Development of near infrared responsive material based on silica encapsulated gold nanoparticles

Huang Chih Lu,1 I Shou Tsai,1,2 Yu Hsiang Lin2

1. Nanotechnology Research Center, Feng Chia University, Taiwan
2. Department of Fiber and Composite Material, Feng Chia University, Taiwan

Abstract

In this research, the silica encapsulated gold nanoparticles with optical resonance located in 700-850 nm spectral region were synthesized by combining gold core and the silica shell. The synthesized composite particles can be potentially used in biological fields, due to the biocompatibility of gold, silica and biopolymers. Nano-gold, which can act a raw material of composite particles, was fabricated by stand citrate reduction method. Then, the polyvinyl pyrrolidone (PVP) and (3-mercaptopropyl)trimethoxysilane (MPTMS) are added to deposit silica shell and control particle size. Finally, a complete silica nanoshell was formed on the gold surface by the one-step method, without a repeated coating process. The controllable absorption wavelength of nano-composite particles can be easily controlled by the concentration ratio of PVP and MPTMS. Transmission electron microscopy (TEM) images and optical absorption spectra clearly showed that silica was successfully deposited onto the gold surface by this novel method. As the decreasing aggregation of gold core by adding PVP, the optical plasmon peaks became blue-shifted, but the optical plasmon resonance became red-shifted and the absorption spectra were functions of addition ratios by MPTMS. We expect to extend these functional nanoparticles for real sample applications in the near future.

Keywords: nanoparticle; optical plasmon resonance, PVP, MPTMS, gold, silica
1. Introduction

Nanostructured materials are of intense interest for the development of the nanofabrication of functional nanodevices, high surface area materials, consolidated materials and biotechnological applications [1-3]. Nanoscale metal particles are well known for their ubiquitous optical plasmon resonance, which allows these materials to be used in the optoelectronic and biological fields such as ultra-fast optical switching, optical stability, chemical and biological sensing, optical filters, surface-enhanced raman spectroscopy, and other surface-enhanced spectroscopies [4-5]. Among them, Au nanoparticles display good biocompatibility as well as fascinating optical and electronic properties, which make it possible to be used for wide biological applications [6-8]. However, the utility of Au nanoparticles is limited because their plasmon resonance is confined to relatively narrow wavelength ranges and cannot be readily shifted.

Until now, there have been several approaches to manipulate the optical resonance of metal nanoparticles by tailoring the particle geometry to metal nanorod or metal nanoshell. Metal nanoshells are composite nanoparticles consisting of a dielectric core coated with a thin metal shell. The plasmon resonance of a metal nanoshell may be shifted throughout the visible and near infrared by varying the ratio of the core radius to the shell thickness. By controlling the core/shell ratios, the optical resonance of gold nanoshell can be extended from the visible region to the infrared region. This spectral range includes the 800–1300 nm and 1600–1850 nm, a region of high physiological transmission which has been demonstrated as the spectral region best suited for optical bio-imaging and biosensing applications [9-11].

In this article, we fabricated completely silica-encapsulated gold particles by combining the standard reduction seeding with one step shell-growing method. Owing to the addition of PVP and MPTMS for nanoshell fabrication, continuous silica nanolayers were easily deposited on gold particles. In this case, the different concentrations of PVP formed around the gold particles acted as a protecting agent to avoid aggregation, and the MPTMS as well as an efficient catalytic surface agent for the formation of silica onto the gold surface. The complete nanoshell was easily formed by the one-step shell growing method, without a repeated coating process for controlling the thickness of the layer. And the optical properties of the composite particles could be easily controlled so that the optical plasmon resonance is located in the near infrared region [12-13]. The spectrum range is ideally suited for in vivo imaging because of minimal light absorption by hemoglobin and water. We expect that the near infrared responsive silica-encapsulated gold particles can be potentially used in targeted bio-imaging and therapeutics applications, due to their good
2. Experimental

