

Synthesis of Au/TiO₂ Core-shell Structure Nanoparticles and the Crystallinity of TiO₂ Shell

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The synthesis of Au/TiO₂ core-shell structure nanoparticles was carried out by the hydrolysis of TOAA (titanium oxide acetylacetonate) in gold sol ethanol solution with water. It was possible to achieve 1 nm thick TiO₂ shell on the surface of gold particles. The morphology and the crystallinity of TiO₂ shell were investigated by TEM and UV-vis absorption spectrometer. The crystal structure of TiO₂ shell was amorphous because the surface plasmon band of gold nanoparticles appeared only when the radioactive ray was irradiated on the TiO₂-coated gold sol ethanol solution.

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1. Introduction

The wet chemical synthesis of small metal and semiconductor particles offers the most economic route for the preparation of nanostructured materials. A variety of applications have already been proposed for such semiconductor particles including solar cells, electrochromic devices,¹⁾ electroluminescent films,²⁾ nonlinear optical switches,³⁾ and high-density information storage systems.⁴⁾ However, a fundamental difficulty to be overcome is the transfer of these materials out of solution while retaining their size-dependent properties. In solution the particles are mobile and will coalesce due to van der Waals forces unless they are protected. Consequently, the synthesis of nanoparticles involves rapid nucleation, homogeneous growth, and final encapsulation stage with polymers, ions, complexing ligands or surfactants to prevent the growth of larger, bulk crystals. Covalently bonded capping ligands are usually employed with both metal and semiconductor particles.⁵⁻⁷⁾

But, the organic capping agents are prone to chemical oxidation, especially under photolysis. To solve this problem, the encapsulation of each nanoparticles with a shell of an inert materials was proposed. The shell allows for stabilization of different types of nanoparticles and nanostructuring in such a way that interparticle distance can be chosen at will.

In addition, 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.^{8,9)} However, at high light intensities, these are susceptible to damage, leading to photofragmentation, ligand desorption, *etc.*^{10,11)} To make these stable at extreme conditions, it is necessary to protect them with a more stable and chemically inert shell such as oxides. This kind of cover also makes it possible to fabricate materials in the form of thin films and disks for applications.

Most of researches in this area are on preparation of noble-metal nanocores and silica shells, and the characterization of

these particles including their optical and catalytic properties.¹²⁻¹⁴⁾ This paper focuses on the synthesis of TiO₂-covered gold particles, and the characterizations of their optical property, and the crystallinity of titania shell. These particles were synthesized by sol-gel method in ethanol.

The metal nanoparticles with TiO₂ shell are very interesting, as their photocatalytic property, the dielectric constant, and the color can be changed with the surface plasmon phenomenon, in which the electron excited from the valence band of TiO₂ by UV irradiation is stored onto the surface of metal core.^{15,16)} But, these changes can occur only when the TiO₂ shell has a crystal structure and the electron excited from TiO₂ can be moved to metal core through the organic layer between shell and metal core for the affinity of titania shell for metal core in synthesis process. However, it is very difficult to evaluate the crystallinity of titania shells on gold particles because very small amount of core-shell metal nanoparticles is generated from dilute solution resulting in a very thin shell. On the other hand, it is very more convenient to evaluate TiO₂-coated gold sol as it is. The following sections describe a simple method to evaluate the crystallinity of titania shell and the movement of electron through organic layer.

2. Experimental Procedures

HAuCl₄, trisodium citrate dihydrate, mercaptoundecanoic acid (MUA), NH₄OH (28%) and titanium oxide acetylacetonate (TOAA) were purchased from Aldrich. Technical grade ethanol and Milli-Q water were used in all the preparations. All the reagents were used as received. A gold sol (500 ml, 5×10^{-4} M HAuCl₄, here M is kmol/m³) was prepared by using a trisodium citrate dihydrate as a reductant. The diameter of the synthesized gold particles determined by TEM was about 12 nm.

