Title

Characteristic optical properties and synthesis of gold-silica core-shell colloids

Journal

Scripta Materialia, 55

Author

Han, Young Hwan

Publication Date

2006

Characteristic Optical Property and Synthesis of Gold-Silica Core-Shell Colloids

Hyung Bock Lee, Young Min Yoo, Young-Hwan Han*
Department of Ceramic Engineering, Myongji University, Yongin, 449-728, Korea
*Department of Chemical Engineering and Materials Science, University of California at Davis, CA 95616 USA and Advanced Materials, Sungkyunkwan University, Suwon, Korea

Corresponding author: Young Min Yoo
E-mail: twil1111@empal.com
Tel: +82-31-330-6459 Fax : +82-31-330-6457

Key words: optical property, Gold-Silica Core-Shell colloid, silica coated gold nanoparticles, nanowire

ABSTRACT

Gold-Silica Core-Shell colloid was synthesized that can be used for the optical instruments like photonic crystal and plasmonic waveguides serving as a building block. Gold nanoparticles could be directly coated with uniform shells of amorphous silica without silane coupling agent to simplify the process. It was confirmed that the thickness of coated silica shells could be varied from tens to several hundred nanometers by controlling the precipitation time and concentration of TEOS.

1. Introduction

Metallic nanoparticles have been applied in many areas such as nonlinear optical element and Raman Spectra devices for their own intrinsic characteristic [1-2]. Much work about colloids of gold and silver has been achieved, and research on stable spectra characteristic by relatively small particles has been done [3]. A characteristic of colloids could make surface coatings uniform like from silica material, and possibly change surface characteristic of materials [4-7]. Generally, chemical composition, structure, and size changes of the core and shell could control their own optical characteristic by using a core-shell colloid. Gold nanoparticles can be coated in a uniform thickness with amorphous silica after several procedures. This homogeneous shell thickness could be

achieved by controlling the concentration of precursor or/and reaction time, ranging from several 10 nm to several 100 nm.
This kind of spherical core-shell colloids could be applied to photonic crystal and plasmonic waveguides as an optical instrument. By changing the thickness of the silica shell and diameter of gold core, direct control of effectiveness in an optical instrument became possible.
To coat nanoparticles of gold and silver with amorphous silica, a technique of coating a monolayer in gold employing an amine terminated silane coupling agent has been reported [8-10], but recently a new technique by Liz-Marzan, a slight modification of Stober method, was reported that direct coating onto nanoparticles of iron oxide and silver nanowire could be possible by applying silica shell with precise control [11-13]. This study was focused on the investigation of scientific characteristic of silica shell thickness coated on gold nanoparticles with applying no silane-coupling agent.

2. Experimental Procedures

Gold-Silica Core-Shell was synthesized from the colloids as shown in Figure 1. For seed manufacturing 1 ml of $HAuCl_4$ (49%, Sigma) was diluted in 20 ml of deionized water, followed by being diluted in 80 ml of boiling deinonized water. When the solution boiled again, 10 ml of 1% Trisodium citrate (99%, MERCK) was added and stirred for 20 minutes, and then cooled down for 100 ml. The processed gold nanoparticles were coated with silica by sol-gel method. This procedure included the mechanism in silica coating covered base-catalyzed hydrolysis by Tetraethoxysilane (TEOS, 98%, Fluka)
for condensation of silica sol and nucleation by silica sol on the surface of gold nanoparticles.
An Ammonia solution (28%, Wak) was used as a catalyst to accelerate hydrolysis speed of TEOS. 4 ml of seed Solution was added to 20 ml of Ethanol (95%, D.S.P., GR Reagent) and kept stirred and then 0.6 ml of Ammonia solution and various amounts of TEOS were added to the reaction mixture. The reaction was run for 24 hours at room temperature with continuous stirring. Gold-Silica Core-Shell colloid can be separated from the intermediate reaction by dialysis and controlling the coating time, concentration, and amount of water, could adjust the thickness of silica from several nano meters to several hundred meters.

The amount of TEOS for the reaction can be calculated by the following equation [8],

$$V_{TEOS} = \frac{V_{TEOS} V_{Au}}{V_{SiO_2}} (Au) 10^3 \left(\left(\frac{R_{tot}}{R_{Au}} \right)^3 - 1 \right) \quad (2.1)$$

Here, V = molar volume
R_{tot}: final radius
R_{Au}: radius of the starting colloid

For the microstructure and particle size of synthesized core-shell particle, TEM (JEOL 200kV, JEOL) were employed, and Zeta Potential measuring System (Zetasizer 300HS, Malvern Instrument Ltd.) for spectra characteristic, UV-VIS-NIR Scanning Spectrophotometer (UV-3101PC, Shimadzu) for optical property.

