Synthesis and physicochemical characterization of tunable silica–gold nanoshells via seed growth method

S. Narjes Abdollahi, Malek Naderi, Ghassem Amoabediny

Department of Mining and Metallurgy, Amirkabir University of Technology, Tehran, Iran
Department of Chemical Engineering, School of Engineering, University of Tehran, Tehran, Iran
Research Center for New Technologies in Life Science Engineering, University of Tehran, Tehran, Iran

Highlights

- SPR of gold nanoparticles below 20 nm shows a red shift by increasing size.
- Excess amount of modifier causes agglomeration of silica cores.
- Using 15 nm gold particles for seeding 100 nm silica causes separated gold islands.
- Shell thickness and tunability of nanoshells depend on size of gold particles.

Abstract

Gold nanoshells are a class of nanocomposites consisting of a core surrounded by a gold shell. They are known to exhibit attractive optical property due to the excitation of surface plasmon resonance. This paper reports synthesis and characterization of gold nanoshells using two different sizes of gold colloids obtained by citrate and borohydride for nucleation step. Silica nanoparticles with an average diameter of 100 nm were synthesized and were modified with 3-aminopropyltriethoxysilane (APTES). The functionalized silica nanoparticles were initially decorated with gold colloids. Then gold hydroxide was reduced into decorated silica particles to obtain gold shell. The results reveal that the silica surface coverage with gold nanoparticles and gold shell thickness depends on size of gold nanoparticles. They show that smaller gold colloids provide better coverage at seeding step; hence, a uniform and complete shell is the consequence for these kinds of particles. Furthermore, tunability of gold nanoshells into appropriate wavelength according to desire application while using 4.5 nm gold nanoparticles for decoration is more facile due to possibility to control shell growth progress and shell thickness.

1. Introduction

In recent years, unique optical, magnetic and chemical properties of nanoparticles lead to a variety of applications such as diagnosis of diseases, drug delivery, catalysis and water treatment. Hence, many researchers have been studied properties and applications of nanostructures and different methods to synthesize them. Recently, synthesis and characterization of nanoshells is an interesting subject for a large number of researches because of their special optical property [1,2].

Nanoshells are a type of nanoparticles composed of a dielectric core such as silica coated with an ultrathin metallic layer, which is typically gold. Nanoshells are capable to absorb or emit different wavelengths from the visible region to the infrared. The optical response of nanoshells depends on core diameter to shell thickness ratio and nanoshell total diameter. In fact, by controlling the core/shell ratio, surface plasmon resonance (SPR) of nanoshells can be extended from visible to IR [3,4]. Due to nanoshells unique optical property, they have gained considerable attention for medical applications especially cancer therapy. Since almost all of them are
gathered in the neoplasm after injection, it is possible to image the tumor by irradiation nanoshells with laser. Furthermore, because nanoshells are able to convert light into heat, they can be used for hyperthermia [4].

Synthesis of silica–gold nanoshells is a multi-step procedure. First, silica nanoparticles are synthesized by Stöber recipe and then they are coated with gold shell [4]. There are two main ways to coat cores with gold [5].

One is changing surface charge by introducing functional groups such as amine, thiol or diethylene phosphine onto the silica [2,4,6]. Then, gold nanoparticles obtained by reduction of chloroauric acid (HAuCl₄) in presence of THPC [1] or tri-sodium citrate [7–9] are seeded onto the cores. The last step involves gold shell growth that gold hydroxide, produced in reaction of chloroauric acid and potassium carbonate, is reduced on gold decorated silica nanoparticles by using reduction agent that the most often one is formaldehyde [2].

Second method to form gold shell is deposition–precipitation (DP), i.e. modification of silica particles and their initial decoration with colloidal gold can be omitted [2]. In this method, gold hydroxide is reduced directly with sodium borohydride [10,11], sodium citrate [6] or formaldehyde [12] onto silica surface.

Although, the DP method is rapid and less expense compared to the method using colloidal gold and modifier [2], but experimental results show that deposition of colloidal gold onto the modified silica particles leads to more uniform distribution of gold nanoparticles [12,13]. Furthermore, using first method leads to more appropriate control over shell growth [12].