TiO₂ was coated on gold particles in ethanol aqueous solution for diminishing the hydrolysis reaction velocity of titanium alkoxides, TOAA. To improve the stability of gold sol in organic solvent, mercaptoundecanoic acid (MUA) is pre-coated on the surface of gold particles. The coating of MUA has a strong effect on the dispersion of gold nanoparticle in ethanol.¹⁷⁾ MUA (0.5 mM) was dissolved into

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2.5 vol% aqueous ammonia solution. The MUA solution was then added to the gold sol and incubated for 2 hours. The gold particles treated with MUA was collected by centrifuging. The gold particles were put into 20 ml of water and re-dispersed by adding about 20 μ l of 28 vol% ammonia solution. This was used as a stock solution of gold sol for coating TiO₂.

TiO₂ coating was preformed by utilizing the Stober method.¹⁸⁾ TOAA was used as a coating reagent. For the preparation of ethanol solution suspending gold sol, 0.4 mM of MUA-coated gold sol (stock solution, 0.3 ml) was mixed with 9.7 ml of ethanol including some water. Here, the water was added for the hydrolysis of TOAA, and the concentration in ethanol was changed in the range of 0~17 M. After the solution became homogeneous, 1 ml of TOAA diluted in ethanol was added to the premixed gold sol ethanol solution with pH 7.5 under vigorous stirring and then the mixture was continuously stirred for 5 hours for the hydrolysis reaction of TOAA. The addition amount of TOAA was adjusted between 1.0 mM and 9.0 mM.

Transmission electron microscopy (TEM) was carried out with a Philips CM 10 microscope. UV-visible spectra were measured with a Hitachi U-2000 spectrophotometer. While Au/TiO₂ core-shell colloid was exposed under ultraviolet light with 254 nm (150 W Xenon lamp) and radioactive lay of ⁶⁰Co in order to evaluate the crystallinity of TiO₂ shell.

3. Results and Discussions

3.1 TiO₂ coating by using TOAA

In this work, TOAA was used as a coating reagent of gold sol, because TOAA is a cyclic compound with two double-bond in atomic structure. Therefore the hydrolysis reaction velocity of TOAA with water is relatively slow compared to other titanium alkoxides. The hydrolysis velocity is also dependent on the concentration of coating reagent.

Figure 1 shows the spectral changes observed after deposition of titania when different amounts of TOAA is

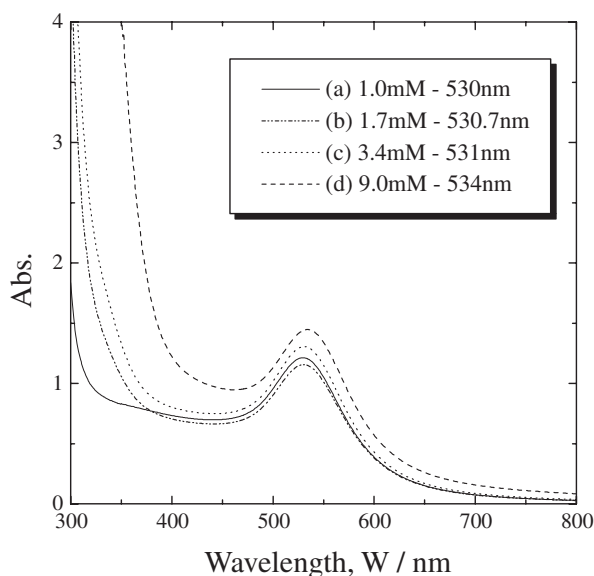


Fig. 1 UV-vis absorption spectrum of TiO₂-coated Au sol synthesized in ethanol with 5 M water at various addition amount of TOAA.

added, when the water in ethanol is 5 M. At 1.0 mM TOAA, the absorption peak appeared at 530 nm and it red-shifted as about 5 nm for gold sol ethanol solution prior to titania deposition. The absorption peaks show red-shift with increase in the amount of TOAA. The other absorption band was observed between 300 nm and 400 nm. Figure 2 shows a series of micrographs of the gold particles obtained at different amounts of TOAA. At 1.0 mM TOAA, the particles have a small coating titania in presence of little colloidal titania generated by spontaneous nucleation in ethanol solution. The thickness of titania shell was about 1 nm. But, as the added amount of TOAA increases, the titania shell does not increase any further, and more separate colloidal titania are formed. Due to faster hydrolysis at higher levels of TOAA, preferential formation of fresh titania takes place on the pre-formed colloidal titania. At 9.0 mM TOAA, the particles are perfectly embedded in a titania matrix. The formation of a cluster of separate colloidal titania is also considered to be due to the fast hydrolysis reaction of TOAA, and therefore the more TOAA is added, the more is the generation of separate colloidal titania. In Fig. 2(d), a larger spot indicated as an arrow is a large cluster of colloidal titania.

