continuous metal nanoshells may utilize the previously formed particles serving as seeds which catalyze metal deposition without nucleation of new particles [8]. Such multi-step processing includes some prospects of fabricating bimetallic structures by varying the metal precursor employed.

In this study we report synthesis and characterization of binary SiO_2/Au nanoshells for clinical applications where surface plasmon-based thermal effect plays a crucial role.

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II. Materials and Methods

Hydrogen tetrachloraurate (HAuCl4) (99.9%), tetraethyl orthosilicate (TOES) (99.9%), 3-aminopropyltrimethoxy silane(APTMS),Tetrakis hydroxymethyl phosphonim chloride (THPC) (80% solution in water), Potassium carbonate (99%), formaldehyde, ammonium hydroxide solution (33%NH3) and ethanol (99%), HPLC grade water and Sodium Hydroxide (99%) were obtained from Sigma- Aldrich Co. Silica nanoparticles prepared using following method: 3mL of ammonia was first added to 50mL of absolute ethanol, and then the mixture was stirred vigorously ; different amounts (1mL (sample A), 1.5mL (sample B)) of TEOS were added drop wise. The induction period was approximately 45 minutes that the solution color became cloudy as silica nanoparticles were grown and eventually turned opaque white. 25µL of APTMS was then added to 50 mL of the vigorously stirred silica nanoparticles solution and allowed to react for 2 hours. The APTMS coated silica nanoparticles were purified by centrifuging at 3500 rpm and redispersion in ethanol. For preparation of colloidal gold nanoparticles, 0.5mL of 1M NaOH and 1 mL of THPC solution (prepared by adding 12 µL of 80% THPC to 1 mL of HPLC grade water) were added to a 45 mL of HPLC grade water. The solution was stirred vigorously for 5 minutes. After this process 2 mL of 1% HAuCl4 in water was added to the stirred solution. THPC gold solution preparation produced a brown color solution within 2-3 seconds after addition of chloroauric acid.

For attachment of colloidal gold to nanosilica particles, 1mL of APTMS-functionalized nanosilica particles dispersed in ethanol was added to 10 mL of gold colloid ($\sim 7\times10^{14}$ particles / mL) in a tube. The tube was shaken for 5 minutes and then was left to settle down for 2 hour. The mixture was subsequently centrifuged at 2000 rpm and a red color pellet precipitated at the bottom of the tube. The supernatant was removed and the remaining red-colour pellet redispersed in HPLC grade water. The purified Au/APTMS/nanosilica particles then redispersed in 5 mL of HPLC grade water.

For growing the gold over the Au/APTMS/silica nanoparticles, 25mg of potassium carbonate was dissolved in 100mL water. After 10 minutes of stirring, 1.5 mL of 1%HAuCl4 was added. This solution was initially yellow and after 30 minutes became colorless. 0.5 mL of the solution containing Au/APTMS/nanosilica was added to the colorless solution. After addition of 20µL of formaldehyde the colorless solution became purple. The nanoshells were centrifuged and redispersed in HPLC water for preparation of final product.

The ultraviolet/visible (UV/visible) extinction spectra of the nanoparticles were measured in solution using the UV/VIS-spectrophotometer (Philips PU 8620) in the wavelength range of 190 to 900 nm with the appropriate mixture of ethanol and water as a reference. The surface topography and roughness as well as the size of nanoshells were studied by AFM (Dual scope/ Raster scope C26, DME, Denmark). Mid-infrared spectra of absorbance peaks of SiO2, APTMS/Silica and Au/APTMS/ SiO2 were obtained by transmission mode of Fourier Transform infrared (FTIR; Brucker, EQUINOX 55, Germany).

III. Results and Discussion

Silica (SiO_2) is a popular material to form core shell particles because of its extraordinary stability against coagulation. Its non-coagulating nature is due to very low value of Hamaker constant, which defines the Van der Waal forces of attraction among the particles and the medium [9]. It is also chemically inert, optically transparent and does not affect redox reactions at core surfaces [10]. For various purposes it is desirable that particles remain well dispersed in the medium which can be achieved by suitably coating them to form an encapsulating shell. It is worth mentioning that the synthesizing of SiO_2 nanoparticles may take place via the procedure developed by Stober et al. [11] This method involves hydrolysis and successive condensation of TEOS ($Si(C_2H_5O)_4$) in alcoholic medium.