In pre-decorated method, in order to grow shell, gold hydroxide must be reduced on seeded gold colloids that it causes gold particles enlargement and finally a continuous gold shell [2]. Hence, the number of gold colloids attached onto silica or the silica coverage degree is an important parameter. Many factors such as type of modifier [1,5,6], volume of linker [1], time of seeding step [1] and type of reduction agent [2] affect the surface coverage of cores with gold particles and as a result, shell thickness and uniformity of shell. In this paper, for the first time, we investigate the effect of gold nanoparticles diameter on surface morphology of gold nanoshells. So, for initial decoration of 100 ± 20 nm and 250 ± 20 nm silica nanoparticles, two gold solutions with different size distribution were used. The gold nanocolloids were produced by using sodium borohydride (gold nanoparticles diameter ~4.5 ± 1 nm) and tri-sodium citrate (gold nanoparticles diameter ~15 ± 3 nm) as reduction agent. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), zeta potential analyser, X-ray diffraction (XRD), UV–vis spectroscopy and Fourier transform infrared spectroscopy (FTIR) were further used to characterize the gold nanoshells. We found that borohydride stabilized gold nanoparticles were deposited more onto silica particles at seeding step in comparison with citrate stabilized ones and for these kinds of particles, a complete shell was the consequence.

2. Experimental

2.1. Materials

Tri-sodium citrate dehydrate (99%), hydrochloric acid (37%), tetraethylorthosilicate (TEOS) (99%), potassium carbonate, ammonium hydroxide (25%) and ethanol (100%) were obtained from Merck. 3-aminopropyltriethoxysilane (APTES) and nitric acid (65%) were purchased from Sigma–Aldrich. Sodium borohydride (98%) and formaldehyde solution (37%) were purchased from Acros and Applichem, respectively. All chemicals were used as received.

2.2. Preparation of modified silica nanoparticles

Silica nanoparticles were synthesized by Stöber method [14,15]. 100 ml ethanol, 5 ml deionized water, 8.5 ml ammonium hydroxide and 1.5 ml tetraethyloxysilicate were stirred at 40 °C for 3 h. The size of synthesized particles was 100 ± 20 nm. By increasing TEOS volume to 2.5 ml, silica particles with average size of 250 nm were obtained.

For modification of silica nanoparticles, 0.1 ml APTES was added to 100 ml silica solution and it was stirred over night. Then, the solution was centrifuged for 30 min and the deposited solid was dispersed in deionized water. In order to investigate the effect of linker quantity on shell formation, the same procedure was repeated for 0.2 ml of APTES.

2.3. Preparation of colloidal gold

Chloroauric acid (HAuCl₄), precursor material for gold nanoparticles, was prepared by evaporation of the solution obtained by dissolving pure gold in aqua regia [16].

For preparation of 4.5 ± 1 nm gold nanoparticles, 1 ml of 1% HAuCl₄ solution was added to 100 ml stirring deionized water in room temperature. Then 2 ml of 1% tri-sodium citrate and 1 ml of fresh 0.075% sodium borohydride in 1% tri-sodium citrate were added and the solution was stirred for 10 min.

In order to prepare 15 ± 3 nm gold nanoparticles, 2 ml of 1% HAuCl₄ solution and 4 ml of 0.04 M tri-sodium citrate were added to 100 ml boiling deionized water, and it was stirred for 15 min. The prepared gold nanoparticles should be kept in fridge for further use.

2.4. Attachment of colloidal gold to silica and shell growth

10 ml functionalized silica nanoparticles solution was added to 100 ml gold nanoparticles, and it was stirred for 5 min. Then, it was left to stand in static situation for further 2 h. The solution was centrifuged for 30 min to remove non-attached gold nanoparticles and the deposited solid was dispersed in deionized water.

In order to grow gold shell, 1.5 ml of 1% HAuCl₄ solution was added to 100 ml of 2 mM potassium carbonate aqueous solution and it was stirred vigorously for 30 min that the yellow colored solution became colorless gradually. The solution kept in dark place over night to form Au(OH)₄⁻ ions. 1 ml of gold seeded silica solution was added to 20 ml gold hydroxide solution and it was stirred in presence of formaldehyde. Slowly, the color of solution changed to blue which is a characteristic of nanoshell formation. Finally, the solution was centrifuged and the deposited pellet was dispersed in deionized water.