In summary, the critical addition amount of TOAA found is 1.0 mM at 5 M water in gold sol ethanol solution. Above this limit, coagulation of gold particles takes place due to spontaneous nucleation of colloidal titania. From these facts, it could be found that the red-shift of absorption peak observed at 1.0 mM as shown in Fig. 3 is caused by the formation of titania shell on the surface of gold particles, but the red-shift appeared above 1.7 mM is mainly due to the coagulation of gold particles because this was accompanied by peak broadening. On the other hand, the absorption band over the wavelength range of 300~400 nm is caused by the undissolved TOAA, and thus the intensity of this band becomes stronger as the addition amount of TOAA increases.

Figure 3 shows the spectral changes observed after deposition of titania at various concentrations of water in ethanol when the addition amount of TOAA is 1.0 mM. The concentration of water was controlled between 0 M and 17 M. At 0 M water, the absorption peak appeared at 542 nm and it red-shifted as about 17 nm for gold sol ethanol solution prior to titania deposition. At 5 M and 10 M water, the absorption peaks showed at 530 nm and the peak width was narrower than that of 0 M water. At 17 M water, the absorption peak appeared at 529 nm. The micrographs of the gold particles obtained at each concentration of water are shown in Fig. 4. The gold particles are extremely flocculated at 0 M water and are gradually dispersed as the concentration of water in ethanol increases. From this result, it could be noted that the gold particles are more stable in water than ethanol.

The intense flocculation of gold particles at 0 M water in Fig. 4 can be explained as follows. The gold sol ethanol solution includes a small amount of water, which 0.4 ml of gold sol has. The amount of water is not enough to hydrolyze all the added TOAA. Consequently, the generated titania is not sufficient to cover the surface of gold particles and the gold particles thus stick to each other by the crosslinkage of irregular titania layer.

At 5 M water in Fig. 4, the thin titania shell on the surface

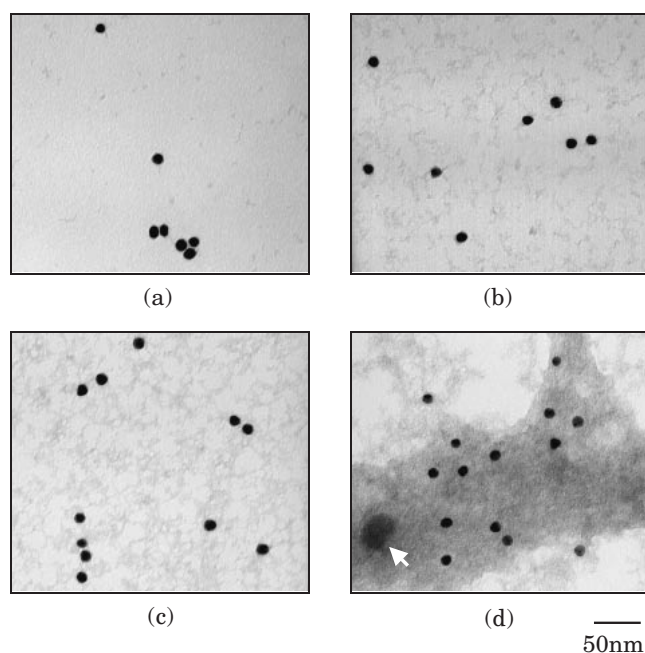


Fig. 2 TEM images of TiO_2 -coated Au particles synthesized in ethanol with 5 M water at various addition amount of TOAA. (a) 1.0 mM, (b) 1.7 mM, (c) 3.4 mM, (d) 9.0 mM.

of gold particles is observed. The thickness of titania shell was about 1 nm. The titania shell was also formed on gold particles at 13 M water. However, no change is found in the thickness of titania layer depending on the concentration of water. In the case of 13 M water, larger amount of separate colloidal titania was generated by spontaneous nucleation. This is also due to the fast hydrolysis reaction of TOAA with water. The separate colloidal titania is more produced at 17 M water and they is flocculated each other.