2.1. Materials and preparation of composite particles

Tetraethoxysilane (TEOS, 99.999+%), ammonium hydroxide (27%), ethyl alcohol, hydrogen tetrachloroaurate(III) (HAuCl₄, 99.9%), sodium citrate (97%), polyvinyl pyrrolidone (PVP, 99.5%), and (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%) were purchased from Aldrich Chemical Co. The deionized water was obtained by Millipore System. All glassware were cleaned with chromic acid and rinsed with deionized water. Gold colloids were prepared by sodium citrate reduction of HAuCl₄ as reported earlier. A 250 mL sample of 1 mM HAuCl₄ was brought to a vigorous boil with stirring in a round-bottom flask fitted with a reflux condenser, and 25 mL of 38.8 mM sodium citrate was rapidly added to the solution. The solution was boiled for another 15 min, during which time the solution changed color from pale yellow to deep red. The solution was allowed to cool to room temperature with continued stirring. The suspension was filtered using a 0.22 μm filter (Corning, NY) and stored at 4 °C until further use.

To synthesize silica-encapsulated gold particles, 12 ml of above gold colloid, 1.6 g of PVP, 6.4 ml of ethanol, and 50 μl of MPTMS were mixed and stirred 12 hours under dark situation. Then the 200 μl of TEOS and 200 μl of ammonium hydroxide were added to the above mixture for further reaction. After 24 hours continuing stir at 4 °C, this mixture was allowed to age in the dark for one day. The different concentration ratios of PVP and MPTMS were prepared to control the size of gold core and the thickness of silica shell. Finally, these composite particles were centrifuged and washed with ethanol for three times to remove excess residuals.

2.2. Characterization of composite particles

The samples for transmission electron microscopy (TEM) were prepared by placing a drop of dilute solution of the sample on a copper grid. The bright field images and energy dispersive analytical X-ray (EDAX) were obtained using JEOL JEM-2010 TEM operating at 200 kV. UV-visible absorption spectra were obtained with a Hitachi U2000 UV-visible scanning spectrometer in the wavelength range from 300 to 1100 nm. Solution spectra were obtained by measuring the absorption of a dilute solution in a methacrylate cell with a path length of 1 cm.
3. Results and discussion

Figure 1a shows the schematic representation of the fabrication process of silica encapsulated gold particles by stand citrate reduction, gold-thiol assembly, and sol-gel method.

\[ \text{HAuCl}_4 + \text{Citrate} \xrightarrow{\text{Reflux}} (\text{Au}) \]

**Step 1:**

**Step 2:**

\[ \text{Au} + \text{PVP} + \text{MPTMS} \rightarrow \text{MPTMS} \]

**Step 3:**

\[ \text{MPTMS} + \text{TEOS} + \text{NH}_3 \rightarrow \]

Figure 1. (a) Schematic representation for the synthesis of silica encapsulated gold particles by stand citrate reduction (step 1), gold-thiol assembly (step 2), and sol-gel method (step 3). (b) The detailed construction of composite particle in this research.

The gold nanoparticle was synthesized in the size of 12 nm by reacting sodium citrate and tetrachloroauric acid; details on the synthesis are in the experimental section and supporting information. Both the shape and size of gold nanoparticle were carefully quantified by TEM and DLS (data not shown), because both variables play an important role for further nanoparticle fabrication. In addition, UV-visible absorbance spectroscopy was used for optical characterization of the gold nanoparticle in solution. The spectra of nanoparticles were measured in aqueous media between 350 and 850 nm, and the maximum absorption wavelength was observed at 520 nm with a narrow bandwidth. This result shows that our gold nanoparticles are well dispersion in water solution, and this material is suitable for further use.

A primary purpose of the introducing PVP was to protect the gold nanoparticles from growing and agglomerating. From our previous study, the diameter of the gold particles should be controlled shorter than 50 nm for various applications, and with the increase in PVP, the particles were dispersed better. This is because that gold particle would coordinate with nitrogen or oxygen atom in PVP, and a covered layer would generate on the surface of the particles. The layer inhibited the growth and agglomeration of the particles. For the gold nanoparticle prepared in this research, both of the two schemes are possible for PVP protection with diameters of about 50
nm. Though the pyrrolidyl has steric effect on the coordination between nitrogen atom and gold, but the electronegativity of nitrogen atom was lower than that of oxygen, and the capability of electron donating of nitrogen was higher than that of oxygen. For the particles with the diameter shorter than 50 nm, the steric effect was not the main factor that influenced the reaction between PVP and gold. As this result, the coordination between PVP and gold was not on oxygen atom, but on nitrogen atom.

