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# Fabrication and characterization of solution processable organosilane-modified colloidal titania nanoparticles and silica-titania hybrid films

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**Colloidal titania nanoparticles were synthesized by a simple sol-gel process. The obtained nanoparticles showed high crystallinity and were of the anatase type. These crystalline colloidal titania nanoparticles were organically modified using methyl- and glycidyl-grafted silanes in order to enhance their stability and solution processability. The stabilized colloidal titania nanoparticles could be dispersed homogeneously without aggregation and converted into silica-titania hybrid films with the heterogeneous Si-O-Ti bonds by a low-temperature solution process. The fabricated silica-titania hybrid films showed high transparency (~ 90%) in the visible range, and low RMS roughness (<1 nm). Therefore, the organosilane-modified crystalline colloidal titania nanoparticles can be used in solution-processable functional coatings for electro-optical devices.**

**Key words : Titania nanoparticle, Organosilane, Silica-Titania, Hybrid.**

## Introduction

Titania has been studied in detail by several researchers because of its outstanding properties such as high refractive index, good chemical resistance, good optical properties, and good electrical properties [1-8]. These desirable properties of titania are strongly related to its crystallinity, and hence, many studies on the fabrication of high-crystalline titania by high-temperature processes such as sintering have been performed [9-11]. Such processes facilitate the production of titania powders comprising particles whose sizes are a few micrometers or larger in the solid state, which can be effectively applied to make the thick and bulky forms. However, the colloidal titania nanoparticles produced from these titania powders have poor solution processability and hence cannot be used for the formation of thin films. Complex processes such as grinding and milling for reducing the particle size, surface treatment of the particles, phase control, and dispersion control must be employed to improve the solution processability of heat-treated titania powders. For this purpose, it is necessary to develop a method for producing solution-processable colloidal titania nanoparticles with high crystallinity. Further, the process parameters affecting the dispersion stability of these colloidal nanoparticles have been also researched [12-15].

This work aims to produce colloidal titania nanoparticles with high crystallinity by a sol-gel process and also increase the solution processability and stability of the colloidal titania nanoparticles by organic grafting using organosilanes. Additionally, the organosilane-modified silica-titania hybrid films, which had high transmittance and low RMS roughness, were fabricated by using a solution-coating process.

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## Experimental procedure

### Fabrication of colloidal-titania nanoparticles by sol-gel process

Titanium (IV) isopropoxide (TTIP, Aldrich) was used as a precursor for synthesizing high-crystalline colloidal titania nanoparticles. Hydrochloric acid (HCl, 37%, Aldrich), distilled water, and isopropyl alcohol (IPA) were used as the catalyst and solvent. TTIP was mixed with IPA on a 1:1 mol ratio and dissolved after stirring for 5 min and then the distilled water containing TTIP (4 mol) was added. TTIP was hydrolyzed upon mechanical stirring of the resulting mixture for 30 min at room temperature. Subsequently, excess water (100 mol) was added to the hydrolyzed TTIP and the mixture was heated to 80 °C in a temperature-controlled oil bath. In order to obtain highly crystalline and transparent colloidal titania nanoparticles, the pH of the sol was maintained in the range of 1~2 by controlling the HCl content. Transparent colloidal titania nanoparticles were produced after reaction process at 80 °C for 2 hours.

### Fabrication of solution processable MTMS-GPTMS-modified colloidal titania nanoparticles

The surface of the colloidal titania nanoparticles was modified with methyltrimenthoxysilane (MTMS, Aldrich, 1.5 M) under magnetic stirring for 3 h at room temperature. Then, glycidoxyoxypropyltrimethoxysilane (GPTMS, Aldrich, 3.0 M) was reacted with the MTMS-treated colloidal titania nanoparticles under magnetic stirring for 3 h at room temperature. After the reaction process for producing the methyl and the glycidyl silane treated colloidal titania nanoparticles, any residual product (such as alcohol and water) was replaced with 2-ethoxy ethanol (Aldrich) at 40 °C with an evaporator. A stabilized and well-dispersed solution- processable MTMS-GPTMS-modified colloidal titania nanoparticle solution was obtained through the surface organosilane treatment and solvent exchange.

### Fabrication of silica-titania hybrid films using solution processable MTMS-GPTMS-modified colloidal titania nanoparticles

The solution processable organosilane-modified titania nanoparticle solution was filtered and spin-coated onto clean glass substrates and Si-wafers. The coated organosilane-modified silica-titania hybrid films were dried at 150 °C for 1 h and then thermally cured organosilane-modified silica-titania hybrid films were produced.

