STUDIES FOR THE CHARACTER OF NANO-SIZED TiO_2 PARTICLE SYNTHESIZED BY MICRO-EMULSION METHOD AND GOLD-DEPOSITED TiO_2 PARTICLE

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SUMMARY

Nano-Sized TiO_2 particles with diameter between 2 and 5 nm are synthesized in Water/ Triton X-100/ n-Hexane microemuelsion. Particles show the amorphous structure and partially hydroxide form.

The optical absorbance of particles appears at 250nm and band edge at 340nm. Gold metal is deposited on the surface of TiO_2 particles by reduction reaction of Au(III) ion with sodium hypophosphite. The size of gold-deposited particles is 20nm, and the optical absorbance appears at 270nm and at 550nm. So particles show the red color. The dense precipitation is formed by aggregation in the TiO_2 nano-sized particles of about 5nm size. But the bulky precipitation is formed by agglomeration phenomena in the gold- deposited particles of 20nm size. And also gold-deposited particles is easily dispersed by being re-dispersed in PEG/Water solution. This study has compared those things measuring the SPF characteristics of the cosmetics made of the synthesized particles. If the particle size is controlled appropriately, then the SPF value will be higher, or more colorless cosmetics will be made.

INTRODUCTION

The metal oxides have been the focus of numerous investigation in the fast few ten years[1]. Particularly, the preparation of the titanium dioxide has been studied by the numerous method because of its applicability as catalytic, ceramic, electronic and optical material[2,3,4].

Recently nanoclusters are interesting as representative of a state of matter intermediate between molecular and bulk solid. Size effects have been observed experimentally that the band gap of nano-sized particle is larger than the bulk crystal band gaps and increase with decrease cluster size[5]. As the size of particles is smaller, the light with the more short wavelength can be absorbed.

In the cosmetic field, TiO_2 has been used as pigment and UV filter. As TiO_2 band gap is about 3.0 eV, it could absorb 380-400nm wavelength. However, if nano-scale particles are synthesized, it can filter UV-ray of 250-400nm irradiated by environmental problem of the earth. Also if particle size is regulated properly, cosmetics can be formulated to filter specific UV wave.

However if TiO_2 particles absorb the energy range of its band gap, the electron of valance band will be transferred to the exciton state or the conduction band. So it will be formed that hole in the valance band and negative charge in the conduction band. As a result of hole and negative charge formation photocatalytic phenomena of the oxidation and reduction appears[6]. In addition, particle size decreases, specific surface area increases. Because of the charge effect between titanium and oxygen, surface of the particles will be an unstable state and the particles will be easily aggregated. To restrain oxi-reduction of cosmetic ingredients caused by aggregation and photocatalytic phenomena, inert metal such as gold should be coated or co-dispersed. As band gap of the gold is comparatively large it can depress surface carrier of hole and electron, increase the size of particles, thus specific surface area can be decreased. Furthermore mechanical dispersion will be easy for it repress the mutual interaction among TiO_2 particles.

Widely adopting synthesizing methods are gas-phase oxidation of $TiC1_4$[7,8,9], hydrolysis of titanium alkoxide[10,11,12], aerosols [13,14] or microemulsion method.

Especially microemulsion method have advantages that can synthesize particles to nano- sized and regulate the particle size according to micelle volume.

Boutonnet et al.[16] synthesized ultra-fine inert metals with this microemulsion method and V.Chhabra et al.[17]reported structural properties and photocatalytic phenomena. As a structure of chemically synthesized particles, however, are amorphous it must be heated to crystallize into anatase or rutile type.

In this paper, to formulate cosmetics going with natural environment change, nano-sized TiO_2 were synthesized and for inhibit structural, chemical and physical phenomena, gold metal was coated or co-dispersed. Aggregation and UV-absorbing phenomena of the particles were investigated and various creams from synthesized particles were prepared to test physical properties.

EXPERIMENTS

MATERIALS

Sulfamic acid, titanium tetrachloride, sodium chloride, sodium acetate, and sodium hypophosphite were purchased from Sigma Co.. Ammonia solution, Triton X-100, n-hexanol, n-hexane, phenol(crystal), and potassium tetrachloro aurate(III) were purchased from Aldrich Chemical Co.. Ethanol(99.9%) and chloroform were purchased from Fisher. All reagents were used without further purification.

Used water was pure water, which was purchased from EM Science.

METHODS

1.) Synthesis of TiO_2 particle

In microemulsion method two emulsion solutions that contains $TiC1_4$ and NH4OH respectively should be prepared. Then these two solutions are mixed with agitation. As a result of collisions, reaction occurs and TiO_2 is synthesized. Micelle volume affects on the shape and size of TiO_2 particles. Table 1 represents composition of two micro emulsions.

Table 1. The Composition of W/O Microemulsion

Function	Microemulsion II	Microemulsion III	%/w/w
Aqueous Phase	$TiC1_4$(0.03M) Solution	Ammonia(0.12M) Solution	8.0
Surfactant	Triton X-100	Triton X-100	19.0
Co-surfactant	n-Hexanol	n-Hexanol	15.0
Continuous phase	n-Hexane	n-Hexane	58.0

Different two aqueous phases were slowly added to the each solution of hydrocarbon phase. Then it mixed homogeneously with homo mixer(Japan, Tokushu kika, Model. Mark II) at room temperature for 10minutes. Microemulsion solution was added as a form of droplets and uniformal, homogeneous nano-sized particles are synthesized. Particle size increases as the concentration of reacting materials increases in the aqueous solution.