The immobilization of silica onto gold nanoparticles from an alcohol solution is easily achieved by exploiting the affinity of gold for thiol groups. In this research, the MPTMS was used to present thiol groups for the surface of gold nanoparticles. Overnight incubation of the thiol-functionalized silane with gold nanoparticles then results in the self-assembly of the MPTMS onto the surface of gold nanoparticles, driven by chemisorption between thiol group and gold nanoparticles. Moreover, MPTMS can perform in the role of linking reagent through its silane terminal. Then, the following addition of TEOS and ammonia hydroxide can help to encapsulate the gold nanoparticles into silica shell by sol-gel reaction.

In order to monitor the surface characteristic of synthesized composite particles, we obtained TEM image and the corresponding EDAX result for the silica encapsulated gold particles (shown in figure 2). The average size of composite particles is \( R = 120 \pm 5 \) nm, which was taken from many different TEM images. After the hydroxylated silica surface was formed by alkaline solution with TEOS, the only visible situation is the presence of small darker dots (gold nanoparticles) within the silica surface. The corresponding EDAX result for composite particle confirms that the silica layer is successfully deposited onto gold particles by our fabrication scheme. Both the Si atom and O atom peaks are clearly shown, which result from silica outer shell without the inner gold particles.

![Figure 2. TEM image (left) and their corresponding EDAX data (right) for silica encapsulated gold particles.](image)

As encapsulated silica grew and emerged, the particles had a distinct optical
Figure 3. UV-visible absorption spectra of silica-coated gold nanoparticles with a different amount of addition for (a)PVP and (b)MPTMS. From the previous discussion, the concentration of PVP may protect gold nanoparticles from aggregating. Figure 3a showed that the increasing addition of PVP could efficiently avoid the aggregation of the gold colloid. And then, the optical plasmon peaks became blue-shifted, which was consistent with theoretical predictions on optical properties of metal coated particles. In addition, MPTMS is another control factor. When the silane based MPTMS attached on gold surface grew, their optical plasmon peak became slightly red-shifted (shown in figure 3b). The peak became distorted into a broad shoulder which was similar to that previously observed in spectroscopic studies of gold platelets in solution, as the growing silica layer began to coalesce and encapsulated the different amounts of gold nanoparticles. This fact also suggests that the silica shell is completed cover and its absorption spectra are functions of the addition ratios by MPTMS. Furthermore, the completed nanoshells, whose optical plasmon resonance peak ranges in the 750–900 nm regions, can be used as a powerful tool in bio-imaging and biosensing applications. This spectrum range is ideally suited for in vivo imaging because of minimal light absorption by hemoglobin and water. The optical absorption spectrum range is relatively broad compared with that of pure gold colloid. Mie scattering theory for the nanoshell geometry quantitatively accounts for the observed plasmon resonance shifts and line-widths. In addition, the plasmon line-width is dominated by electron surface scattering.
4. Conclusions

In conclusion, we have prepared silica nanolayer-encapsulated gold particles by combining stand citrate reduction, gold-thiol assembly, and sol-gel methods. Because the PVP and MPTMS attached onto a gold surface could act as protection agent and linker molecule for the coating of silica layers, only two pretreatment steps were needed to fabricate a continuous outer silica shell. It was also demonstrated that we could control the amount of silica deposition by changing the functional agents to the metal colloid solutions, without repeating the coating step. Because this method is easy, novel and effective in producing silica-encapsulated particles, the fabrication technique can be also applied to produce other silica-encapsulated metal particles for various potential applications such as photonic devices, catalysis, and biosensing materials.

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