

## Synthesis and Characterization of Au/TiO<sub>2</sub> Core-shell Structure Nanoparticles

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**Abstract**—Au/TiO<sub>2</sub> core-shell structure nanoparticles were synthesized by sol-gel process, and the morphology and crystallinity of TiO<sub>2</sub> shell were investigated by TEM and UV-vis absorption spectrometer. Au/TiO<sub>2</sub> core-shell structure nanoparticles could be prepared by the hydrolysis of TOAA (titanium oxide acetylacetonate) in gold sol ethanol solution with water. The thickness of TiO<sub>2</sub> shell on the surface of gold particles was about 1 nm. To investigate the crystallinity of TiO<sub>2</sub> shell, UV light with 254 nm and radioactive ray of <sup>60</sup>Co were irradiated on the TiO<sub>2</sub>-coated gold sol ethanol solution. The surface plasmon band of gold nanoparticles appeared only when the radioactive ray was irradiated on the TiO<sub>2</sub>-coated gold sol ethanol solution. From these results, it was found that the TiO<sub>2</sub> shell was amorphous and the MUA (mercaptoundecanoic acid) layer on the Au particle for its dispersion in ethanol did not act as an obstacle to disturb the movement of electrons onto the surface of Au particles.

Key words: Core-shell Structure Nanoparticle, Gold, Titania, Crystallinity

### 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 [Bedja et al., 1993], electroluminescent films [Dabbousi et al., 1995], nonlinear optical switches [Neeves et al., 1989], and high-density information storage systems [Micheletto et al., 1995]. 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 [Motte et al., 1995; Giersig and Mulvaney, 1993; Hayes et al., 1989].

But, the organic capping agents are prone to chemical oxidation, especially under photolysis. To solve this problem, the encapsulation of each nanoparticle 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 metal nanoparticles are occasionally used under extreme conditions such as optical limiters and three-dimensional optical memories using high intensity lasers. Gold and silver nanoparticles are some of the best optical limiters known thus far [Philip et al., 2000; Sun et al., 1999]. However, at high light intensities, they are susceptible to damage, leading to photofragmentation, ligand desorption, etc. [Kamat et al., 1998; Link et al., 2000]. To

make them stable at extreme conditions, it is necessary to protect them with stable and chemically inert shells such as oxides. This kind of cover also makes it possible to fabricate materials in the form of thin films and disks for application.

Most of the research in this area has been on noble-metal nanocores and silica shells and characterization of their properties such as optical and catalytic [Mulvaney et al., 2000; Chang et al., 1994; Aliev et al., 1999]. In this paper, we focus on the synthesis of TiO<sub>2</sub>-covered gold particles, and the characterizations of their optical property and crystallinity of titania shell.

The preparation of uniform oxide-protected metal colloid can be facilitated by a slow and steady growth of oxide layer on metal core and the stability of metal colloid. The metal nanoparticles coated by some polymeric stabilizer are very stable in aqueous solution, but not usually in organic solvents such as ethanol. On the other hand, the titanium alkoxides used as precursors to make titania shell on gold particles are very fast hydrolyzed in water. Therefore, it is important to diminish the reaction velocity of hydrolysis of titanium alkoxide in order to get excellent titania shell, and thus gold sol is needed to move into organic solvent with low polarity, such as ethanol and toluene. However, the stability of gold sol in organic solvent is not good. In this work, to circumvent this problem, mercaptoundecanoic acid (MUA) is pre-coated on the surface of gold particles before coating TiO<sub>2</sub>. The coating of MUA has a strong effect on the dispersion of Au nanoparticles in ethanol. The synthesis of Au/TiO<sub>2</sub> core-shell nanoparticles is attempted by sol-gel method in ethanol.