These results was confirmed by HR-TEM(high resolution transmission electron microscopy. Japan, JEOL, Model. JEM-200FXII). Synthesized nano-sized TiO_2 in the aqueous core was applied immediately to the centrifugal separator(Korea, Hanil Ind., Model. HMR-1601V) for 10 minutes. Then the precipitation was washed three times with ethanol /chloroform mixture (1:1 v/v). To measure optical absorbance of prepared particles its solvent was changed to PEG / Water(1: 1 v/v) solution, and them UV-visible spectrometer(UK, ATI unicam. Model. UV2) was applied.

2) Gold deposition on the surface of TiO_2 particle.

Table 2. Represents Gold Bath Composition for Deposition on the TiO_2 Surface.

	A (w / v)	B (w / v)
Potassium tetrachloroaurate(III)	0.2 g / l	0.02 g / l
Sodium chloride	0.5 g / l	0.05 g / l
Sodium acetate	0.5 g / l	0.05 g / l
Sulfamic acid	0.5 g / l	0.05 g / l
Sodium hypophosphite	1.5 g / l	0.15 g / l

It was reported that in the reducing reaction of potassium tetrachloro aurate(III) by sodium hypophosphite, phosphorus was detected in the gold metal phase. To eliminate phosphorus element, hydrazine, reductant have been used[15]. However, phosphorus element would not have an effect on the purpose of this paper and reducing power of hydrazine is so strong that gold would not deposit and educe as a gold cluster. Metal educt reaction in the gold solution depends on the temperature. To delay reaction time it was reacted in the ultra sonicator at relatively low temperature 50°C.

Table 3 represents the relation between the concentration of the gold bath and adding TiO_2. As concentration of TiO_2 decrease, deposition of gold on the surface of TiO_2 particles were decreased and formation of gold clusters was increased.

Table 3.Deposition Test with the Concentration of TiO_2 and Gold(III).

Conc.of Gold Bath	A			B		
Conc. of TiO_2 particles.	1 g/l	10 g/l	100 g/l	1 g/l	10 g/l	100 g/l

These synthesized particles were centurifugated with the same condition and washed several times with the pure water. Then it was re-dispersed in the PEG/Water (1:1 v/v) solution to observe the shape of particles and aggregation by UV-visible spectrometer and TEM.

To analyze composition and oxidation state of elements in the synthesized TiO_2 and gold-deposited TiO_2 particles ESCA(electron spectroscopy for chemical analysis. UK, V.G. Scientific., Model. ESACLAB 220i) was applied. Because analyzer chamber of the ESCA is ultra high vacuum system below $1x10^{-9}$ torr, it can desorb almost physically adsorbed chemical species. Therefore it was analyzed after sputtering with Ar ion for 5 minutes. Relative composition and oxidation state of the elements can be analyzed from the peak position.

3) Aggregation charactor

Aggregation property of the synthesized nano- sized TiO_2 and gold deposited TiO_2 was analyzed with UV-visible spectrometer and TEM. Each TiO_2 particles were dispersed in PEG/Water(1 : 1 v/v) solution to measure optical absorbance. Particles were re-dispersed in the ethanol solvent and analyzed with TEM.

4) The measurement of SPF values.

UV-ray protecting ability was evaluated for synthesized nano-sized TiO_2 and commercial micro-sized TiO_2,(mean particle size:21nm). Each particles were applied to two types of cosmetic cream, and their compositions are presented in Table 4 and Table 5. Thease creams were applied to the subject(20 people) and then SPF values were measured.

Experiment method :

(a) The ultraviolet intensity of each probe in the Multiport Solar Simulator(USA, Solar Light., Model. 601) was adjusted to 6 steps(25% increments, i.e., 0.66, 0.83, 1.04, 1.28, 1.6, 2.0 MED/min) with erythema UV & UVA Intensity Meter(USA, Solar Light., Model. 3D-600). Then the ray was emitted to the back of the subject for 1minute.

(b) 20-24 hours later, appeared erythema was observed and MED(minimal erythema dose) was calculated.

(c) 2 types of the prepared testing material were applied evenly on the testing area with 2.0mg/cm2. Then 30 minutes later, fixed ultraviolet was emitted, and after 24 hours, SPF was calculated with the MED value calculated from the (b).

SPF = MED after the testing material / MED before the testing material.

Table 4. Composition of Cosmetic Gel Cream.

Components	1	2
Purified Water	To.100	
Disodium EDTA	0.02	
glycerin	5.0	
Polyglycerylmethacrylate/ propylene glycol	10.0	
PEG - 4M	2.0	
Carbomer	0.25	
Triethanolamine	-	-
Synthesized TiO_2	3.0	-
Micro TiO_2	-	3.0

Table 5. Composition of Cosmetic Emulsion Cream.

Component	5	6
Purified Water	To.100	
Triethanolamine	1.0	
Disodium EDTA	0.02	
Methylparaben	0.3	
Glycerin	5.0	
Xanthangum	0.1	
Synthesized TiO_2	3.0	-
Micro TiO_2(Rutile)	-	3.0
Cetearyl alcohol	2.0	
Stearic acid	1.3	
Palmitic acid	0.9	
Butyl paraben	0.1	
Squalane	4.0	
Liquid paraffin	5.0	
Polysorbate 60	0.2	
C10-30 Cholesterol / Lanesterol ester	5.0	
Sorbitan sesquioleate	0.65	
Glyceryl stearate / PEG-100 stearate	1.3	
Cetyl Esters		2.0

RESULTS AND DISCUSSION

1) The Characters of Synthesized TiO_2 particle

The size and the shape of particles depend on the forming type of micelle and the result of measuring the TEM of TiO2 particles synthesized in this study shows that the particle is 2-5 nm globular one just as in the Fig. 1. Many other experiments are trying various methods to restrain the growth of particle but this study does not try the equal(even) re-dispersal because the object is to study the formation and the characteristics of aggregation of pure particles. We have found that three-dimensional aggregation takes place because the synthesized TiO_2 particle is a globular symmetry.

