



## Deposition of Titania Nanoparticles on Spherical Silica

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**Abstract.** Titania coated silica nanoparticles were prepared through a sol-gel process using peptized  $\text{TiO}_2$  nanosols. The  $\text{TiO}_2$  sols were obtained by peptization, the process of redispersing a coagulated colloid, and were coated on  $\text{SiO}_2$  particles by the control of the weight ratio of  $\text{TiO}_2/\text{SiO}_2$  and the pH of the mixture in aqueous solution. At pH 4.5 the difference of zeta-potential between  $\text{SiO}_2$  and  $\text{TiO}_2$  maximized and then the  $\text{TiO}_2$ -coated  $\text{SiO}_2$  particles with highest  $\text{TiO}_2$  contents ( $\sim 20\%$ ) were obtained without the self-aggregation of  $\text{TiO}_2$  sols. The morphologies of particles were characterized with field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) and the isoelectric points (IEP) of particles were measured by zeta potential. The nature of exposed titanium ions on the surface of titania-coated silica nanoparticles was elucidated by X-ray photoelectron spectroscopy (XPS).

**Keywords:** isoelectric point (IEP), nano sol, peptization, pH, titania-coated silica

### 1. Introduction

Titania nanoparticles have many interests in various fields, such as photocatalyst, catalyst support and so on. However the use of titania when present as a high surface area has some serious drawbacks, because it is not thermally stable and decreases surface area readily. Therefore many efforts have been devoted in recent years to improve the stability of titania surface area at higher temperature.

Several procedures have been reported in the literature to coat titania on monodisperse silica spheres. In one of the procedures, Srinivansan et al. [1] added 270 nm silica spheres to a solution of titanium tert-butoxide in tetrahydrofuran under a dry nitrogen atmosphere. After the mixture was stirred for 0.25 h, the suspension was filtered under nitrogen, washed with

tetrahydrofuran, and dried in a vacuum. Only up to a monolayer of titania could be coated with this method.

In another procedure, Hsu et al. [2] worked with silica spheres of different mean diameters from 0.40 to 1.30  $\mu\text{m}$  and used a solution of titanyl sulfate in sulfuric acid as the starting material.

Hanprasopwattana et al. [3] have modified the procedure using titanium alkoxide as a precursor. In their method, an ethanol solution of titanium *n*-butoxide was refluxed after a certain amount of water was added. Recently Xing-cai Guo and Peng [4] have carried out titania coating on monodisperse silica spheres in ethanol solution with a multistep method using titanium *n*-butoxide.

In this paper we have investigated nanoparticle the titania coatings using the peptized titania sol, and studied the effect of pH change on the homogeneous coating processes under open atmosphere using only water solvent.

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## 2. Experimental

Monodisperse  $\text{SiO}_2$  nanoparticles were prepared through the procedure originally described by Stöber et al. [5].

$\text{TiO}_2$  nano-sols were prepared the peptization process. Coagulated titanium oxide was precipitated by adding titanium isopropoxide (7.38 ml) in excess distilled water under magnetic stirring, which is then filtered after 1 h.

The coagulated  $\text{TiO}_2$  particles obtained in this manner were added to an aqueous solution containing nitric acid (36 ml of  $\text{H}_2\text{O}$ ,  $x$  ml of  $\text{HNO}_3$  ( $0.10 < x < 3.85$ )). Depending on the pH, a clear white-blue solution was observed, which is indicated the resuspension of the precipitate and reduction of the particle size.

Stöber  $\text{SiO}_2$  spheres (1 g), 300 nm in diameter, were sonicated in 40 ml of water for 1 h and then mixed with a stock solution containing peptized  $\text{TiO}_2$  sol. The pH of  $\text{SiO}_2$  solution was adjusted to that of peptized  $\text{TiO}_2$  sol, leading to prevent homo-aggregation of  $\text{TiO}_2$  after mixing. The amount of peptized  $\text{TiO}_2$  sol

was varied from 1 ml to 5 ml. A fresh solution of 1 g NaOH in 100 ml water was added to the above mixture. The total volume of reaction was maintained at 100 ml. The final mixture was stirred for 3 h and then filtered. The uniformity of coating was affected by the control of the final pH and the concentration of the peptized sol.

