English

Characterization and Synthesis of GSCS Nanoparticles by Sol–Gel Method   with Controlling of Adding Water Amount

Yeong-Her Wang[1,*], Pin-Hsiang Chiu[2] and Chien-Jung Huang[3]

[1]Institute of Microelectronics, Department of Electrical Engineering, Institute of Electro-Optical Science and Engineering/ NCKU
[2]Institute of Electro-Optical Science and Engineering/ NCKU
[3]Department of Applied Physics, National University of Kaohsiung
yhw@eembox.ncku.edu.tw

The development of materials with a different structure has been a fundamental focus of scientific research, which promotes advances in both the academic and industrial fields. Among these materials, the various types of core–shell nanostructures exhibited unique properties of electronics, catalysis, magnetism, and optics owing to their composite structure and design. Very recently, gold nanoparticle cores with silica shells have been the most widely studied due to the potential applications of gold nanoparticles in many fields, such as surface-enhanced Raman scattering (SERS) detection, deoxyribonucleic acid (DNA) sensors, optical sensors, surface Plasmon resonance (SPR) sensors, and fluorescence signals. The gold nanoparticles are only stable as suspensions in solution and tend to irreversibly aggregate over time. This nature depresses their nanoscale properties and limits their application. Hence, the coating of silica shell is usually used, which has several advantages. First, silica shell is chemically inert and does not affect redox reactions at the surface of the gold core. Second, the silica shell is optically transparent, so that chemical, physical, and optical properties can be monitored by spectroscopy. Third, the silica shell can also increase a gold core's mechanical, thermal, and chemical stability. Finally, silica is well-known to form ordered colloid crystals, so silica coating may be a useful precursor to the creation of two- and three dimensional (2D) and (3D) arrays of any type of nanoparticle system. Such gold–silica core–shell (GSCS) nanoparticles may be further applied to photonic crystals and plasmonic waveguides to act as an optical instrument. By changing the thickness of the silica shell and the diameter of the gold core, direct control of the effectiveness of the optical instrument would become possible. Therefore, synthesis of GSCS nanoparticles will be a subject of significant research for the fabrication of advanced materials.

In this paper, we developed a simple procedure by slightly modifying the Stöber process so it could be applied to coat gold nanoparticles with well-controlled silica shells. In this procedure, gold nanoparticles acted as the nucleation agents in the reaction solution so that the silica could nucleate and condense onto the surfaces of gold nanoparticles via the sol–gel process of tetraethyl orthosilicate (TEOS) without using any primers, surfactants, or surface modification of the core. The thickness of the silica shell can

be easily controlled by varying the added water amount. For uniform coating of silica on gold nanoparticles, we further investigate the pH of the reaction solution. Therefore, the authors have focused on the growth mechanism of silica shell via varying the amount of added water in the present work. Morphology, chemical composition, and optical properties of the gold–silica core–shell (GSCS) nanoparticles are also presented.