We did not show the X-ray diffraction of TiO_2 particles synthesized by the method of microemulsion but it shows the amorphous structure. The TiO_2 synthesized by the microemulsion method is an amorphous structure and there is a transition as an anatase at the 500°C and as a rutile structure at the 900°C. But we can find out in the Fig. 2, 3, and 4, the measuring results of ESCA that the particle synthesized by this method exists not as a stoichiometric composition but partly as a hydroxide form.

The Fig. 2 is the result of wide scanning synthesized particles by ESCA. Titanium-oxide, being an insulator and because of the charge effect, shows its peak shift by wholly about 2 eV to higher energy position and the carbon C1S peak appears because of the impurity of the washing solution and the surfactant.

The Fig. 3 represents the titanium $Ti_2P_{3/2}$ and $Ti_2P_{1/2}$ peak of particles, and considering the charge effects it shows the typical Ti^{+4} condition of 460.0±0.2 eV.

The Fig 4 is the oxygen O_{1S} peak and considering the charge effects the oxide condition of 530.6±0.2 eV and the hydroxide peak of 532.4±0.2 eV appears and this means that the particles exist partly as a hydroxide form.

The nano-sized particle is usually called as "Quantum State" and as for the semi conductor, many studies report that the optical absorbance becomes the "blue shift" as the size of the particle is being decreased.

This study shows the absorbance of the UV-region of synthesized TiO_2 particles in the Fig. 5 and Fig. 6.

The main absorbance appears at 300 nm and the two peak shoulders which appear in the shorter position than this are by the impurity. The band edge of particles are 370 mm.

The main absorbance of the synthesized particles, centrifuged after being washed by the alcohol/chloroform solution, is 250 nm and the absorbance is sharp because the band edge is 340 nm. This shows that centrifuged particles are uniform and a mono-sized form. And the size of the synthesized particle depends on the $TiC1_4$ concentration

in the aqueous phase. If we increase the $TiC1_4$ concentration as 0.3M, the particle size increases as 10-15nm. We make this experiments with regular cmc concentration and without changing the concentration of the surfactant.

2) The character of gold deposited TiO_2

The reaction by the reduction reagent of metal ion differs in its reduction kinetics, according to the concentration of metal ion, temperature and the concentration of the reduction reagent. The deposition by the reduction method of metal ion differs resting upon the reduction reagent such as hydrogen, hydrazine, borohydride and so on.

Unless the reaction kinetic in the reduction reaction of metal ion is controlled, the gold metal is not deposited on the surface of core particles.but grows as metal cluster and owing to this phenomena the particle size becomes the non-uniform condition.

This study made a reduction of Au(III) by using sodium hypophosphite, which is the method to control the reduction kinetic properly. Much phosphorus is deposited in Au(III) metal but this does not effect on the object of this study.

The experiment of this study shows that the size of the gold-deposited particle is about 20-25 nm by the nuclear growth, as in the TEM analysis of the Fig 7. and Fig.8 But if we keep the concentration of gold solution evenly and the adding quantity (1g/l) of the TiO_2 is relatively small, much is formulated separately as gold cluster. But if the concentration of particles are 100g/l, the deposition is comparatively uniform. And also the growth of the deposited particle, as in the Fig. 8 appears not as a three-dimensional aggregation but as a branch-type agglomeration. This shows that particles are deposited more bulky than non-deposited TiO_2 particles.

Fig. 9 and Fig. 10 represents the EDAX(Energy Disperse X-ray Analysis) measuring results of the gold-clustered particle and the gold deposited TiO_2. This results shows that there is a partial formation of gold cluster.

Fig. 11 represents the optical absorbance of gold-deposited particles. Unlike the absorbance of non-deposited particles, the band edge appears broadly as about 400 nm, and this means that the particle is grown by the gold deposition. And also there appears an secondary absorption peak, at the position of 550 nm, by the gold cluster and deposited particles. Therefore centrifuged particles after the deposition reaction show red color.

As there are enormous ingredients to the cosmetics. there must be wide-range and continual experiments in the photocatalytic reaction on the electron-hole of synthesized particle. Not yet published in this paper, Some facts are found out about the photocatalytic properties of particles synthesized on organic materials including the double bond or the functional group of alcohol among the cosmetic ingredients. The transition $\pi \rightarrow \pi^*$ of double bond or the oxidation-reduction reaction of the alcohol func-

tional group needs the quantitative analysis based on the evidence according to the shift of IR, UV-visible Spectrometer, conductivity, pH, Zeta-potential etc., of solution, and studies on this view point is now continually being kept.

But this study has compared those things measuring the SPF characteristics of the cosmetics added by the synthesized particle.

3) Synthesized TiO_2 in the SPF point of view

The results of SPF measurement was represented in Fig. 12, 13 and <Table 6>. Of the SPF value of each cosmetics which was added synthesized TiO_2 and commercial TiO_2 respectively. SPF value of the former was a little higher than the latter.