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad (2)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \quad (3)$$

UV-visible spectra recorded for two different samples are shown in fig.1. For gold nanoparticles synthesized by 1mL TEOS a peak at about 535 nm was observed. However, when 1.5mL was used the peak showed a red-shift at about 556 nm. This is thought to be associated with a SPR phenomenon. The resonance peak position depends on the plasmon interaction between separate inner and outer gold layers. As it can be seen in this figure, the increasing addition of TEOS could efficiently cause the optical plasmon peaks to undergo a red-shift, which is consistent with the theoretical predictions of optical properties of metal coated particles. As the nanoshell growth progresses their optical plasmon peak is slightly red-shifted. Also the peak broadening is similar to the results observed by Wiesner [12] in spectroscopic studies of gold platelets in solution. In their case, the growing silica layer began to coalesce and encapsulated the different amounts of gold nanoparticles.

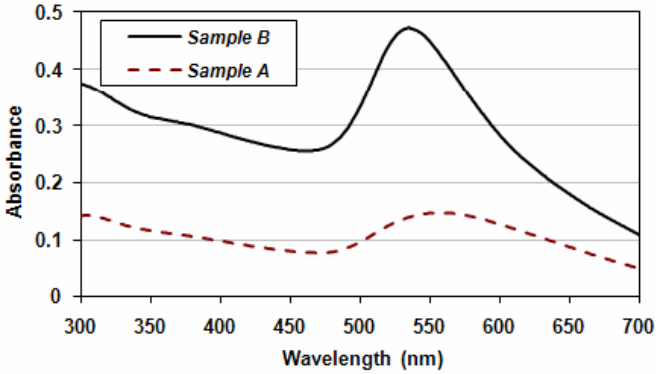


Fig.1 UV-visible spectroscopy of gold nanoshell synthesized by different amount of TEOS

This phenomenon suggests that the silica core is completely covered by gold layer and its absorption spectra are function of the addition ratios of TEOS. Furthermore, the complete synthesized nanoshells, whose optical plasmon resonance peak ranges in the 500- 600 nm regions, can be used as a powerful tool in bio-imaging and bio sensing applications. The optical absorption spectra shown in this figure are

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relatively broad compared with that of pure gold colloid. According to Mie scattering theory, the nanoshells geometry can quantitatively accounts for the observed plasmon resonance shifts and line-widths. In addition, the plasmon line-width is dominated by surface electron scattering [13].

Infrared spectroscopy offers a wealth of information regarding the structure of the surface of the nanoparticles. In particular, IR spectroscopy affords insight into the order and packing of the surface chains. The surface of the core particles is often modified with bi-functional molecules to enhance coverage of shell material on their surfaces [14]. Surface of core particles such as silica can be modified using bi-functional organic molecules such as APTMS. This molecule has a methoxy group at one end, and NH group at the other end. APTMS forms a covalent bond with silica particles through the OH group and their surface becomes NH-terminated. The FTIR spectra of SiO_2 functionalized with APTMS and gold coated nanoparticles for sample A is shown in fig.2. The main peaks are 3431 cm^{-1} (NH_2 asymmetric stretch), 1634 cm^{-1} (O-H bending) and 466 cm^{-1} for Si-O-Si bending mode. The shells showed Si–O–Si symmetric stretching at 801cm^{-1} and characteristic Si–O–Si asymmetric stretching at around 1100 cm^{-1} respectively [15].

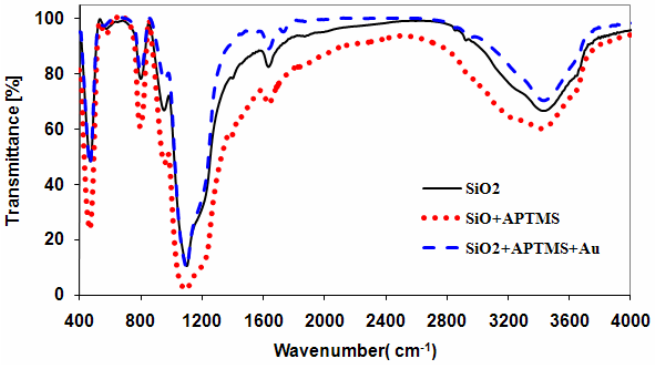


Fig.2 FTIR of SiO_2 functionalized with APTMS for sample A

In order to indicate identity of the particles, X-ray diffraction (XRD) analysis was performed. The XRD pattern of nanoshells shown in Fig.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.