Figure 1a-e shows the TEM images of gold nanoparticles whose surface had been coated with silica shells using the addition of 0, 1, 3, 5, 7, and 9 mL of water by the sol–gel method. The experimental results clearly indicate that the thickness of the silica shell can be changed by altering the amount of added water. Figure 1a shows a TEM image of the GSCS nanoparticles without water addition. The silica show the sol phase. Almost all the gold nanoparticles were distributed in the interior of the silica sols. These silica sols could not be uniformly coated onto the surface of the gold nanoparticles. When the amount of water is added at 1 mL, the silica shell is not perfectly coating, but practically the entire surface of all the gold nanoparticles appears to be coated, as shown in Fig. 1b. It can be seen that the thickness of the silica shell is about 10 nm. The surface of the silica shell is very rough. If the formation of silica shells is slow and the thickness of the silica shell is thin, the dispersion forces are still strong enough to cause coalescence of the nascent coated particles. As the amount of water is increased in the range from 3 to 7 mL, the thickness of the silica shell is increased, as shown in Fig. 1c-e. It also can be seen that this colloid silica shell is thicker, resulting in reducing the van der Waals interactions between the gold cores. The coverage monolayer is insufficient to prevent gold core coalescence, leading to multiple gold core formation, as shown in Fig. 1e. When the amount of water was 9 mL, the gold core was almost covered with uniform silica shells. The thickness of the silica shell is increased to about 120 nm, as shown in Fig. 1f. However, the amount of water is a dominant factor to control the thickness of the silica shell.
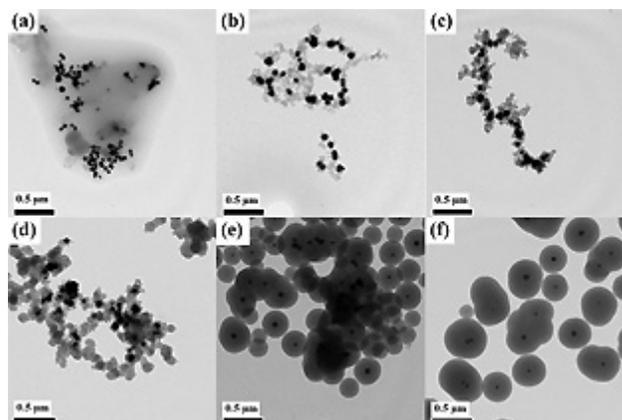

Figure 1. (a) TEM image of GSCS nanoparticles without additional water by sol–gel method. (b)–(f) TEM images of GSCS nanoparticles with 1, 3, 5, 7, and 9 mL of additional water by sol–gel method.

The large amount of water can promote the hydrolysis and condensation reaction, resulting in the nucleation and growth of the silica being enhanced and causing the thickness of the silica to be increased. As seen in Fig. 2, thicknesses of silica shell increase nonlinearly with the amount of water. Figure 2 also shows an incubation period prior to the start of the active phase silica shell growth when the amount of water is below 5 mL. The formation of the silica shell is considered as the nucleation and growth of silica particles, which is an aggregation process of small subparticles several nanometers in size. According to thermodynamics, phase transformations begin
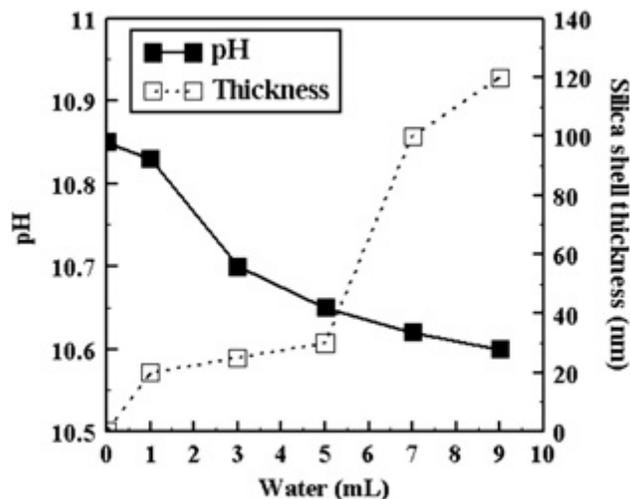

Figure 2. pH of reaction solution and shell thickness as a function of the amount of added

with the appearance of a number of very small particles of the new phase. During this period, the growth of a new particle relies on a particle's ratio of surface area to volume, small particles tending to redissolve and large ones tending to grow. Thus, there is a critical size which separates particles that redissolve from those that grow. Hence, the silica shell is slowly growing during the period of below 5 mL. When the incubation period has passed, the thickness of the silica shell rapidly increases with the amount of water from 5 to 7 mL. Moreover, it seems that the thickness of the silica shell tends to saturate at the amount of water from 7 to 9 mL. However, the amount of water can be used as a tool for adjusting the growth thickness in this paper.