Therefore we supposed that, in a field of UV-B, UV filtering ability of particles of which particle size was relatively small than the other at first was more predominant. The specific point was that the degree of clarity was more higher in a cream containing synthesized TiO_2. The result was shown that if the particle size is controlled properly, the SPF value will be higher or more colorless cosmetics can be formulated. Besides, from the results of gel cream it was supposed that dispersibility of TiO_2 particles have a great influence on the SPF value.

CONCLUSION

The dense precipitation is formed by aggregation in TiO_2 nano-sized particles with about 5nm size. The bulky precipitation is formed by agglomeration phenomena in gold-deposited particles of 20nm size. And also gold-deposited particles are easily dispersed by being re-dispersed in PEG/Water solution.

And then, if the particle size is controlled appropriately, the SPF value of cosmetics will be higher, or more colorless one will be made. We can develop new cosmetics filtered a specific UV-ray if we control the size properly, because nano-sized particles synthesized by the microemulsion method absorbs its own UV-ray region due to the size. Moreover we need more studies on the photocatalytic characteristics and skin care of cosmetics made of the synthesized nano-sized particles.

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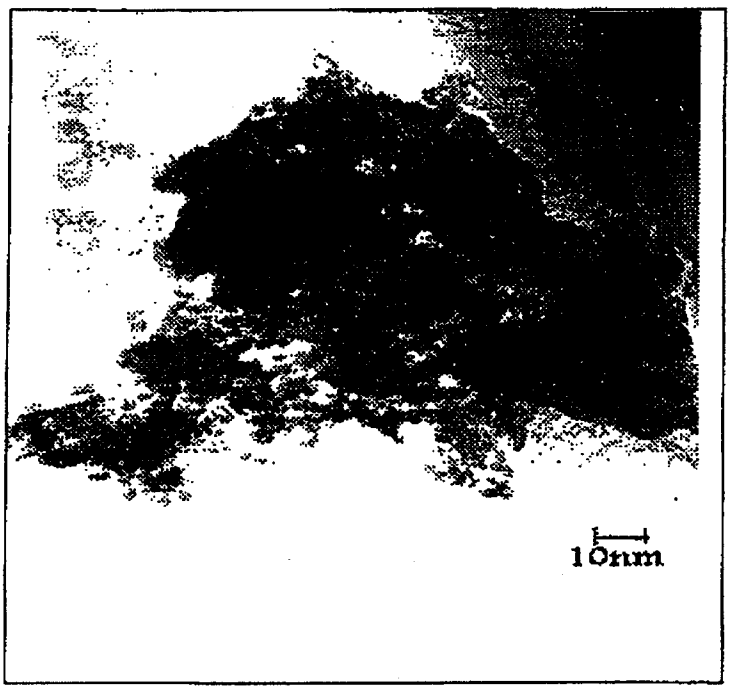


Fig. 1. TEM image of TiO_2 particles synthesized by microemulsion method.

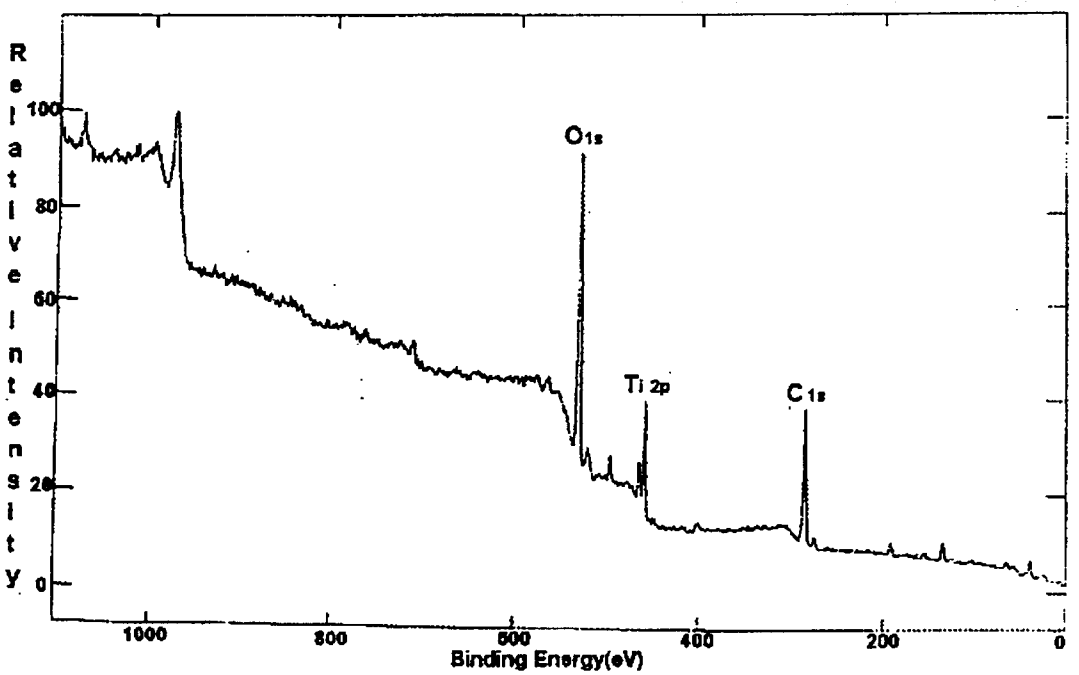


Fig. 2. Xp wide scan spectrum of TiO_2 particles synthesized by microemulsion method.