2.5. Characterization

Fourier transformed infrared spectroscopy spectra were obtained using a Tensor 27 FTIR spectrometer (Bruker) and samples were dried at 50 °C. A ZEN 3600 zetatarsizer (Malvern) was used to measure the zeta potential of the nanoparticles. The UV–vis absorption spectra were measured by a V–550 spectrophotometer (Jasco). The X-ray diffraction patterns of the samples were recorded in an X-pert Pro diffractometer (PANalytical) using CuKα radiation (λ = 1.5418 Å) in the 2θ range of 5°–100°. SEM images were obtained using a XL30 scanning electron microscope (Philips) operating at 30 kV. Sample was dropped on a cylinder, was dried in a desiccator at room temperature, and was covered with a thin gold layer. TEM was performed with EM 208 and CM 120 electron microscope operating (Philips) at a bias voltage of 100 and 120 kV, respectively. Samples were dropped onto a carbon-coated grid and were dried at room temperature.
3. Results and discussion

3.1. Characterization of modified silica nanoparticles

The silica nanoparticles with an average diameter of 100 nm were synthesized as described before (Fig. 1). Fig. 2 presents the X-ray diffraction pattern of silica nanoparticles shown in Fig. 1. Since silica nanoparticles are amorphous, they just produce a single broad diffraction peak around 24° in XRD pattern.

In Fig. 3, the solid curve shows FTIR spectrum of unmodified silica nanoparticles and Table 1 presents the observed peaks assignments. Zeta potential of silica particles was measured and it showed a negative potential of about −34.3 mV at pH = 11.47 because of silanol groups (Si—OH). So, the affinity between silica and negatively charged gold nanoparticles is low and the attachment of gold onto silica is limited [2]. Hence, in this paper, we modified silica nanoparticles by hydrophilic amine group (—NH₂) in order to change their surface charge.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>468</td>
<td>deformation vibration of O—Si—O [17]</td>
</tr>
<tr>
<td>568</td>
<td>stretching vibration of Si—O [17]</td>
</tr>
<tr>
<td>800</td>
<td>symmetric stretching vibration of Si—O—Si [17]</td>
</tr>
<tr>
<td>949</td>
<td>stretching vibration of Si—OH [17–19]</td>
</tr>
<tr>
<td>1100</td>
<td>asymmetric stretching vibration of Si—O—Si [17,19]</td>
</tr>
<tr>
<td>1400</td>
<td>symmetric deformation vibration of C—H [17,18,20]</td>
</tr>
<tr>
<td>1642</td>
<td>molecular water physically adsorbed [17,19]</td>
</tr>
<tr>
<td>2355</td>
<td>stretching vibration of NH group of ammonium hydroxide [21]</td>
</tr>
<tr>
<td>3282</td>
<td>stretching vibration of Si—OH and adsorbed water [17,19]</td>
</tr>
</tbody>
</table>

3. FTIR spectra of bare (solid line) and modified (dash line) silica nanoparticles.
Due to presence of silica hydroxide groups, APTES formed a covalent bond with silica nanoparticles and their surface became amine terminated [4]. Hence, the sharp peak observed at 3417 cm$^{-1}$ for dashed curve in Fig. 3 demonstrates introduction of amine group onto silica nanoparticles.

### 3.2. Characterization of gold nanoparticles attachment into silica

Fig. 4 shows absorption spectra of synthesized gold nanoparticles which were normalized at their maximum surface plasmon absorption for comparison. It can be understood that when the diameter of particles was ~4.5 nm, the plasmon peak was ~510 nm and as gold nanospheres increased in size, the SPR peak showed a slightly red shift to longer wavelengths and the plasmon bandwidth was decreased.

For nanoparticles below 20 nm, it can be considered that only the dipole oscillation is dominated, but for nanoparticles larger than 20 nm, since the light can no longer polarize the nanoparticles homogeneously, the higher order electron oscillations start to take important roles. Hence, electromagnetic retardation effect in larger particles must be considered. So, the higher order modes peak at lower energies, and therefore, the plasmon band shows a red shift by increasing particle size [22–24]. Fig. 4 shows that for nanoparticles below 20 nm, the same result was obtained and the absorption band shifted to longer wavelengths by enhancing the diameter of gold particles.

Fig. 4 demonstrates that the plasmon bandwidth was increased by decreasing gold nanoparticle diameter. According to Drude model, the imaginary part of dielectric constant describes the broadening of spectrum due to damping and dephasing of the electron oscillations. In fact, the mean free path of the conduction electrons in metal nanoparticles is limited by the physical dimension. If the electrons scatter on the surface of particles in a random way, the coherence of the overall plasmon oscillation is lost. As a consequence, dephasing and damping will be occurred. For smaller particle, since the electrons can come into the surface faster, they can scatter at the surface and lose the coherence more quickly than larger nanoparticles [22,23]. Therefore, the plasmon bandwidth is inversely proportional to the particle size. Hence, the SPR band of nanoparticles below 5 nm is strongly damped and its absorption becomes weak and broad and it completely disappears for nanoparticles less than about 2 nm in diameter [22,25,26]. Therefore, our experimental results are in a good agreement with calculated ones.