Nanoparticles with TiO<sub>2</sub> shell are very interesting, as the photocatalytic property, the dielectric constant and the color can be changed with the surface plasmon phenomenon, which the electron excited from the valence band of TiO<sub>2</sub> by UV irradiation is stored onto the surface of metal core [Ueno et al., 1985; Nasr et al., 1997]. But, these changes are susceptible to occurring only when the TiO<sub>2</sub> shell has a crystal structure and the electron excited from TiO<sub>2</sub> can be moved to metal core through the organic layer between shell and

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metal core for the affinity of titania shell for metal core in the synthesis process. However, it is very difficult to evaluate the crystallinity of titania shell with X-ray diffraction analysis because very small amount of core-shell metal nanoparticles is generated from dilute solution. In the following, we describe a simple method to evaluate the crystallinity of titania shell and the movement of electrons through organic layers.

## EXPERIMENTAL PROCEDURES

HAuCl<sub>4</sub>, trisodium citrate dihydrate, mercaptoundecanoic acid (MUA), NH<sub>4</sub>OH (28%), titanium isopropoxide (TIPO) 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,  $5 \times 10^{-4}$  M HAuCl<sub>4</sub>) 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. MUA (0.5 mM) was dissolved into 2.5% aqueous ammonia solution. The MUA solution was then added to the gold sol and incubated for 2 hours. The gold particles treated with MUA were collected by centrifuging. The gold particles were put into 20 ml of water and re-dispersed by adding about 20  $\mu$ l of 28% ammonia solution. This was used as a stock solution of gold sol for coating TiO<sub>2</sub>.

TiO<sub>2</sub> coating was performed by utilizing the Stober method [Turkevich et al., 1949]. For the preparation of ethanol solution suspended 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, water was added for the hydrolysis of titanium alkoxide, and the concentration in ethanol was changed in the range of 0–17 M. After the solution became homogeneous, 1 ml of titanium alkoxide diluted in ethanol was added to the premixed gold sol ethanol solution under vigorous stirring and then the mixture was continuously stirred for 5 hours to completely terminate the hydrolysis reaction of titania alkoxide.

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/TiO<sub>2</sub> core-shell colloid was exposed under ultraviolet light with 254 nm (150 W Xenon lamp) and radioactive layer of <sup>60</sup>Co in order to evaluate the crystallinity of TiO<sub>2</sub> shell.

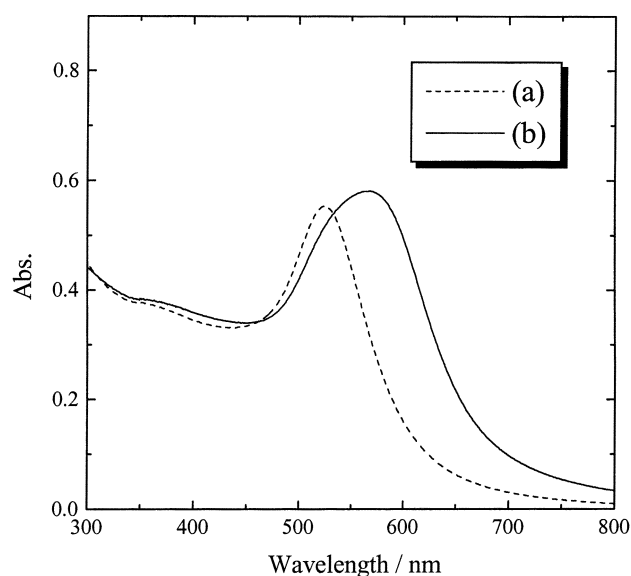
## RESULTS AND DISCUSSION

### 1. Effect of pH on Dispersion of Gold Colloid

The stability of MUA-coated gold particles in ethanol is very important for obtaining monodispersed Au/TiO<sub>2</sub> core-shell nanoparticles. The stability of MUA-coated gold particles is usually affected by the solution pH. To investigate the dependence of time on stability and optimize the pH of gold sol ethanol solution, 0.3 ml of the MUA-coated gold sol was mixed with 9.7 ml of ethanol, and the stability was determined by UV-vis spectrometer with time. The results are shown in Table 1. The absorption peak of MUA-coated gold sol appeared at 524.7 nm, and no clear change in the absorption spectrum is observed with time. However, on the other hand, when a small amount of additional NH<sub>4</sub>OH (0.1 M) was added into the MUA-coated gold sol ethanol solution, the absorption peak was