Figure 3 gives the UV-vis absorption spectra of GSCS nanoparticles with altering the amount of water. The redshift in the SPR band of GSCS nanoparticles from 528 to 537 nm was observed with increasing the amount of water from 0 to 9 mL. Furthermore, as the amount of water is increased, there is a decrease in the intensity of the SPR band. A much more drastic effect on the SPR band of GSCS nanoparticles was found when the thickness of the silica shell was changed. The inset of Fig. 3 shows the relationship between the thickness of silica shell and the SPR band of GSCS nanoparticles with various amounts of water. This curve suggests that the thickness of the silica shell increased from to 10 to 120 nm with a redshift in the SPR band from 528 to 537 nm.

Figure 3. UV-vis absorption spectra of GSCS nanoparticles under various reaction conditions, as a function amount of added water. The inset shows the relationship between the thickness of silica shell and the SPR band.

Silica shell is electronically inert. It does not exchange change with the gold nanoparticles. But, the medium surrounding it is influenced by the refractive index of the silica shell. In this study, the thickness of the silica shell is increased with decreasing the intensity of the SPR band, as well as a redshift in the wavelength position of the SPR band. This redshift is caused by the change in refraction index around the colloid particles after silica coating. The refractive index of the silica shell is higher than that of the solvent. The larger shift is found with the thicker dielectric silica coating around the particles. In Fig. 4, the photograph shows a solution of GSCS
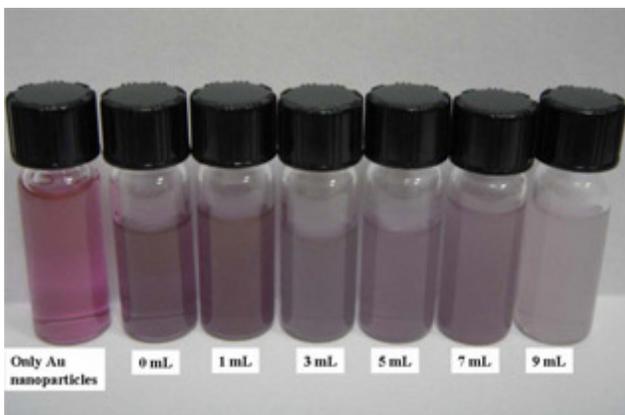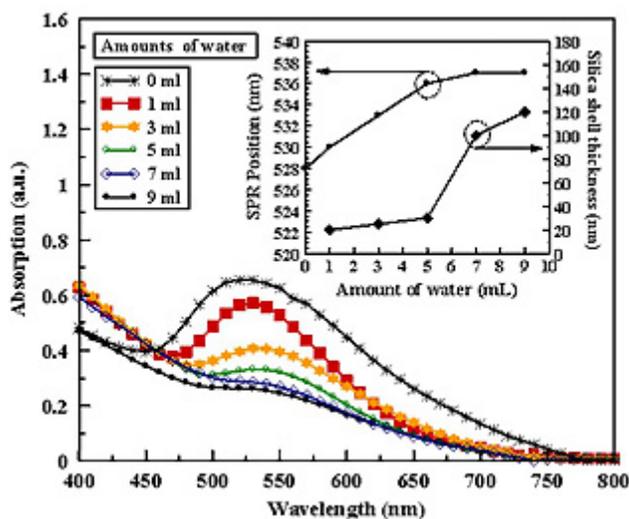

Figure 4. Photograph of solution of GSCS nanoparticles in various amounts of added water. Left bottle is only gold nanoparticles in IPA solvent.

nanoparticles with various amounts of water. The bottle on the left side contains original gold nanoparticles in IPA solvent, which shows the original cherry-red color. When the thickness of the silica shell is increased with increasing the amount of water, the color of the solution varies from purple red to pale red. This result is because the thickness of the

silica shell altered the solvent refractive index.

In summary, we have demonstrated the sample of GSCS nanoparticles fabricated by the sol–gel method. It has been shown that the amount of added water plays an important role in the formation of GSCS nanoparticles. Changing the amount of water from 1 to 9 mL strongly affected the thickness of the silica shell from ~10 to ~120 nm, and the SPR band is redshifted from 528 to 537 nm. The pH of the reaction solution indicated that the silica was not coated at pH > 10.85.