The size and morphology of particles were determined with JEOL JEM-6340F FE-SEM. The microstructure of the  $\text{TiO}_2$  coated  $\text{SiO}_2$  was observed by JEOL EM-2000EX II TEM. Zeta-potential was measured on Malvern Instrument Zetasizer 3000. The nature of exposed titanium ions on the surface of titania-coated silica nanoparticles was elucidated by X-ray photoelectron spectroscopy (XPS).

## 3. Results and Discussion

Monodisperse spherical  $\text{SiO}_2$  nanoparticles were prepared by sol-gel process, known as Stöber method. The mean diameter of  $\text{SiO}_2$  nanoparticles is about 300 nm with an isoelectric point (IEP) of 2.57 (Fig. 1).

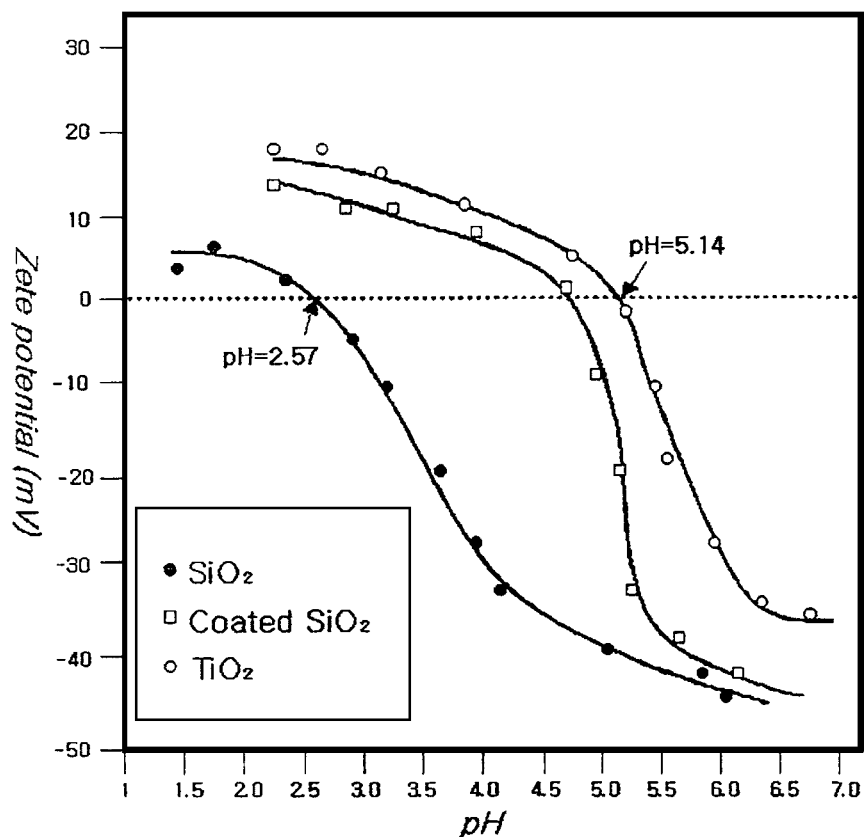


Figure 1. Variation of zeta potential with pH values for silica spheres, peptized titania, and titania-coated silica.