Most of particles exhibit a positive charge at low pH and the surface charge decreases almost linearly to a negative charge by raising pH. Point of zero charge (PZC) for nanoparticles depends on pH of solution [27]. Leong reported that PZC of silica particles is about pH = 2 [28]. The PZC of nanoparticles changes after treatment with different functional groups, Pham et al. noticed that the PZC of silica particles was shifted to about pH = 7 after modification of 30 nm silica particles with APTES [29]. In our experiments, surface charge of nanoparticles was −1.94 mV at pH = 10.4 after modification. It can be concluded that the PZC of modified silica particles was about pH = 10. It was higher than previous result may because of larger particle size in our experiment [30]. Since, pH of solution in nucleation step in the experiment was about 9, surface charge of modified silica particles was positive. Therefore, after mixing of gold colloids and modified silica solution; negatively charged gold nanoparticles attached onto silica particles electrostatically.

In Fig. 5, TEM images of silica–gold nanoshells after nucleation step are presented. Since surface charge of gold nanoparticles depends on their particles size and increasing gold nanoparticles diameter increases surface charge [8], therefore surface charge of gold nanoparticles obtained by citrate method is more negatively than one for 4.5 ± 1 nm gold particles. Because of repelling inter-particle Coulomb interactions between negatively charged gold particles, they deposited onto substrate separately [2,31]. Hence, separation between larger attached gold colloids was more than smaller ones. Therefore, degree of silica surface coverage with gold colloids was limited for larger ones that Fig. 5a and b reveal this fact.

Although, increasing the amount of silica modifier enhances the silica surface coverage with gold nanoparticles due to increasing positively available sites for nucleation, but Fig. 5c indicates that excessive amount of modifier showed opposite effect on surface coverage (15 ± 3 nm gold colloids were attached onto silica particles). By increasing the APTES volume, the neutral ethoxy groups of APTES deposited onto silica surface and covered some of the positively charged sites, so less nucleation sites were available for gold deposition [1] and as a consequence gold nanoparticles distribution on silica became restricted. Furthermore, excessive volume of APTES caused coagulation and aggregation of silica nanoparticles.

### 3.3. Characterization of silica–gold nanoshells

Fig. 6 presents TEM images of silica–gold nanoshells obtained by using 15 ± 3 nm gold colloids for nucleation stage. For silica nanoparticles with average size of 100 nm, surface coverage with 15 ± 3 nm gold particles was limited and since gold hydroxide must be reduced on seeded gold colloids; a uniform shell did not form (Fig. 6a). For silica particles with an average diameter of 250 nm, although repelling between gold nanoparticles caused separation, but due to larger size of silica, more gold colloids were seeded and degree of surface coverage was more than 100 nm silica particles. Therefore, a better shell was obtained for these types of silica particles (Fig. 6b).

TEM images of gold nanoshells with silica diameter about 100 nm which were decorated with 4.5 ± 1 nm gold particles are shown in Fig. 7. Due to better silica surface coverage with gold colloids (explained before), more gold hydroxide was reduced onto attached colloids. Therefore, a uniform and complete shell about 20 nm was obtained for these types of gold seeded silica particles. The zeta potential of obtained nanoshells was −12.2 mV at pH = 6.2–7. Hence, deposition of gold particles onto silica caused the positive potential to become negative again; or in fact, it shifted the ZPC of particles to low pH.
Fig. 5. TEM images of gold decorated silica nanoparticles. (a) 15 ± 3 nm, (b) 4.5 ± 1 nm gold colloids used for seeding and (c) 0.2 ml APTES used for functionalizing.

Fig. 6. TEM images of gold nanoshells with core size of (a) 100 nm and (b) 250 nm initially decorated by 15 ± 3 nm gold colloids.

Fig. 7. TEM images of gold nanoshells with core size of 100 nm initially decorated by 4.5 ± 1 nm gold colloids.

Fig. 8. XRD pattern of silica-gold nanoshells shown in Fig. 9.
Synthesized nanoshells presented in Fig. 7 were characterized with X-ray diffraction (Fig. 8). The XRD pattern exhibits diffraction peaks for 2θ at 38.35°, 44.66°, 64.75°, 77.67° and 81.95° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of the face centered cubic structure of gold [32] (same as JCPDS 04-0784) which indicates that the crystalline gold shell was obtained and Au (1 1 1) plane was preferred orientation for shell growth. Furthermore, no specific peak was observed around 24° assigned to amorphous silica. It is due to complete gold coverage on silica particles that demonstrates formation of a uniform gold shell. The mean thickness of shell was calculated by Scherrer’s equation. It was 22.9 nm confirming TEM results.

