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Synthesis of Au/TiO₂ Core-Shell Nanoparticles from TTIP and Thermal Resistance Effect of TiO₂ Shell

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Abstract

This work presents the synthesis of Au/TiO₂ core-shell structure nanoparticles and the evaluation method of crystallinity of TiO₂ shell. Au/TiO₂ core-shell structure nanoparticles were synthesized by sol-gel process, and the morphology and crystallinity of TiO₂ shell were investigated by TEM and UV-vis absorption spectrometer. Au/TiO₂ core-shell structure nanoparticles could be prepared by the hydrolysis of the mixed solution of titanium(IV) isopropoxide (TTIP) and triethanolamine (TEOA) with water. The average size of synthesized Au nanoparticles was 15nm. The thickness of TiO₂ shell on the surface of gold particles was about 10nm. The crystal structure of TiO₂ shell was amorphous structure similar to anatase.

1. Introduction

Nowadays the metal nanoparticles are occasionally used under extreme conditions such as optical limiters and three-dimensional optical memories using laser with high intensity. Gold and silver nanoparticles are some of the best optical limiters known thus far [1-2]. However, at high light intensities, they are susceptible to damage, leading to photofragmentation, ligand desorption, etc [3]. To make them stable at extreme conditions, it is necessary to protect them with stable and chemically inert shells such as oxides. TiO₂ is able to become a good shell material, because TiO₂ has the same effect with silica shell for durability and re-dispersing property of nanoparticles.

The metal nanoparticles with TiO₂ shell are very interesting, as the photocatalytic property, the dielectric constant and the color can be changed with the surface plasmon phenomenon [6]. So, it is expected that these kinds of core-shell nanoparticles can be used as nanocapacitor, high activity photocatalyst, biosensor, 4-dimensional optical data storage material and FL (fluorescence) material.

Most of research in this area has been on noble-metal nanocores and silica shells and characterization of their properties such as optical and catalytic [4-5]. In this paper, we focus on the synthesis of TiO₂-covered gold particles, and the characterizations of their optical property and effect of thermal resistance of titania shell. The synthesis of Au/TiO₂ core-shell nanoparticles is attempted by sol-gel method.

2. Experimental

Synthesis of Au Colloid

A gold colloid (500mL, 5×10⁻⁴M HAuCl₄) is prepared according to the standard sodium citrate reduction method.

This method produces a stable, deep-red dispersion of gold particles with an average diameter of around 15nm. Mercaptoundecanoic acid (MUA) was dissolved into 2.5% aqueous ammonia solution ([MUA] =1mM). The MUA solution was then added to the gold colloid and incubated for 2h [7]. MUA can improve the mutual affinity between Au nanoparticle and TiO₂ [8]. Then, 1M HCl was added dropwise until pH 3, to make the MUA-gold particles flocculate. The flocculate was left for one night to sediment. The collected gold was washed with water by centrifuging (3800 rpm). The gold particles were put into 20mL of water and re-dispersed by adding about 20 μl of 28% ammonia solution

Preparation of Ti⁴⁺ Stock Solution

A stock solution of Ti⁴⁺ was prepared by mixing titanium(IV) isopropoxide (TTIP) with triethanolamine (TEOA) under nitrogen atmosphere at a molar ratio of TTIP: TEOA = 1:2 to form a stable complex of Ti⁴⁺ [9].

Synthesis of Au/TiO₂ Core-Shell Nanoparticle

The concentrations of Ti⁴⁺ in stock solution were adjusted to 0.01~0.3mM. Then, 0.33mL of the MUA-Au colloid is added to 10mL of the stock solution. The resulting solution was placed into a screw-capped Pyrex bottle and aged for 24h at 80 °C

Characterization of the Au/TiO₂ Nanoparticle

The particles were observed using a transmission electron microscope (JEOL JEM-2010 Electron microscope). To investigate the optical property of the Au/TiO₂ nanoparticles and to identify the stability of Ti⁴⁺ stock solution, UV-vis spectra were taken by a UV-vis spectrophotometer (Shimadzu UV-2550).

The crystallinity of the obtained Au/TiO₂ nanoparticles was evaluated by XRD.

3. Result and discussion

In this work, TTIP was used as a coating reagent for gold sol, but it has very high rate of hydrolysis reaction with water. To control of hydrolysis reaction velocity, TTIP was mixed with TEOA as the complexing agent.

To synthesize the Au/TiO₂ nanoparticle with core-shell structure, we controlled the concentration of Ti⁴⁺ in stock solution. Shown in Fig. 1 is the TEM photographs of Au/TiO₂ particles obtained in the range of Ti⁴⁺ concentration from 0.01mM to 0.3mM at 80 °C. Heterogeneous nucleation of TiO₂ on the surface of Au nanoparticles was obtained by

the hydrolysis of Ti^{4+} stock solution. The separated colloidal titania can not be found and almost TiO_2 was formed only on the surface of Au nanoparticles in this photographs. At 0.01mM Ti^{4+} , Au/ TiO_2 composite fine particle with perfect core-shell structure was obtained and the thickness of TiO_2 shell was about 15nm, as shown in Fig. 1(a). However, in Fig. 1(c), the Au nanoparticles were coagulated slightly and were perfectly embedded in a titania matrix. It was caused by relatively high Ti^{4+} content as compared with that of Au nanoparticles.