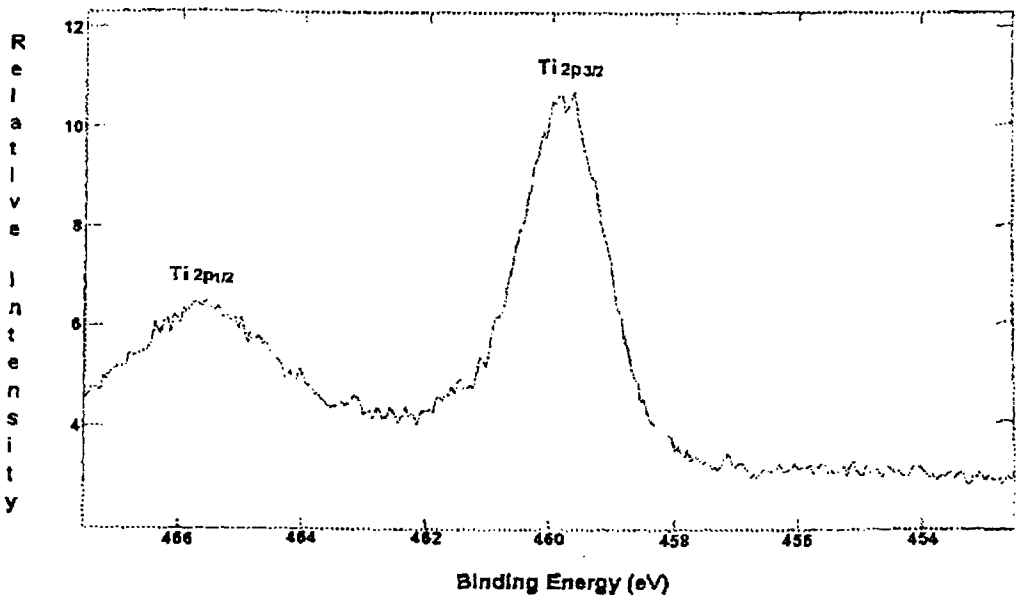


Fig. 3. Xp spectrum of Ti in TiO_2 particles

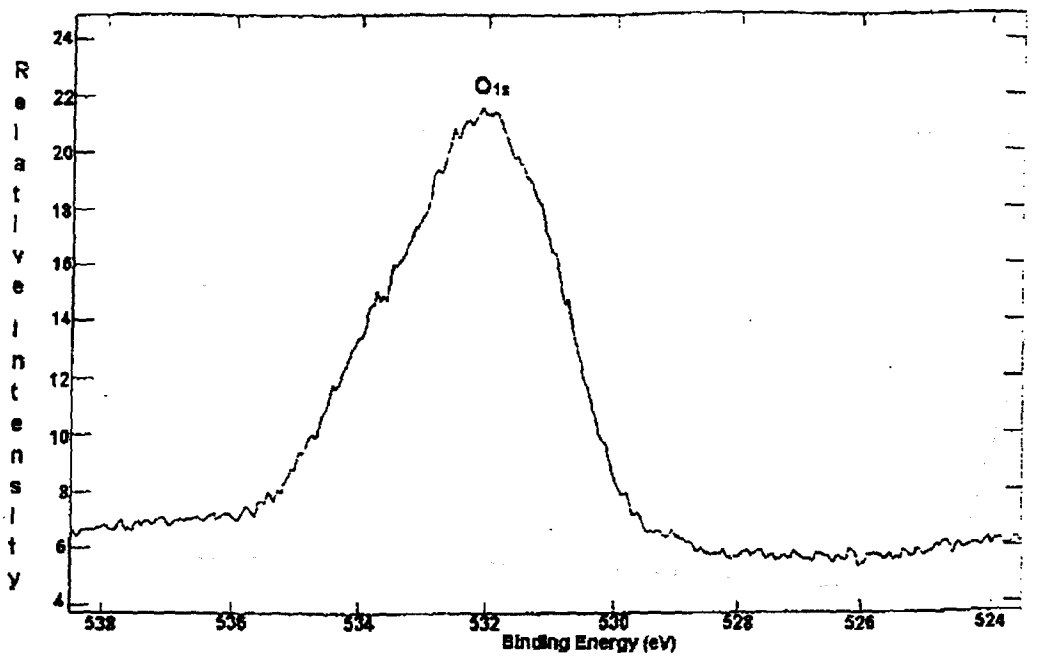


Fig. 4. Xp spectrum of Oxygen in TiO_2 particles

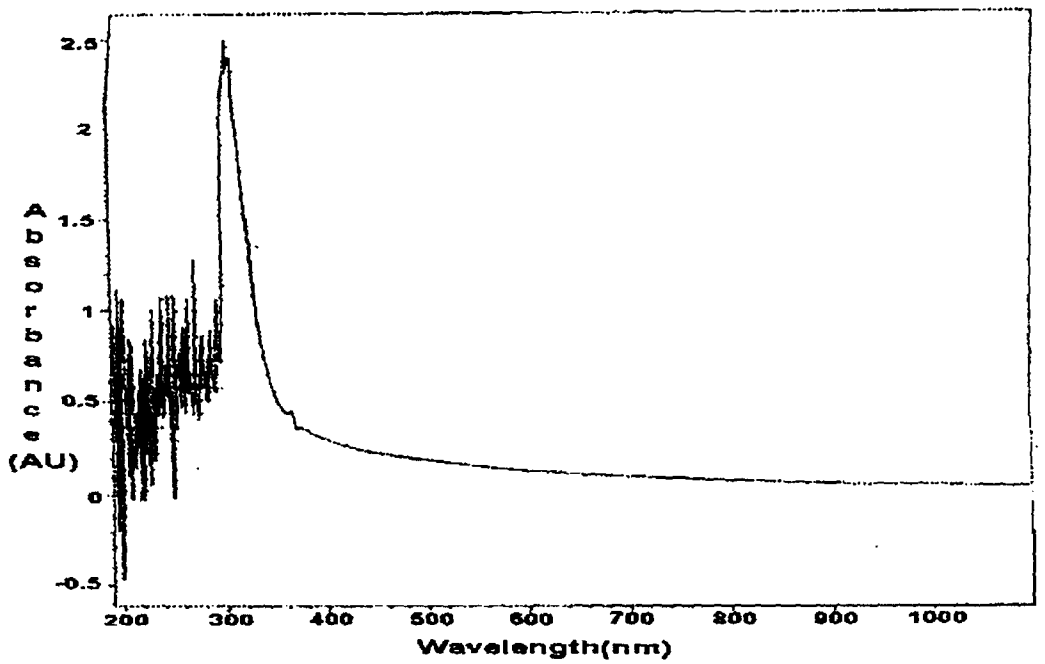