UV–vis spectra of gold nanoshells during shell growth presents in Fig. 9 (decorated with 4.5 ± 1 nm gold particles). It can be seen that as the gold shell growth progressed, the UV–vis spectrum increased in absorption because the density of attached gold particles was enhanced. Besides, the absorption peak initially showed a red shift during shell growth and then shifted to shorter wavelengths and a secondary peak rose up indicating that the shell growth was completed.

When two metal nanoparticles are brought in proximity each other, their near-field can interact with each other, and as a consequence, plasmon oscillations of the two nanoparticles become coupled and it causes a red shift in SPR [33]. Aggregation of gold nanoparticles on silica surface leads to decreasing the distance between neighboring gold nanoparticles. Hence, plasmon coupling between gold particles occurred. The plasmon coupling depends on the number of particles and the distance between the nanoparticles in the assembly [33,34]. By increasing the density of attached gold particles onto silica, each particle was subject to the near-field of a large number of closer particles, resulting in a much stronger coupling. Hence, a red shift to longer wavelengths was observed in plasmon resonance for our results as shell growth progressed.

Based on hybridization model, the SPR spectrum of nanoshells is a result of an interaction between plasmon response from a nanosphere and a nanocavity leading to hybridization of plasmon resonance into antisymmetric mode (higher energy) and symmetric mode (lower energy) that shows up in the visible and near infrared region [4,35,36]. The position of maximum SPR depends on the strength of plasmon coupling or mainly the metal shell thickness. In fact, while the core diameter is constant, dipolar coupling for a thin shell is stronger than a thick one, since a thinner shell induces stronger near-filed coupling [4,35]. Hence, the red shift of absorption spectrum for a thin shell is more than one for a thick shell and it is another reason for initially red shift of absorption spectrum to 570 nm in Fig. 9.

Initially, the absorption peak of nanoshells is mostly due to the dipolar plasmon resonance. As the shell grows, the higher order multipole mode (i.e. quadrupolar plasmon resonance) becomes more dominant that leads to advent of secondary peak at shorter wavelengths [24,37] like one observed around 410 nm for curve h in Fig. 9. Besides, the broadening of absorption spectrum seen in Fig. 9 is because of increased interparticle interactions introduced by a low order aggregation of the nanoshells [38].

Fig. 10 compares SPR spectra of nanoshells shown in Fig. 6a and Fig. 7. Since, no secondary peak appeared in curve a, it can be understood that shell growth did not complete and just some separated gold islands formed on silica surface emphasizing TEM image. Furthermore, due to more reduction of gold hydroxide onto silica surface i.e. thicker shell, the blue shift of curve b was more than curve a.

4. Conclusions

In this paper we investigate the effect of gold nanoparticles size on shell growth progress using two different size gold colloids. In conclusion, since repelling between borohydride stabilized gold nanoparticles is less than citrate stabilized ones, using 4.5 nm gold colloids for seeding onto 100 nm silica particles leads to more uniform shell. Increasing silica particles size provides more available sites for deposition of gold colloids; as a consequence increasing the possibility to obtain a complete shell in case of 250 nm silica particles by using citrate stabilized gold nanoparticles.

Besides, we studied optical properties of gold nanoparticles and nanoshells. Our results show that absorption spectrum of gold colloids below 20 nm shows a blue shift to shorter wavelengths and it broadens because of rapid dephasing and damping by decreasing the particles size. In case of gold nanoshells, the position of maximum SPR depends on the density of attached gold particles, space between them and the thickness of gold shell and the mode of electrons oscillation determines the advent of secondary peak.
Therefore, tunability of silica–gold nanoshells initially decorated with 4.5 nm gold particles is more than ones decorated with larger particles while 100 nm silica particles are used.

Acknowledgments

Authors would like to thank staff members of Research Center for New Technologies in Life Science Engineering and department of Mining and Metallurgy of Amirkabir University of Technology (Tehran Polytechnic) for supporting this research.

References


[28] Y.K. Leong, Yield stress and zeta potential of nanoparticulate silica dispersions under the influence of adsorbed hydrolysis products of metal ions—Cu(II), Al(III) and Th(IV), J. Colloid Interface Sci. 292 (2005) 557–566.