**Table 1.** Peak locations of UV-vis absorption spectrum for MUA-coated gold sol ethanol solution according to the passage of time and the addition of NH<sub>4</sub>OH

Holding time in EtOH (min)	10	30	60	120	600	After 10 min from adding 0.1 M NH <sub>4</sub> OH
Peak location of UV-Vis. spectrum (nm)	524.7	524.7	524.7	524.7	524.7	566.8



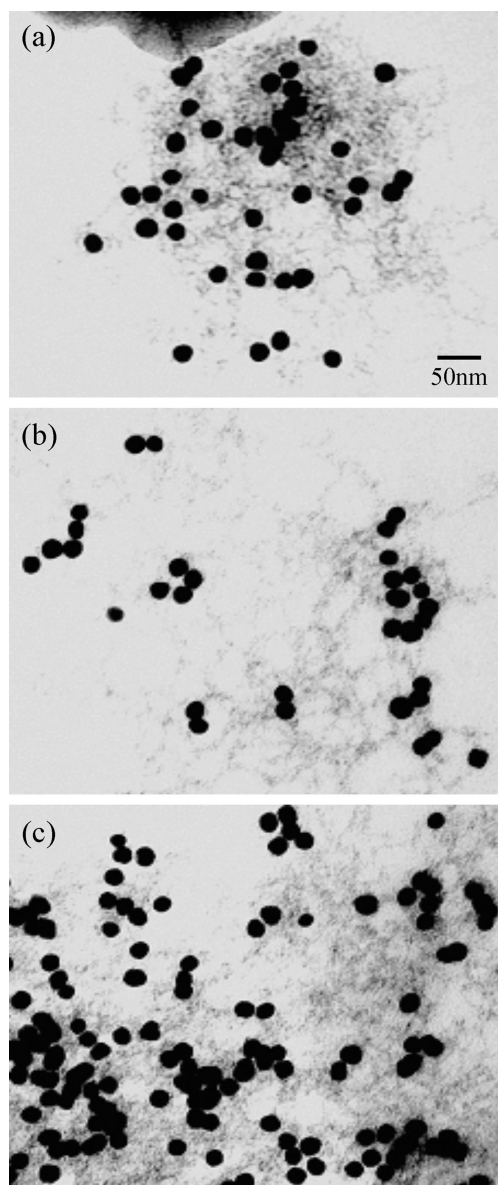
**Fig. 1.** Peak change of UV-vis absorption spectrum of Au sol ethanol solution according to the addition of NH<sub>4</sub>OH.

(a) No addition, (b) 0.1 M

shifted to 566.8 nm and the peak width became broad as shown in Fig. 1, and also the pH of gold sol ethanol solution was changed from 7.1 to 9.5. This result indicates that adding NH<sub>4</sub>OH causes the MUA-coated gold particle to coagulate in ethanol solution. In general, MUA can act as a flocculent and dispersant. An MUA-coated gold particle is very stable in aqueous media when pH is higher than the pK<sub>a</sub> (6.3) of the carboxyl group, because the mercapto group of MUA has a strong affinity with gold and the carboxyl group is considered to face to the dispersion media. The acid addition makes the particles flocculate by diminishing its surface charge and starts to sediment down [Kane and Mulvaney, 1998]. However, in ethanol media, the MUA-coated gold particle is aggregated though the pH of gold sol is higher than 6.3. This flocculation of gold particles is probably considered to be due to the high solubility of MUA in ethanol. Thus, in the following experiment, TiO<sub>2</sub> coating of gold particles was performed in MUA-coated gold sol ethanol solution which pH is about 7 without adding additional NH<sub>4</sub>OH.