Fig. 5. Optical absorption spectrum of particles in microemulsion phase

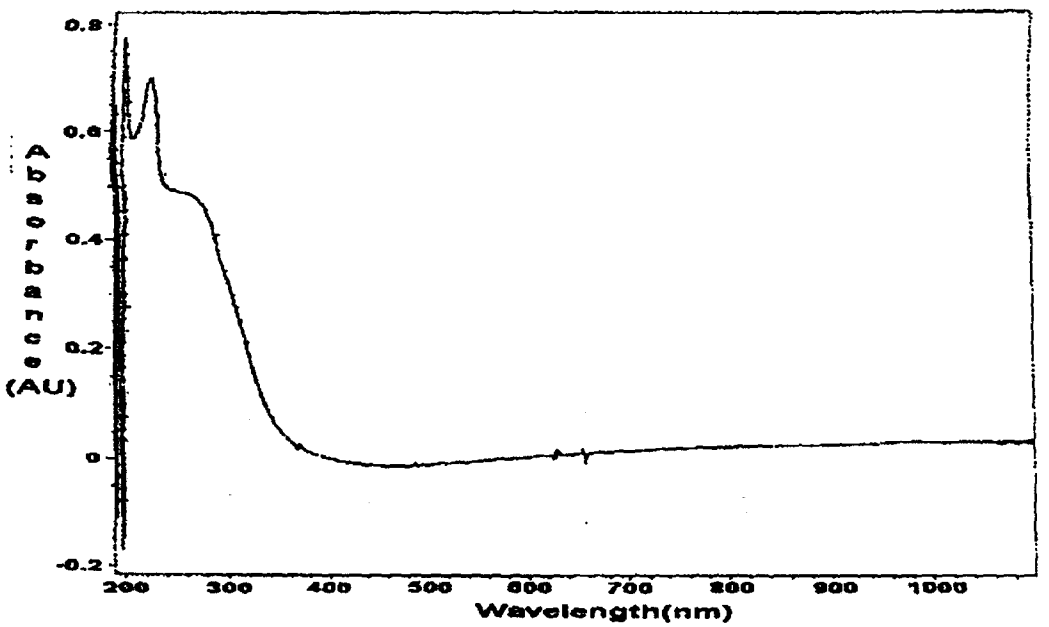


Fig. 6. Optical absorption spectrum of particles re-dispersed in PEG/Water solution.