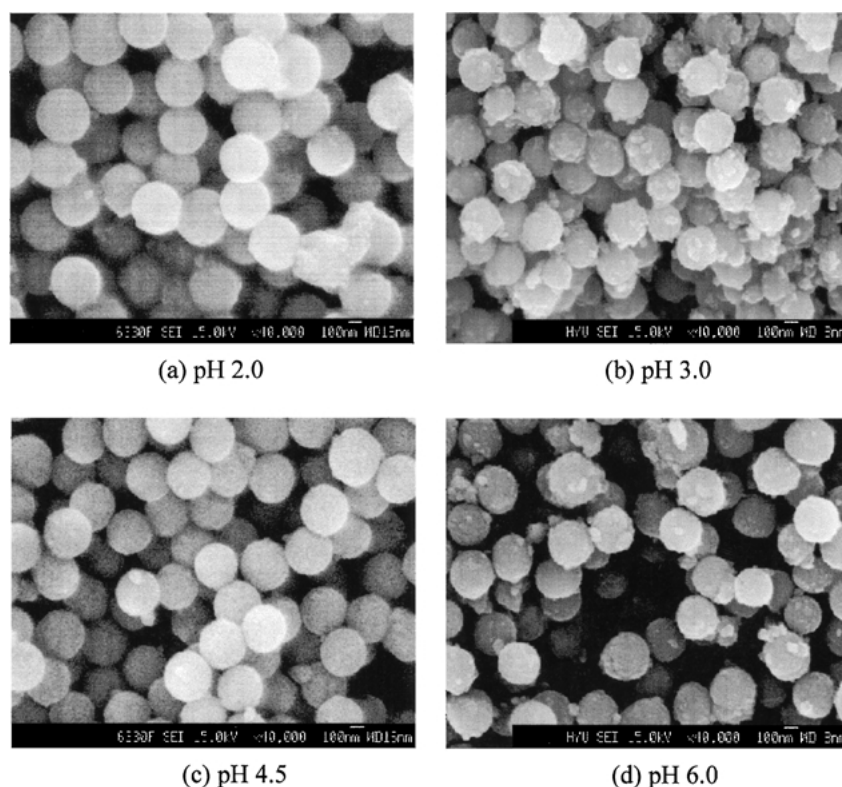


Figure 2. SEM images of the titania-coated silica with the various pH.

Figure 1 shows the variations of zeta potentials with pH values for  $\text{SiO}_2$  spheres,  $\text{TiO}_2$ -coated  $\text{SiO}_2$  spheres, and peptized  $\text{TiO}_2$  sol. The behaviors are very similar to those in the literature [2]. No additional heat treatment or drying procedure was carried out for samples prepared in this work.

In the first step peptized  $\text{TiO}_2$  sol was added to  $\text{SiO}_2$  solution that was acidified with nitric acid. The stability of peptized  $\text{TiO}_2$  sol is very sensitive to pH change, so the pH of  $\text{SiO}_2$  solution must be equalized to that of peptized  $\text{TiO}_2$  sol to prevent the homo-aggregation of  $\text{TiO}_2$ . In the second step, the pH of mixed solution was then raised by adding NaOH solution to induce the interaction between  $\text{TiO}_2$  and  $\text{SiO}_2$  spheres. The most important factors that affect the uniformity of coating are the final pH and the concentration of the  $\text{TiO}_2$  sol, therefore our attention has focused on the effect of pH value and  $\text{TiO}_2/\text{SiO}_2$  ratio in this study.

Figure 2 shows scanning electron micrographs of  $\text{TiO}_2$ -coated  $\text{SiO}_2$  at different pHs. At pH 2.0, it can be seen from micrograph that the presence of  $\text{TiO}_2$  particles could not be observed. The reason is

that the peptized  $\text{TiO}_2$  sol used here has the electrostatically stabilized region below pH 3.0 and thus the both reactant oxide particles have net positive charge at pH 2.0, resulting in preventing two particles from attracting each other. As a result  $\text{TiO}_2$  sols neither react with  $\text{SiO}_2$  surface and nor aggregate themselves.

At pH 3.0 and 6.0,  $\text{TiO}_2$  particles adsorb on the  $\text{SiO}_2$  surface but the second phase precipitates of  $\text{TiO}_2$  were also observed. As shown in Fig. 2(c), smooth and uniform coating of  $\text{TiO}_2$  on  $\text{SiO}_2$  can be achieved at pH 4.5. Furthermore no second phase precipitates of  $\text{TiO}_2$  were seen in SEM. These results can be explained through the charge difference between  $\text{TiO}_2$  and  $\text{SiO}_2$ . The charge difference is relatively small at pH 3.0 and 6.0. However, at pH 4.5, the charge difference between two reactants oxide particles maximized.  $\text{TiO}_2$  sols, thus, deposited onto silica surface uniformly and strongly.