### 2. TiO<sub>2</sub> Coating by using TIPO

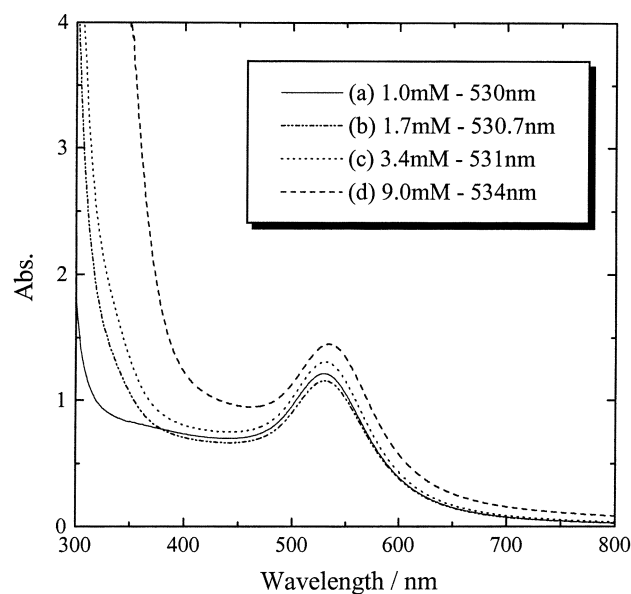
The TiO<sub>2</sub> coating of MUA-coated gold particles was pursued by titanium isopropoxide (TIPO). For titania coating on gold particles, TIPO solution diluted in ethanol is added to the gold sol ethanol solution with 0.4 ml of MUA-coated gold sol. The amount of TIPO



**Fig. 2. TEM images of  $\text{TiO}_2$ -coated Au particles obtained at various contents of TIPO.**

(a) 1.0 mM, (b) 1.7 mM, (c) 3.4 mM

was varied between 1.0 mM and 3.4 mM when the content of water in ethanol solution was 13 M. Fig. 2 shows the micrographs of the gold particles coated at various amounts of TIPO. The gold particles were flocculated in separate colloidal titania matrix and the coagulation was more extreme as the amount of TIPO was higher. This result implies that the nucleation of titania occurred spontaneously in solution as well as heterogeneously on the surface of gold particles, and thus the gold particles were more extremely flocculated by the separate colloidal titania. This spontaneous nucleation of titania is considered to be caused by the fast hydrolysis reaction of TIPO with water. From this result, therefore, it should be noted that the hydrolysis velocity of titanium alkoxide must be more diminished for preparing titania shell on gold particles though the hydrolysis reaction of titanium alkoxide is performed in ethanol rich solution.



**Fig. 3. UV-vis absorption spectrum of  $\text{TiO}_2$ -coated Au sol synthesized in ethanol with 5 M water at various amounts of TOAA.**

### 3. $\text{TiO}_2$ Coating by using TOAA

In order to diminish the hydrolysis reaction velocity of titanium alkoxide, titanium alkoxide was changed to titanium oxide acetylacetonate (TOAA). The hydrolysis reaction velocity of TOAA with water is expected to be relatively more slow than TIPO because TOAA is a cyclic compound including two double bonds in the atomic structure. The amount of TOAA was changed between 1.0 mM and 9.0 mM. In this case, the content of water in gold sol ethanol solution for hydrolysis reaction was adjusted between 0 M and 17 M.