### Characterization

The crystalline phase of the fabricated titania nanoparticles was analyzed by powder X-ray diffraction (XRD, CuK, 40 kV, 30 mA, PW 3830, PAN analytical). Organosilane modification of the titania surface was confirmed by Fourier-transform infrared (FT-IR) spectroscopy (JASCO, FT-IR 460plus). The shapes, crystallinity, sizes, and dispersion states of the organosilane-modified titania nanoparticles were investigated by transmission electron microscopy (TEM, 300 kV, JEM 3010 of JEOL) observations. The Si-O-Ti bonds with Si-O-Si bonds of organosilane-modified silica-titania hybrid films were confirmed through X-ray photoelectron spectroscopy (XPS, ESCALAB 250, VG Scientifics). In addition, the optical transparency and surface morphology of the organosilane-modified silica-titania hybrid films were examined through ultraviolet-visible near-infrared (UV/Vis/NIR) spectroscopy and atomic force microscopy (AFM, SFI 3800N, SEIKO) studies, respectively.

## Results and Discussion

Fig. 1 shows the XRD patterns of the titania nanoparticles synthesized by sol-gel process. The synthesized titania nanoparticles exhibits the peaks assigned to anatase phase titania at 25.5°, 38.0°, 48.2°, 54.5° and 62.8° [16, 17] and possessed high crystallinity. This result should be emphasized because these nanoparticles were produced under very simple reaction condition which maintains at a low temperature of 80 °C for 2 hrs.

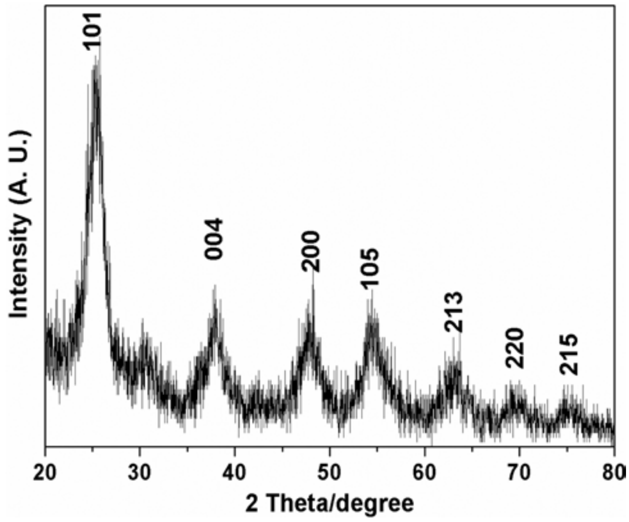


**Fig. 1.** XRD patterns of the titania nanoparticles synthesized by the sol-gel process.

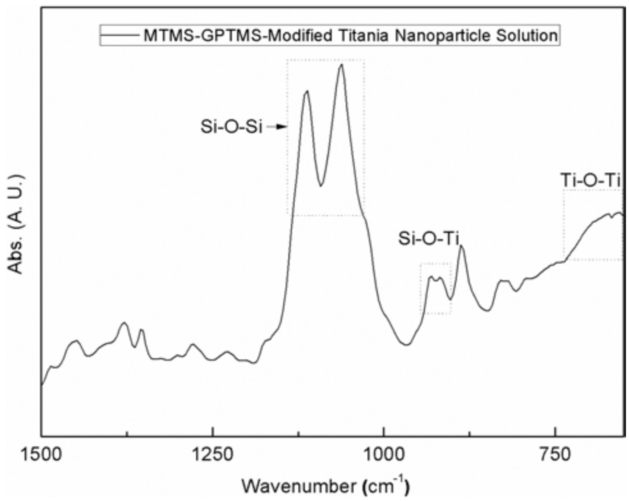


**Fig. 2.** FT-IR absorption spectra of the MTMS- and GPTMS-modified titania nanoparticle solution.

These high crystalline colloidal titania nanoparticles synthesized by the simple sol-gel process were organically modified by the MTMS and GPTMS for the solution stability and processibility.

Fig. 2 shows the FT-IR absorption spectra of MTMS-GPTMS-modified titania nanoparticle solution in the important region of 1500-650 $cm^{-1}$ in order to confirm the chemical modification of organosilanes on the surface of titania nanoparticles. The bands in the range of 1000~1110 $cm^{-1}$ represent the Si-O-Si asymmetric stretching mode, indicating that the used oganosilanes such as MTMS and GPTMS were well condensed by a sol-gel reaction. The bands below 750 $cm^{-1}$ represent the Ti-O-Ti asymmetric stretching mode [18-20]. In particular, the bands around 910~930 $cm^{-1}$ represent the Ti-O-Si bonds, indicating that the hetero-condensation of Si-O-Ti was well performed on the surface of titania nanoparticles by the modification of MTMS and GPTMS. Therefore, the FT-IR analysis confirms the