Figure 3 shows the  $\text{TiO}_2$ -coated  $\text{SiO}_2$  prepared with various weight ratios of  $\text{TiO}_2/\text{SiO}_2$ . At weight ratio of 15%, the  $\text{TiO}_2$  was present uniformly over the sample. As shown in Fig. 3 (15%), at a low magnification, the

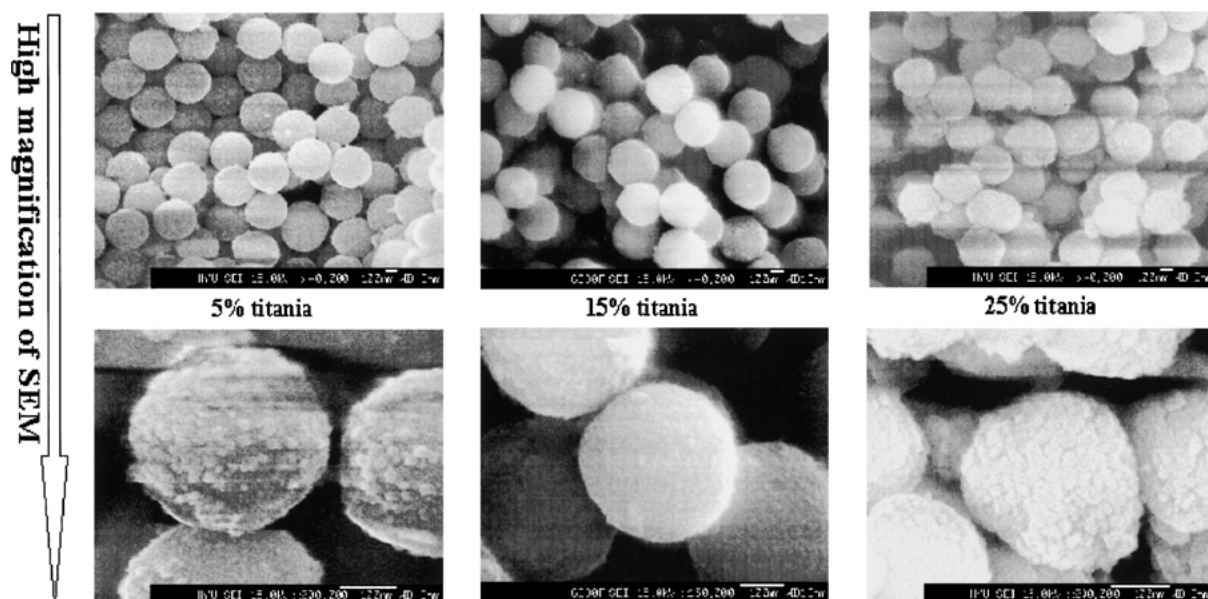


Figure 3. SEM images of the titania-coated silica prepared at various weight ratios of  $\text{TiO}_2/\text{SiO}_2$ .

$\text{TiO}_2$ -coated  $\text{SiO}_2$  spheres look very similar to the uncoated spheres suggesting that the  $\text{TiO}_2$  has uniformly adsorbed on the surface of the  $\text{SiO}_2$ .

The ‘saturation uptake’ was defined in other previous work as the amount of the  $\text{TiO}_2$  that could be deposited on  $\text{SiO}_2$  surface [3]. When the  $\text{TiO}_2$  loading is less than the saturation uptake (5%), the  $\text{TiO}_2$  is present in the form of isolated units bound to the oxide support (Fig. 3). The presence of isolated  $\text{TiO}_2$  is evident from the texturing of the  $\text{SiO}_2$  surface. But, when the  $\text{TiO}_2$  loading is increased more than saturation uptake (25%), in every instance this procedure led to necking of the spheres and formation of agglomerates. There was also a significant amount of second phase  $\text{TiO}_2$  precipitates in addition to the coated parts.