Fig. 3 shows the spectral changes observed after deposition of titania at various amounts of TOAA when the content of 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 increasing amount of TOAA. Also, the other absorption band appeared between 300 nm and 400 nm. Shown in Fig. 4 is a series of micrographs of the gold particles obtained at various amounts of TOAA. At 1.0 mM TOAA, the particles are all slightly coated with titania and a small amount of separate colloidal titania generated by spontaneous nucleation appeared in ethanol solution. The separate colloidal titania is spreaded with increasing the amount of TOAA, but the growth of titania shell is not more achieved. This is the reason why the hydrolysis reaction is faster with increasing the amount of TOAA and the formation of fresh titania happened preferentially on the separate colloidal titania generated already. At 9.0 mM TOAA, the particles are perfectly embedded in a titania matrix. The formation of cluster of separate colloidal titania is also considered to be due to the fast hydrolysis reaction of TOAA though the velocity is not as fast as TIPO, and thus the more TOAA is added, the greater the amount of separate colloidal titania generated.

In summary, the critical addition amount of TOAA found is 1.0 mM when the content of water in gold sol ethanol solution is 5 M. Above this limit, there is the coagulation of gold particles by the

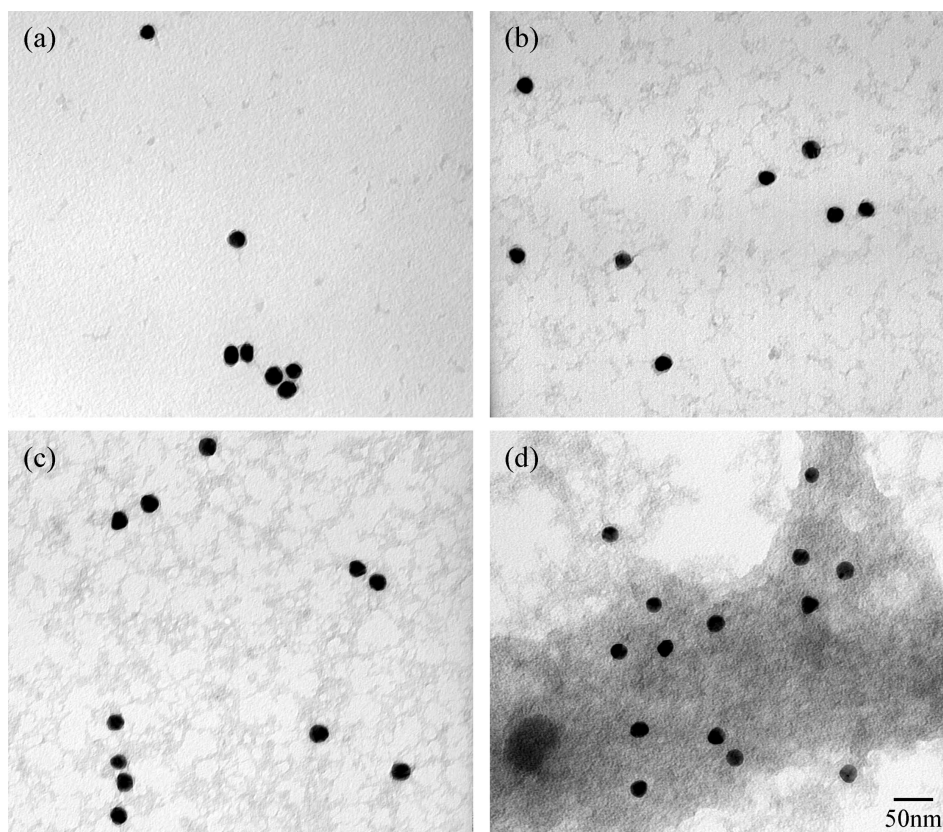


Fig. 4. TEM images of TiO<sub>2</sub>-coated Au particles synthesized in ethanol with 5 M water at various amounts of TOAA.

(a) 1.0 mM, (b) 1.7 mM, (c) 3.4 mM, (d) 9.0 mM

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 appearing above 1.7 mM

is mainly due to the coagulation of gold particles because this red-shift 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 the absorption band is more strong as the amount of TOAA increases.