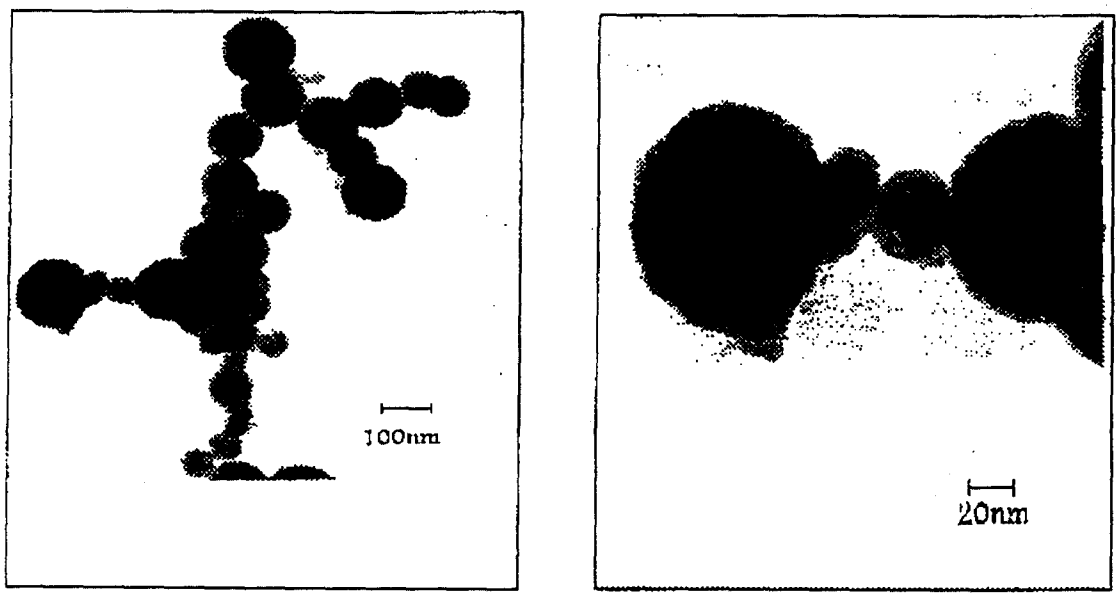
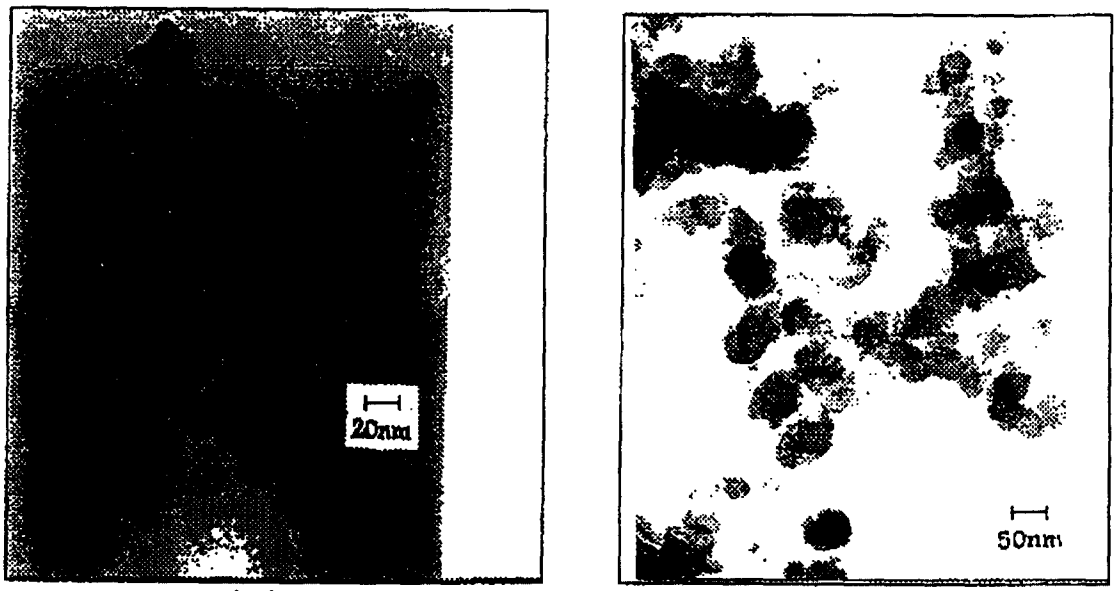


Fig. 7. The TEM image of gold-deposited particles.
The concentration of TiO_2 particles in the gold bath is 1 g/l.



(a) (b)

Fig. 8. The TEM image of gold-deposited particles.
(a) The concentration of TiO_2 particles in the gold bath is 100 g/l.
(b) The concentration of TiO_2 particles in the gold bath is 10 g/l.

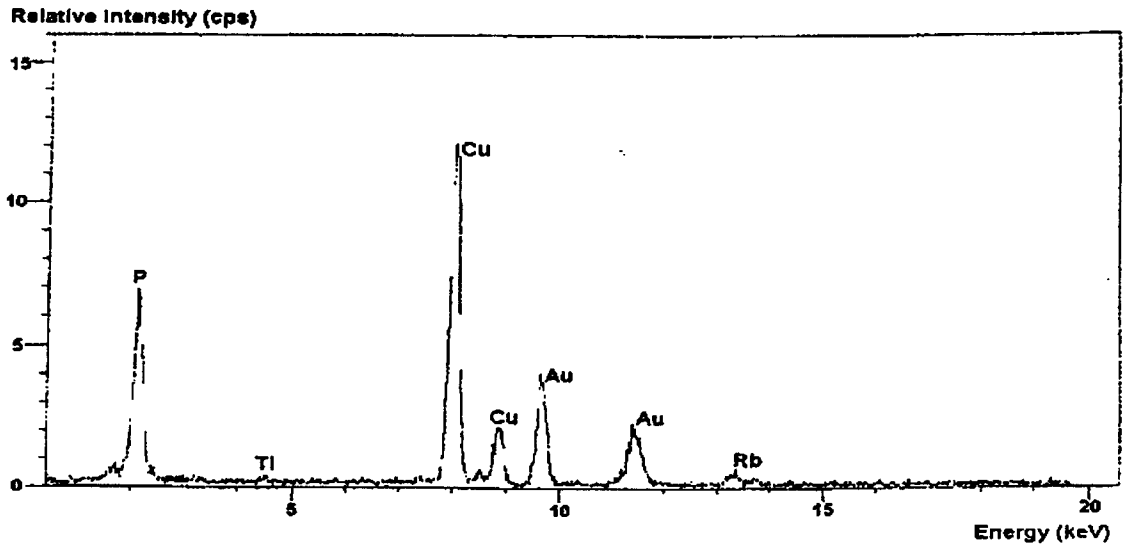


Fig. 9. EDAX spectrum of gold-rich phase in gold-deposited particles.