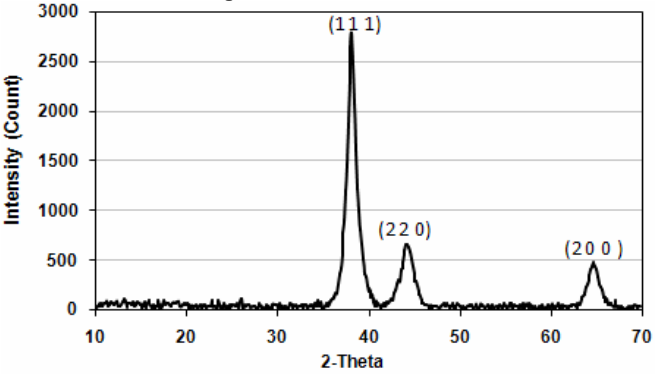


Fig.3 XRD spectra of gold nanoshells

By varying relative ratio of TEOS to solvent we could synthesize these particles in various sizes. Reduction in TEOS concentration led to the formation of smaller particles. Silica particles synthesized by this procedure were amorphous and porous. Fig. 4a shows an AFM image of functionalized silica nanoparticles synthesized by the procedure described earlier in the material and methods section. An example of Au coated SiO_2 nanoshell is shown in fig. 4b. Small colloids of the gold particles are attached to APTMS – functionalized silica nanoparticles core which were then used to template the growth of gold over layer. The size of the nanoshells determined by AFM ranged between 90 and 110 nm. These images provided useful information about surface topography and the size of the gold nanoparticles with well defined clarity, which effectively is correlated to optical absorption spectra.

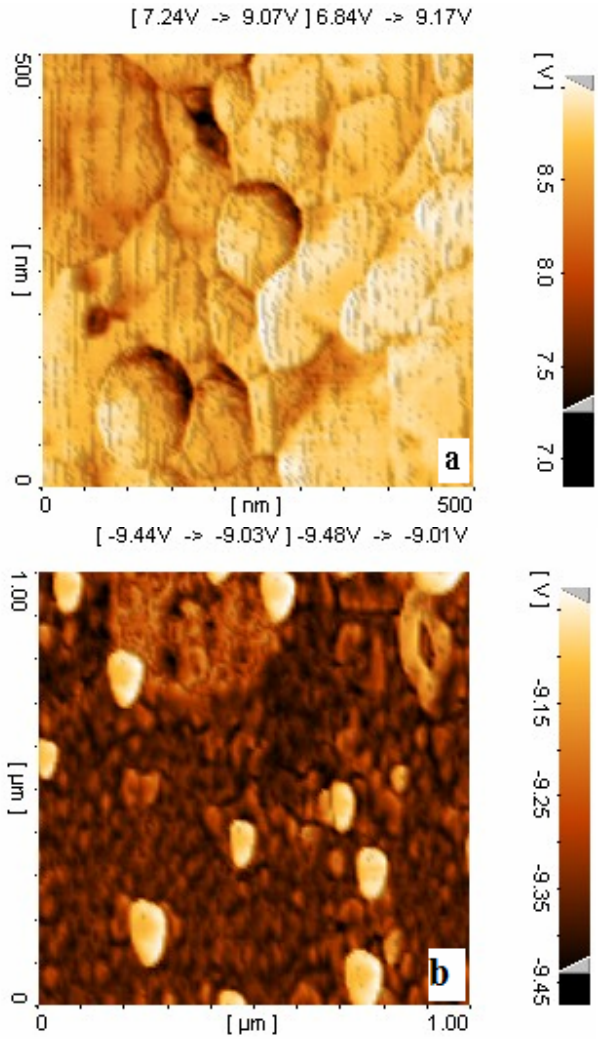


Fig.4 AFM photographs of surface topography of SiO_2 core (a) and SiO_2/Au nanoshells

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IV. Conclusion

Gold nanoshells were deposited on the surfaces of silica core and their chemical and optical properties were investigated. The unique, tunable and optical responses of gold nanoshells are most desirable as exogenous agent for biophotonics applications. In summary, we have demonstrated that gold nanoshells with tunable thickness can be fabricated on silica dielectric with diameters ranging from 90 to 110nm, where the shell thickness and roughness were controlled by the amount of TEOS and checked by AFM. Higher concentration of gold nanoparticles provided a higher temperature rise. Based on the gold layer thickness and the LSPR effect the degree of light absorption varied between 470-600 nm. A variety of parameters can influence the self-assembly of gold nanoparticles into clusters attached to the surfaces of functionalized silica nanoparticles which in this case hydrophilic functional groups such as NH_2 led to the attachment of gold nanoparticles.

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