The charge of the Ti atom of titania/silica has a change due to the interface formation of  $\text{TiO}_2\text{—SiO}_2$ . The formation of interface  $\text{Ti—O—Si}$  bond, decreases the positive charge of the Ti atoms at the interface [6], resulting in the lower binding energy of the 2p-electron of Ti of  $\text{TiO}_2/\text{SiO}_2$ , which was confirmed by XPS. The binding energy of the 2p-electron of Ti of pure  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SiO}_2$  was 458.6 eV and 458.2 eV, respectively.

The photocatalytic activity of the  $\text{TiO}_2$ -coated silica prepared was investigated with a dye, Rhodamine B, after redispersing the particles sintered for 2 h in

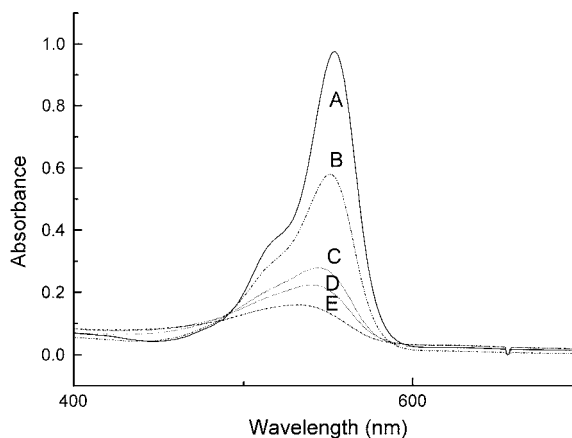


Figure 4. The absorption band of Rhodamine B measured by UV-vis spectroscopy. The test samples, containing  $1.0 \times 10^{-5}$  M of Rhodamine B, were prepared by redispersion of titania-coated silica before (A and B) and after (C: 400°C, D: 500°C, and E: 600°C) sintering for 2 h. Before measurement, all samples except for A were irradiated with UV-Hg lamp for 30 min.

given temperatures (400, 500, and 600°C). Figure 4 shows that the intensity of absorption band of Rhodamine B decreases with decomposition of the dye by  $\text{TiO}_2$ -coated  $\text{SiO}_2$  as a photocatalyst. It indicated that the particles sintered at 600°C have the highest photocatalytic activity. It was attributed to higher crystallinity

(anatase) of titania on the surface (XRD data is not shown in this paper).

#### 4. Conclusions

In this study, titania-deposited silica was prepared by using titania nano-sol. The  $\text{TiO}_2/\text{SiO}_2$  ratio and pH of the solution were two major factors on the morphology and uniformity titania coated onto silica. The optimal condition of deposition of titania onto silica surface was pH 4.5 at which was maximized the charge difference between titania and silica. The charge in the binding energy of Ti (2p) for titania-coated silica indicated that titania nano-sols are adsorbed onto silica particles by chemisorption. The photocatalytic activity of titania-coated silica was proven by the decomposition of Rodamine B. The coated silica sintered at  $600^\circ\text{C}$  exhibited the highest activity among prepared.

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#### References

1. S. Srinivansan, A.K. Datye, M. Hampden-smith, I.E. Wachs, G. Deo, J.M. Jehng, A.M. Turek, and C.H.F. Peden, *J. Catal.* **131**, 260 (1991).
2. W.P. Hsu, R. Yu, and E.J. Matijevic, *J. Colloid Interface Sci.* **156**, 56 (1993).
3. A. Hanprasopwattana, S. Srinivansan, A.G. Sault, and A.K. Datye, *Langmuir* **12**, 3173 (1996).
4. G. Xing-Cai and D. Peng, *Langmuir* **15**, 5535 (1999).
5. W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
6. J. Rubio, J.L. Oteo, M. Villegas, and P. Duran, *J. Mater. Sci.* **32**, 643 (1997).