Fig. 2 is the absorption peaks of Au/ TiO_2 particles according to the amount of Ti^{4+} in stock solution at 80 °C. The absorption peak of pure Au nanoparticle was 519nm. At 0.05mM Ti^{4+} in stock solution, the absorption peak appeared at 522nm and this peak was red-shifted as about 3nm as compared with that of the pure Au nanoparticle. It is found that the red-shift of absorption peak observed at 0.05mM is caused by the formation of titania shell on the surface of gold particles. However when the amount of Ti^{4+} in stock solution was changed between 0.025mM and 0.1mM, the position of UV-vis absorption peak according to the amount of Ti^{4+} was not changed. It was thought that titania was independently not coated on Au nanoparticles because of high Ti^{4+} content.

The effect of heat treatment temperature on the crystallinity of Au/ TiO_2 core-shell nanoparticle has investigated. Fig. 3 is the XRD patterns of (a) pure Au nanoparticles (b) Au/ TiO_2 core-shell nanoparticles (synthesized at $[\text{Ti}^{4+}] = 1\text{mM}$) heated at various temperature. This result shows that the thermal resistance of Au nanoparticles in Au/ TiO_2 core-shell is larger than that of pure Au nanoparticles, because Au nanoparticles were protected by TiO_2 shell.

4. Conclusions

The Au/ TiO_2 core-shell nanoparticle could be synthesized by the hydrolysis of TEOA/TTIP complex when the temperature of hydrothermal reaction was at 80 °C and the concentration of Ti^{4+} was in the range of 0.01mM~0.05mM. The thickness of TiO_2 shell on Au nanoparticles was about 10nm. The peak position of UV/vis absorption spectrum for the Au/ TiO_2 core-shell nanoparticles was shifted towards the red end of the spectrum by 3nm as compared with that of Au nanoparticles, and it was expected that the red shift was caused by TiO_2 shell. The thermal resistance of Au nanoparticles in Au/ TiO_2 core-shell at high temperature was confirmed from X-ray diffraction analysis.

References

- [1] R. Philip, G. R. Kumar, N. Sandhyarani and T. Pradeep, Phys. Rev. B **62** (2000) 13160.
- [2] Y. Sun, J. E. Riggs, H. W. Rollins and R. Guduru, J. Phys. Chem. B **103** (1999) 77.
- [3] S. Link, C. Burda, B. Nikoobakht and M. A. El-sayed, J. Phys. Chem. B **104** (2000) 6152.
- [4] P. Mulvaney, L. M. Liz-Marzan, M. Giersig and T. Ung, J. Mater. Chem. **10** (2000) 1259.
- [5] S. Chang, L. Liu and S. A. Asher, J. Am. Chem. Soc. **116** (1994) 6739.
- [6] C. Nasr, S. Hotchandani, W. Y. Kim, R. H. Schmehl and P. V.

Kamat, J. Phys. Chem. B **101** (1997) 7480.

[7] Liz-Marzan, L. M, Giersig, M and Mulvaney, P, Langmuir, the ACS journal of surfaces and colloids, v. 12 no. **18** (1996) 4329.

[8] Kane, V. and Mulvaney, P, Langmuir : the ACS journal of surfaces and colloids, v. **14** no.12 (1998) 3303.

[9] Sugimoto, T, Okada, K and Itoh, H, Journal of colloid and interface science, v. **193** no.1 (1997) 140.

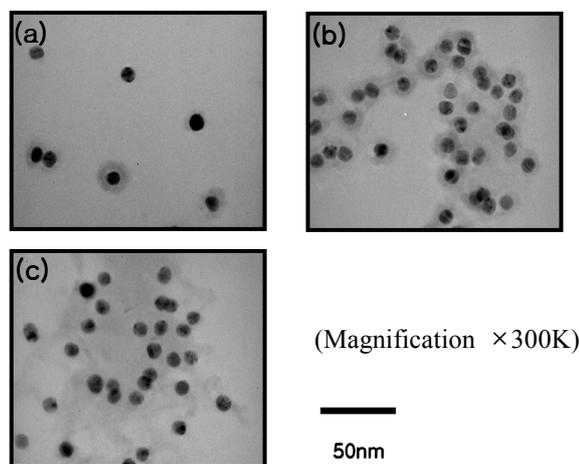


Fig. 1 TEM images of Au/ TiO_2 nanoparticles synthesized according to the various amount of Ti^{4+} in stock solution at 80 °C under the standard conditions : (a) 0.01mM, (b) 0.05mM, (c) 0.3mM

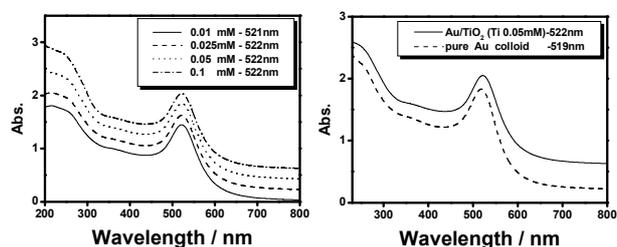


Fig. 2 UV-vis absorption spectrum of Au/ TiO_2 particles according to the various amount of Ti^{4+} in stock solution at 80 °C under the standard conditions.

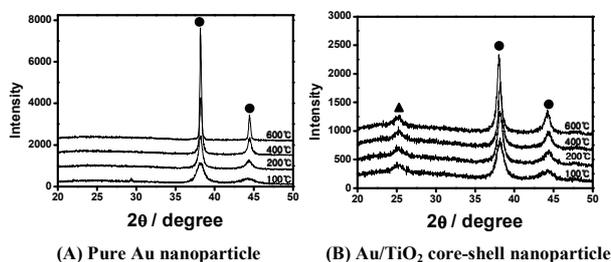


Fig. 3 XRD patterns of (a) pure Au nanoparticles (b) Au/ TiO_2 core-shell nanoparticles (synthesized at $[\text{Ti}^{4+}] = 1\text{mM}$) heated at various temperature. (Au; ●, TiO_2 ; ▲)