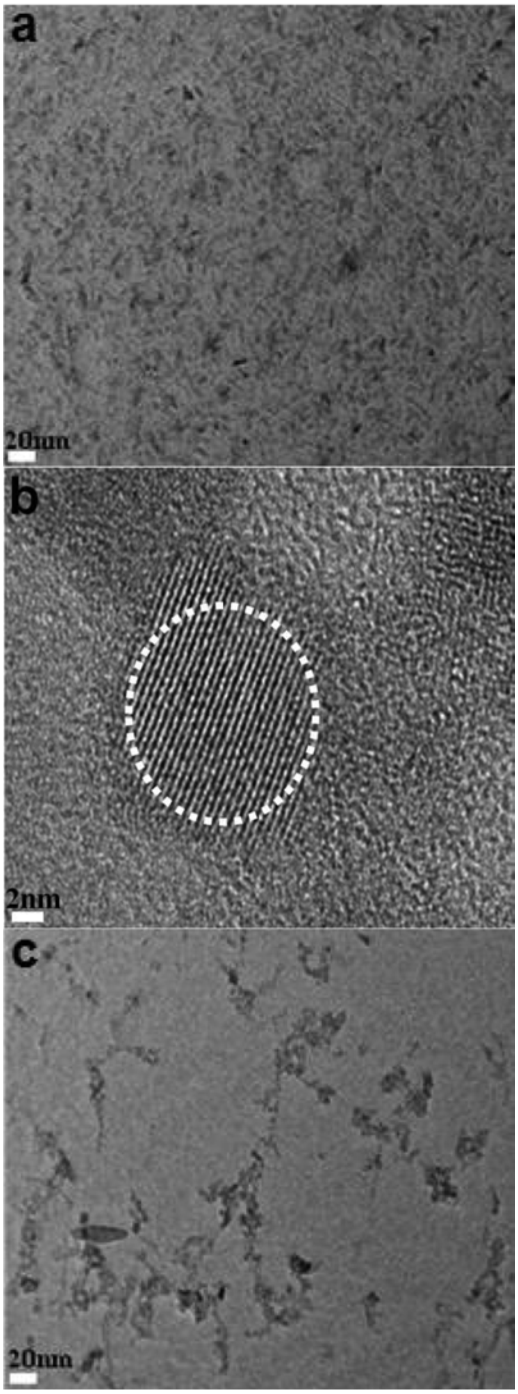


**Fig. 3.** TEM images of the titania nanoparticles with diameters of around 10 nm, indicating (a) well-dispersed organosilane-modified titania nanoparticles (scale bar: 20 nm), (b) the high crystallinity of silane-modified titania nanoparticles (scale bar: 2 nm), and (c) the agglomeration of colloidal titania nanoparticles without organosilane modification (scale bar: 20 nm).

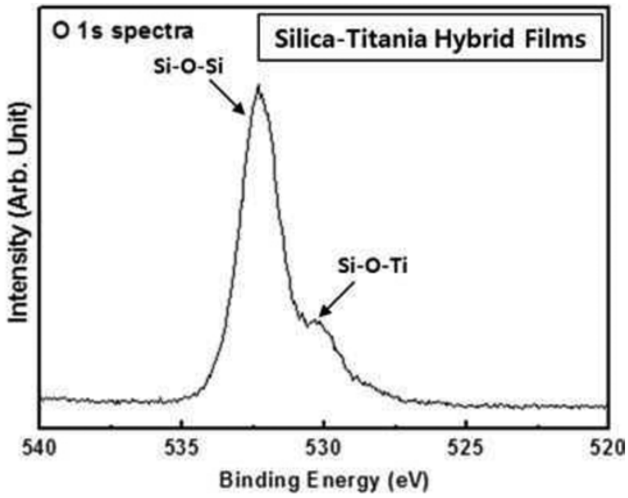


**Fig. 4.** XPS spectra of the organosilane-modified silica-titania hybrid films fabricated from the organosilane-modified titania nanoparticle solution.

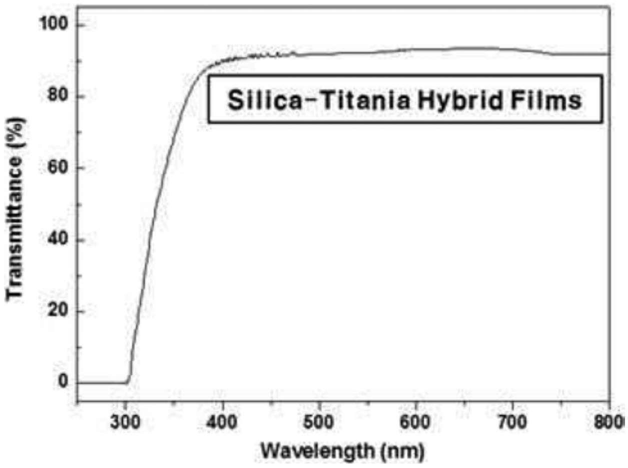


**Fig. 5.** Optical transparency of the organosilane-modified silica-titania hybrid films fabricated from the organosilane-modified titania nanoparticle solution.

fabrication of titania nanoparticles and the surface modification of organosilanes on the obtained colloidal titania nanoparticles.