3. Results and Discussion

In Figure 2(a), the TEM image shows seed colloid with about 15 nm in diameter, and in Figure 2(b), the TEM image shows the gold nanoparticles coated with amorphous silica. In this stage, the silica coated gold nanoparticles show themselves to be relatively large and various sizes of the gold core's original shape. The silica-coated gold particles with diameters of comparable thickness were surely scattered simply and showed a spherical shape different from gold core's original shape. As shown in Figure 2(d), each silica shell increased 80 nm in thickness and showed a homogeneous overview image on the overall surface of gold core.

Peak localization in soluble gold sol has been reported variously between 512 nm and 514 nm [14-16]. The used gold sol in the experiment showed a maximum at 522 nm and the effect of silica layering on optical property is shown in Figure 3. The direction showing diffracted silica expresses slight higher than water and this dual peaks confirm a change in direction to 540 nm when the surface was coated with silica shell. The localization of the peaks was not sensitive to the change of coating thickness, but hardness increased with the formed silica shell thickness. In initial stage, increase of shell thickness observed with increase of intensity in the Plasmon absorption band as much as red-shift, which was due to the increase of partial diffraction ratio in around. However, in case of a big

enough silica shell, the reason for scattering to increase strong absorption in shorter wavelengths is caused by the blue-shift of surface Plasmon band and by a definite decrease in intensity of Plasmon absorption band. Finally, scattering has covered the most of surface Plasmon band in the above of 80 nm shell thickness. The final colloid color is opaque and slight pink. Figure 4 shows maximum localization of Plasmon band, and it is assumed that the scattering observed in the experiment was distributed partially due to silica particles without unabsorbed gold. Figure 5 shows distribution diagram of colloid, which seems to be related to the detected mobility in the materials used in the individual distribution experiment. So, surface potential density from precipitation of processed powder is presumed to contribute to distribution degree.

4. Conclusions

Gold nanoparticles were coated with amorphous, homogeneous silica shell using sol-gel method. By adjusting reaction time and controlling TEOS precursor material, the coating thickness of silica varied from several ten nm to several hundred nm, and it improved efficiency and performance of Photonic Crystals and Plasmonic waveguides as a optical instrument by changing silica shell’s thickness. Therefore, well-controlled silica coated gold nanoparticles could serve as a building block in a nano-sized optical science area. As a result, structural scattering from induction of controlled photon cannot be limited by wavelength of light anymore.

5. References

1. G. Carotenuto, G. P. Pepe, L. Nicolais, Eur. Phys. J. B, 16(1), 11-17 (2000).
2. C. L. Haynes, R. P. Van Duyne, J. Phys. Chem. B, 105(24), 5599-5611 (2001).
3. Kenneth R. Brown, Daniel G. Walter, and Michael J. Natan, Chem. Mater., 12, 306-313, (2000).
4. K. S. Mayya, D. I. Gittins, F. Caruso, Chem. Mater. 13(11), 3833-3836 (2001).
5. L. M. Liz-Marzán, P. Mulvaney, New J. Chem., 22(11), 1285-1288 (1998).

6. G. Wang, A. Harrison, J. Colloid Interface Sci., 217(1), 203-207 (1999).
7. C. Graf and A. van Blaaderen, Langmuir, 18(2), 524-534 (2002).
8. L. M. Liz-Marzán, M. Giersig, P. Mulvaney, Langmuir, 12(18), 4329-4335 (1996).
9. Robert I. Nooney, T. Dhanasekaran, Yimei Chen, Robert Josephs, and Agnes E. Ostafin, Adv. Mater., 14(7), 529-532 (2002).
10. V. V. Hardikar, E. Matijevic, J. Colloid Interface Sci., 221(1), 133-136 (2000).
11. Yoshio Kobayashi, Miguel A. Correa-Duarte, and Luis M. Liz-Marzán, Langmuir, 17(20), 6375-6379 (2001).
12. Werner Stöber, and Arthur Fink, J. Coll. and Inter. Sci., 26, 62-69 (1968).
13. T. Li, J. Moon, A. A. Morrone, J. J. Mecholsky, D. R. Talham, and J. H. Adair, Langmuir, 15(13), 4328-4334 (1999).
14. J. P. Wilcoxon, R. L. Williamson, and R. Baughman, J. Chem. Phys. 98(12), 9933-9950 (1993)
15. L. M. Liz-Marzán, A. P. Philipse, J. Phys. Chem. 99(41), 15120-15128 (1995).
16. B. V. Enüstün, J. Turkevich, J. Am. Chem. Soc., 85(21) 3317-3328 (1963).

Captions

Fig. 1. Flow chart of experimental procedure

Fig. 2. TEM photographs of Silica Coated Gold Nanoparticles with different Silica thickness (a: 0 nm, b: 20 nm, c: 50 nm, d: 80 nm, e: 100nm)

Fig. 3. UV-Visible Absorbance Spectra of Silica Coated Au Nanoparticles with different Silica thickness

Fig. 4. Variation in the position of Silica Coated Gold Nanoparticles

Fig. 5. Zeta Potential and Mobility with dispersion of Silica Coated Gold Nanoparticles