Fig. 5 shows the spectral changes observed after deposition of titania at various concentrations of water in ethanol when the added 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 appeared 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. 6. 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. 6 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 and 13 M water, the thin titania shell on the surface of

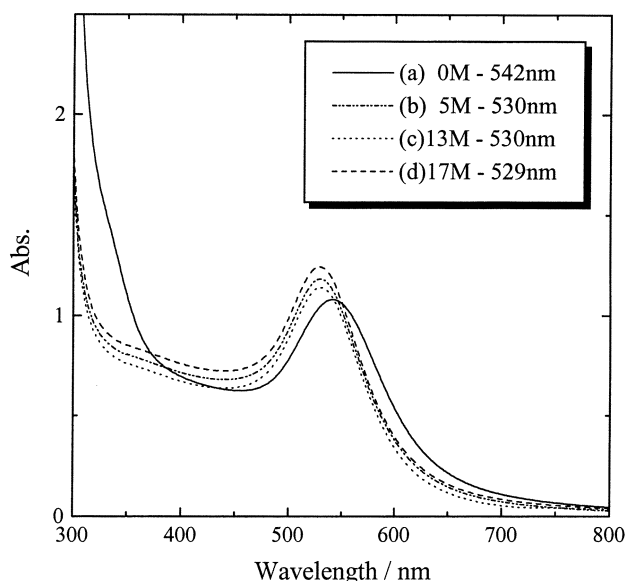
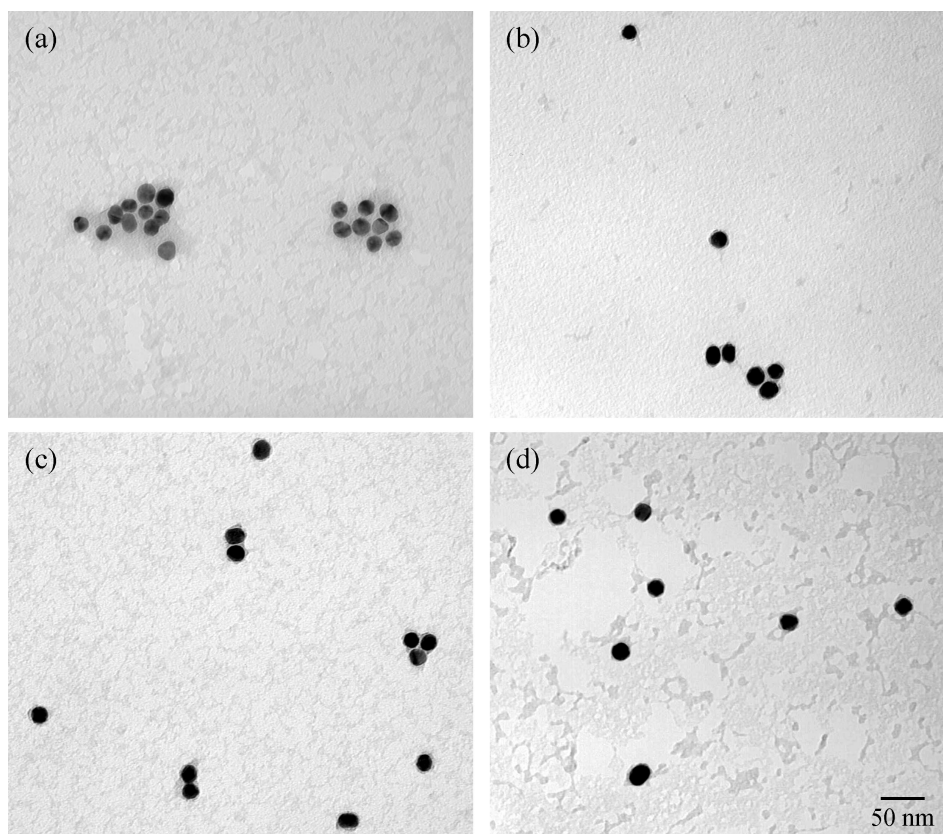
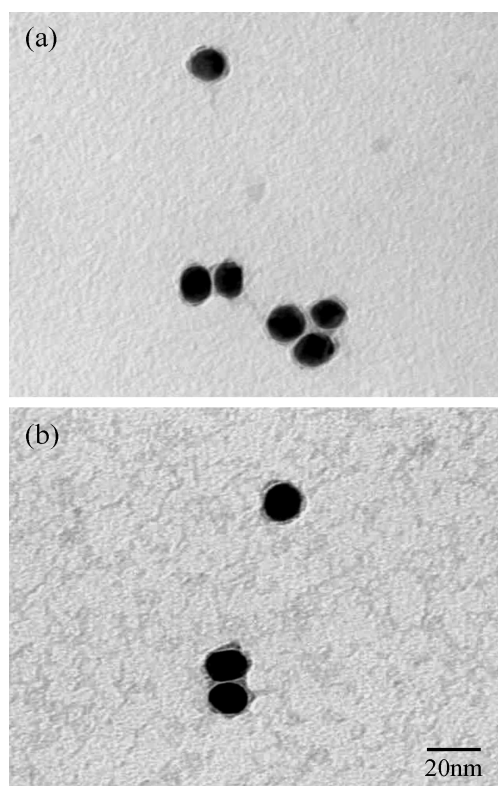