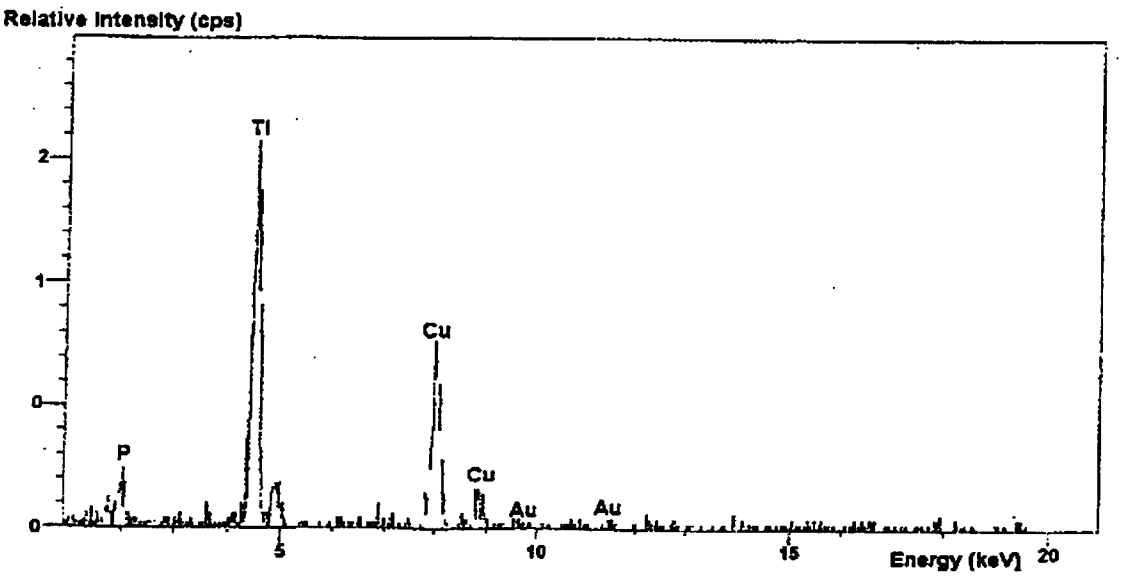


Fig. 10. EDAX Spectrum of titanium-rich phase in gold-deposited particles.

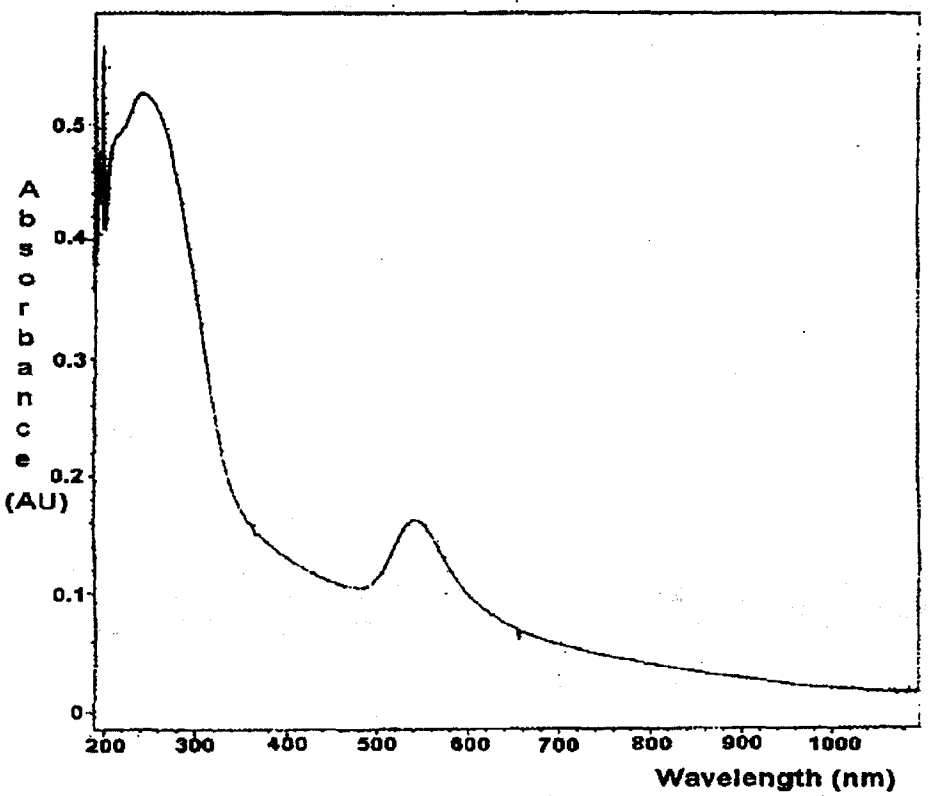


Fig. 11. Optical spectrum of gold-deposited particles.
(TiO_2 Concentration : 100 g/l)

				Sample A		Sample B	
No	SEX	AGE	The Value of MED	SPF Value of G-1	SPF Value of E-1	SPF Value of G-2	SPF Value of E-2
1	M	32	1.28	10.0	8.12	10.0	10.0
2	M	33	1.28	10.0	10.0	8.12	10.0
3	M	30	1.28	10.0	8.12	8.12	8.12
4	M	32	0.83	12.5	12.5	12.5	10.0
5	M	29	1.04	12.5	12.5	10.0	12.5
6	F	21	1.04	10.0	10.0	10.0	10.0
7	F	22	1.60	10.0	10.0	12.5	8.12
8	F	22	1.28	8.12	10.0	6.48	8.12
9	F	25	1.28	8.12	8.12	8.12	12.5
10	F	23	1.28	12.5	12.5	10.0	10.0
Mean Value			1.22	10.37	10.12	9.58	9.94

Table. 6. The SPF values measured from each samples.

(a) Before applied
(Emitted time: 1 minute)

(b) After applied
(Emitted time : 10 minutes)

Fig. 12. The SPF measurement of gel cream that formulated with commercial TiO_2 (These pictures were taken 24 hours later from emmiting UV-rays).

(a) Before applied
(Emitted time: 1 minute)

(b) After applied
(Emitted time : 10 minutes)

Fig. 13. The SPF measurement of gel cream that formulated with synthesized TiO_2 (These pictures were taken 24 hours later from emmiting UV-rays).