TEM observation was performed in order to investigate the shapes, crystallinity, sizes and dispersion states of the fabricated silane modified colloidal titania nanoparticles. Fig. 3 shows the TEM images of the titania nanoparticles with diameter of around 10 nm. The organosilane-modified colloidal titania nanoparticles exhibited the homogeneous dispersion state, which is attributed to the good surface modification of MTMS and GPTMS, and were not agglomerated and phase-separated even upon exposure to a high-energy electron beam of 300 kV TEM accelerating voltage (Fig. 3(a)). Also, the obtained organosilane-modified colloidal titania nanoparticles exhibited the high crystallinity (Fig 3(b)), even though they were obtained by the simple sol-gel reflux method. On the other sides, colloidal titania nanoparticles without surface modification of organosilanes were not only agglomerated but also precipitated and their solution stability was low.

These colloidal titania nanoparticles, which are well-dispersed and organically modified, could be applied to form the thin films by a solution coating process. Fig. 4 shows XPS spectra of the organosilane-modified silica-titania hybrid films, indicating that the heterogeneous Si-

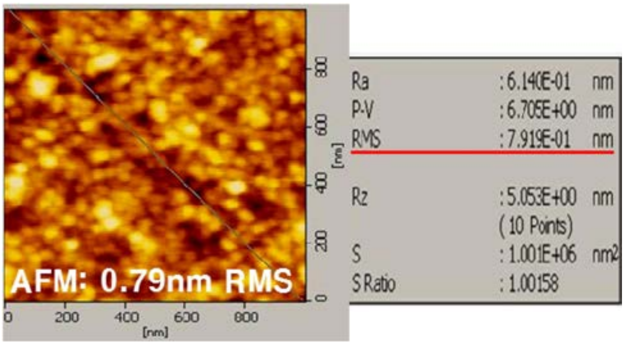


**Fig. 6.** RMS roughness of the organosilane-modified silica-titania hybrid films fabricated from the organosilane-modified titania nanoparticle solution.

O-Ti bonds with Si-O-Si bonds are formed. The 535 eV and lower 532 eV represents oxygen bonding energy with silicon and heterogeneous Si-O-Ti bonding energy, respectively [18]. It is concluded that the fabricated films showed the well heterogeneous condensation through the modification of organosilanes such as MTMS and GPTMS on the surface of titania nanoparticles.

Fig. 5 shows the optical transparency of the organosilane-modified silica-titania hybrid films fabricated from the organosilane-modified titania nanoparticle solution. The analysis was carried out with the films coated on the quartz substrate in the visible wavelength range of 400~800 nm. The silica-titania hybrid films exhibited high transparency of above 90% in the visible wavelength regions, which is highly related to the homogeneous dispersion of the fabricated titania nanoparticles by the surface modification of organosilanes without particle agglomeration. The high transparency of the organosilane-modified silica-titania films has a good advantage for optical applications.

Fig. 6 shows the RMS roughness of the organosilane-modified silica-titania hybrid films fabricated from organosilane-modified titania nanoparticle solution. The RMS roughness was measured from the AFM image. The silica-titania hybrid films showed the good surface smoothness of below 1 nm, which is very favorable for the device and functional coatings. The characteristics with good RMS roughness are thought to be attributed to the well dispersion and size control within several nanometer scales in the organosilane-modified colloidal titania nanoparticles.

## Conclusions

Colloidal titania nanoparticles were synthesized by a simple sol-gel process. The obtained nanoparticles had high crystallinity and were of the anatase type. The surfaces of the high-crystalline titania nanoparticles were successfully modified with organosilanes and the heterogeneous bonds of Si-O-Ti were confirmed by the FT-IR. TEM investigation confirms that the organosilane-treated titania nanoparticle solution showed good homogeneous dispersion as well as high crystallinity. The fabricated organosilane-modified silica-titania hybrid films exhibited the heterogeneous Si-O-Ti bonds and also possess high transparency and good RMS roughness. It can be concluded that the silica-titania hybrid films fabricated from the organosilane-treated titania nanoparticle solution have promising applications as functional coatings for electro-optical devices.

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