Fig. 5. UV-Vis absorption spectra of TiO<sub>2</sub>-coated Au particles synthesized in ethanol with various contents of water (at 1.0 mM TOAA).



**Fig. 6.** TEM images of  $\text{TiO}_2$ -coated Au particles synthesized in ethanol with various contents of water (at 1.0 mM TOAA). (a) 0 M, (b) 5 M, (c) 13 M, (d) 17 M



**Fig. 7.** TEM images of  $\text{TiO}_2$ -coated Au particles synthesized in ethanol with (a) 5 M and (b) 13 M (at 1.0 mM TOAA).

gold particles is observed. The thickness of titania shell was about 1 nm. To examine whether the titania layer grows when more water is added, the micrographs of  $\text{TiO}_2$ -coated gold particles obtained at 5 M and 13 M water are magnified as shown in Fig. 7. However, no change is found in the thickness of titania layer depending on the concentration of water. In the case of 13 M water, a large amount of separate colloidal titania generated by spontaneous nucleation was formed. 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 are flocculated with each other.

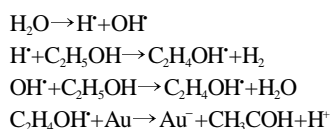
As a result, it is found that the critical content of water in gold sol ethanol solution to get the titania shell is 5–13 M when the amount of TOAA is 1.0 mM. Below this limit, the gold particles are intensely coagulated. Above this limit, the uniform titania shell is also not obtained because the formation of separate colloidal titania occurs preferentially. From above the results, in Fig. 5, the red-shift of the absorption peak appearing 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.

#### 4. Crystallinity of $\text{TiO}_2$ Shell

If the titania shell obtained by the hydrolysis of TOAA is a crystal, such as anatase or rutile, the electron of titania in valence band will be excited to the 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 [Mulvaney, 1996; Jakob and Levanon, 2003; Mock et al., 2002]. However, we could not find a change in the absorption band of TiO<sub>2</sub>-coated gold particles after the irradiation of ultraviolet light with 254 nm for 1 hour. From this result, it can be determined that no electron is generated from titania shell and thus the shell does not have a crystal structure.