As the result, it is found that the critical content of water in gold sol ethanol solution to get the titania shell is 5~13 M when the addition amount of TOAA is 1.0 mM. Below this limit, the gold particles are intensely coagulated. Above this limit, the uniform titania shell is also not obtained because the formation of separate colloidal titania occurs preferentially. From above the results, in Fig. 3, the red-shift of absorption peak appeared at 0 M water is caused by the flocculation of gold particles, and the red-shift observed at 5 M, 13 M and 17 M water is due to the titania shell on gold particle even if the titania layer is not so uniform in the case of 17 M water.

3.2 Crystallinity of TiO_2 shell

If the titania shell obtained by the hydrolysis of TOAA is a crystalline such as anatase or rutile, the electron of titania in valence band will be excited to conduction band by UV irradiation and the excited electron will be stored on the surface of gold particles. This is called surface plasmon phenomenon. This phenomenon can be observed by UV-vis spectrum because the absorption band of the gold particles charged with electron will be blue-shifted.^{19,20)} However, no such change was observed in the absorption band of TiO_2 -coated gold particles after the irradiation of ultraviolet light at 254 nm for 1 hour. From this result, it may be concluded that no electron is generated from titania shell and thus the shell

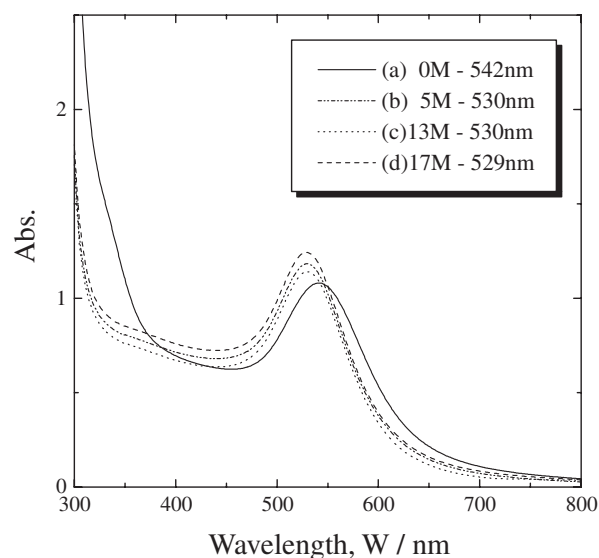
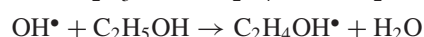
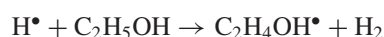


Fig. 3 UV-Vis absorption spectra of TiO_2 -coated Au particles synthesized in ethanol with various content of water. (at 1.0 mM TOAA).

does not have a crystal structure.

However, in order to achieve that the determination is true, it should be needed to check whether the excited electron from titania shell can penetrate through the MUA organic layer between gold particle and titania shell and arrive at the surface of gold particles. To test this, an electron was generated from TiO_2 -coated gold sol ethanol aqueous solution by irradiation with radioactive ^{60}Co . The surface plasmon band from gold particles was observed with UV-vis spectrum. The reaction for electron generation from ethanol by radioactive ray can be described as follows;



H_2O generates $\text{H}^\bullet$ and $\text{OH}^\bullet$ radical by irradiation of radioactive ray. These radicals react with ethanol and form $\text{C}_2\text{H}_4\text{OH}^\bullet$ radical. The $\text{C}_2\text{H}_4\text{OH}^\bullet$ radical gives an electron to gold particle and is transformed to acetaldehyde. Here, if the electron given from $\text{C}_2\text{H}_4\text{OH}^\bullet$ radical cannot penetrate through MUA layer, the absorption band from the gold sol ethanol aqueous solution will be similar to that prior to irradiation.