However, in order to determine if this is true, it should be checked whether the excited electron from the titania shell can penetrate through the MUA organic layer between the gold particles and titania shell and arrive at the surface of the gold particles. To determine this, we attempted to generate an electron from TiO<sub>2</sub>-coated gold sol ethanol aqueous solution by using irradiation of radioactive material, <sup>60</sup>Co, and observe the surface plasmon band from gold particles with UV-vis spectrum. The reaction for electron generation from ethanol by radioactive ray can be described as follows:



H<sub>2</sub>O generates H<sup>·</sup> and OH<sup>·</sup> radical by irradiation of radioactive ray. These radicals react with ethanol and form C<sub>2</sub>H<sub>4</sub>OH<sup>·</sup> radical. The C<sub>2</sub>H<sub>4</sub>OH<sup>·</sup> radical gives an electron to gold particles and is transformed to acetaldehyde. Here, if the electron given from C<sub>2</sub>H<sub>4</sub>OH<sup>·</sup> radical cannot penetrate through the MUA layer, no change in absorption band from the gold sol ethanol aqueous solution will be observed as compared with that prior to irradiation of radioactive ray.

Fig. 8 shows the spectral changes observed from TiO<sub>2</sub>-coated gold sol ethanol solution after radioactive irradiation for 1 hour. In this absorption spectrum, the blue-shift of the absorption peak is observed in the spectrum and is due to the electrons stored on the

surface of the gold particles. This result indicates that the electrons can penetrate through the MUA organic layer. As a result, it is found that the titania shell has an amorphous structure and the MUA layer on gold particles does not act as an obstacle to disturb the movement of electrons onto the surface of Au particles.

## CONCLUSIONS

The synthesis of Au/TiO<sub>2</sub> core-shell structured nanoparticles was attempted by sol-gel method, and two kinds of titanium alkoxides, TIPO and TOAA, were used as a starting material of titania.

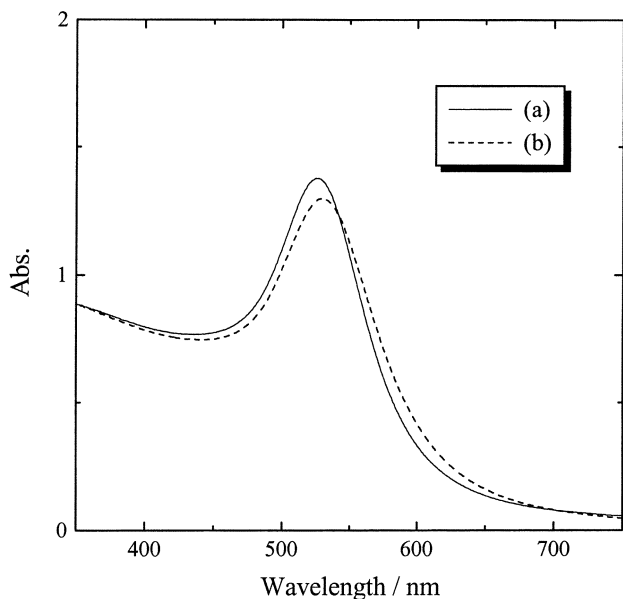
In the case of TIPO, the gold particles were flocculated in separate colloidal titania matrix and the titania shell on gold particles could not be obtained because of the fast hydrolysis reaction of TIPO with water in ethanol.

In the case of TOAA, titania shell was formed on gold particles and the shell thickness was about 1 nm. This is caused by the lower velocity of hydrolysis reaction of TOAA than that of TIPO. However, the further growth of titania shell was not achieved because the hydrolysis reaction is gradually faster as the amount of TOAA increases and the formation of fresh titania happens preferentially on the separate colloidal titania generated already. The critical condition for obtaining TiO<sub>2</sub>-coated gold particles is when the amount of TOAA found is 1.0 mM and the content of water in gold sol ethanol solution is 5-13 M.

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 TiO<sub>2</sub>-coated gold sol solution. Also, it was 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 particles.

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**Fig. 8.** UV-Vis absorption spectra of TiO<sub>2</sub>-coated Au particles irradiated by <sup>60</sup>Co.  
(a) Au/TiO<sub>2</sub> particles irradiated by <sup>60</sup>Co, (b) Au/TiO<sub>2</sub> particles prior to irradiation.

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