Figure 5 shows the spectral changes observed from TiO_2 -coated gold sol ethanol solution after irradiation of radioactive ray for 1 hour of the sample shown in Fig. 1(a). In this absorption spectrum, a blue-shift of the absorption peak is observed, and this is due to the electron stored on the surface of gold particles. This indicates penetration of the electron through the MUA organic layer. As the result, it is concluded that the titania shell has an amorphous structure and the MUA layer on gold particles doesn't act as an obstacle to disturb the movement of electron onto the surface of Au particle.

4. Conclusions

The studies showed the formation of TiO_2 coating on gold

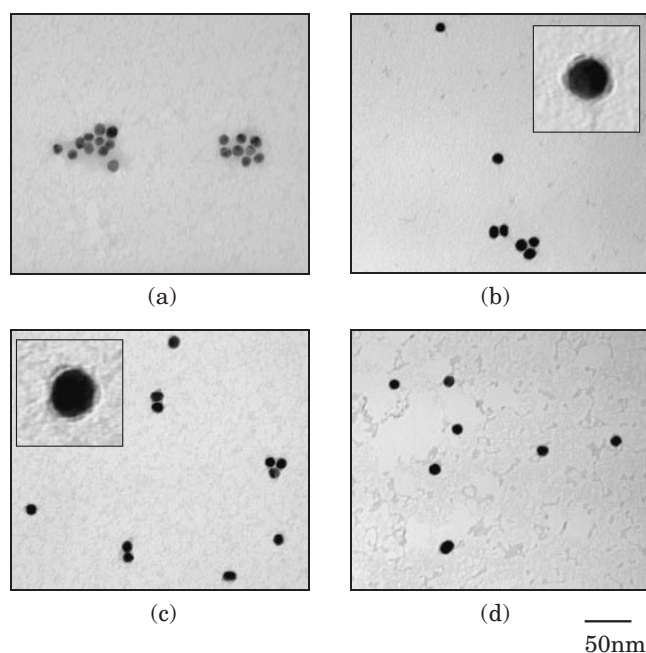


Fig. 4 TEM images of TiO₂-coated Au particles synthesized in ethanol with various content of water. (at 1.0 mM TOAA). (a) 0 M, (b) 5 M, (c) 13 M, (d) 17 M.

nanoparticles takes place when 1 mM TOAA is added to gold sol ethanol solution containing 5 M water. The shell thickness at this concentration was about 1 nm. Any further addition of TOAA does not increase the thickness of the coating, but resulted in the formation of titania nucleating on colloidal titania. This is due to faster hydrolysis of TOAA.

The crystallinity of titania shell was evaluated by observing the blue-shift in UV-vis absorption spectrum. The crystal structure of titania shell formed on gold particles was considered to be amorphous because the blue-shift in the absorption band did not appear after ultraviolet light was irradiated on TiO₂-coated gold sol solution. It was also found that the MUA layer on gold particles did not act as an obstacle to disturb the movement of electron onto the surface of Au particle.

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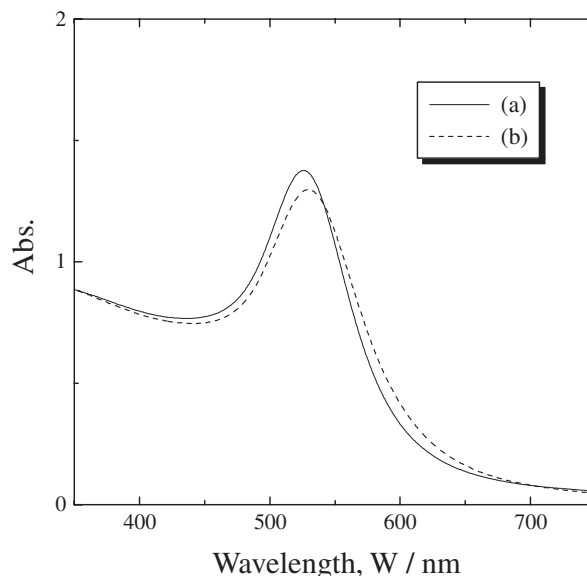


Fig. 5 UV-Vis absorption spectra of TiO₂-coated Au particles irradiated by ⁶⁰Co. (a) Au/TiO₂ particles irradiated by ⁶⁰Co, (b) Au/TiO₂ particles prior to irradiation.

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