

## TiO<sub>2</sub> Coated Core-Shell Nanoparticles Fabricated through Sol-Gel Reaction of Titanium Precursor on Surface of Silica Core Templates

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### 1. Introduction

Fabrication of TiO<sub>2</sub> materials with high refractive index, strong oxidizing power, and long-term stability have been reported due to their potential applications such as catalysis, low dielectric constant materials, and photonic crystals [1]. Particularly, TiO<sub>2</sub> hollow capsules have been mainly investigated through various methods using soft and hard templates such as polymer latex and silica nanoparticles (NPs). However, fabrication of these materials inevitably involves the removal process of polymer latex and silica template used through calcination at high temperature and etching with toxic etchants, respectively. As a result, these processes result in the generation of chemical waste as well as serious environmental concerns. Also, these processes are required to the time-consuming and costly etching process to remove the core templates.

To overcome above mentioned problems, although studies on in situ recrystallization transformation of silica into more useful functional nanostructured silica materials such as microporous zeolites or mesoporous silicas instead of removal of the silica templates were reported in recent [2], the additional process, including hydrothermal reaction and calcination at high temperature in the removal of the organic templates used is required to fabricate these materials.

In this work, we report the fabrication of the TiO<sub>2</sub> coated core-shell NPs through sol-gel reaction of titanium(IV) butoxide as a precursor on the surface of the silica core templates. Structural properties for the TiO<sub>2</sub> coated core-shell NPs were investigated through various methods such as TEM and SEM images, powder XRD analysis, EDX elemental mapping analysis and so on. Resulting TiO<sub>2</sub> coated core-shell NPs showed a smooth surface and uniform TiO<sub>2</sub> shell layer. TiO<sub>2</sub> shell layer after the calcination processes at high temperature under air flowing exhibited the crystal structure corresponding to the anatase phase.

### 2. Methods and Results

#### 2.1 Preparation of Silica Core Templates

The silica NPs were synthesized using previous reported method, Stöber modified method. Typically, silica precursor, TEOS (tetraethyl orthosilicate, 98%) was added into mixture solution consisted of ammonium hydroxide (28 wt.%), DI water, and absolute ethanol and stirred at ambient temperature for 6 h. The core-

shell NPs with mesoporous shell as silica core templates were synthesized following the process reported in our previous work [3]. The suspended silica NPs in mother liquor were added into the surfactant solution, including CTABr (cetyltrimethylammonium bromide), ammonium hydroxide (28 wt.%), and DI water after stirring for 30 min, stirred for 1 h more, and then aged at 343 K overnight. As-synthesized samples were retrieved using centrifugation, dried at 343 K overnight, and calcined at 823 K for 5 h in air.

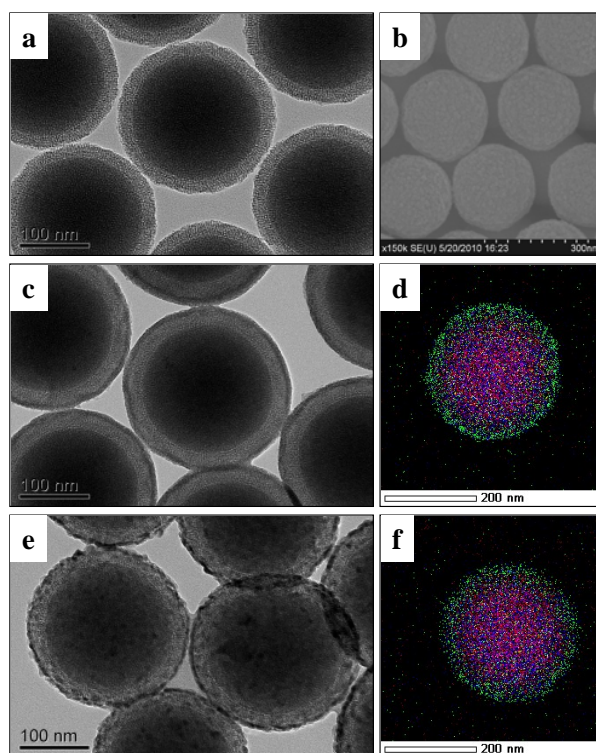


Fig. 1. (a) and (b) TEM and SEM images of core-shell silica NPs, (c) and (d) TEM image and EDX elemental mapping analysis of A-TiO<sub>2</sub> coated core-shell NPs, (e) and (f) TEM image and EDX elemental mapping analysis of C-TiO<sub>2</sub> coated core-shell NPs.

#### 2.2 Fabrication of TiO<sub>2</sub> Coated Core-Shell NPs

TiO<sub>2</sub> coated core-shell NPs were fabricated through the sol-gel reaction of titanium (IV) butoxide on the surface of the silica core templates synthesized in this work [4]. Silica core templates were dispersed in the mixture solution consisted of DI water and acetone. The TiO<sub>2</sub> precursor prepared after adding titanium (IV) butoxide in ethylene glycol and stirring at ambient

temperature for 1 h was added into the above mixture solution containing silica core templates and stirred for 3 h. As-synthesized TiO<sub>2</sub> coated core-shell NPs (denoted as A-TiO<sub>2</sub> core-shell NPs) were retrieved using centrifugation, dried at 343 K overnight, and calcined at 973 K for 5 h in air, where calcined TiO<sub>2</sub> coated core-shell NPs were denoted as C-TiO<sub>2</sub> core-shell NPs.

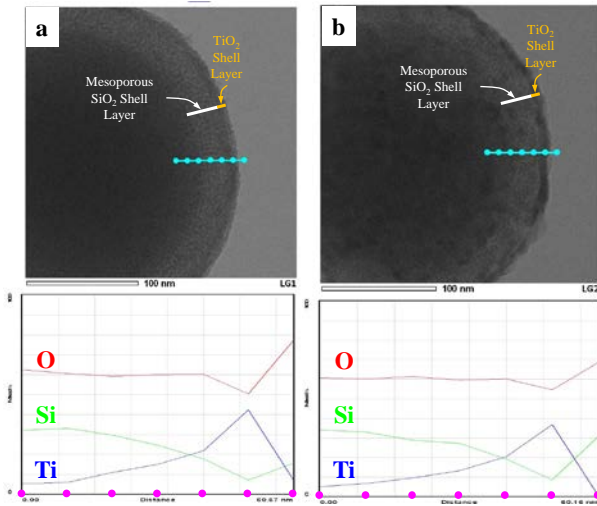


Fig. 2. Point and line analysis of (a) A-TiO<sub>2</sub> coated core-shell NPs and (b) C-TiO<sub>2</sub> coated core-shell NPs.

### 2.3 Characterization

Various analyses were performed to investigate the structural properties of the A- and C-TiO<sub>2</sub> coated core-shell NPs. Fig. 1(a) and (b) show the TEM and SEM images for the silica core templates with mesoporous silica shell synthesized to fabricate the TiO<sub>2</sub> coated core-shell NPs. Resulting materials exhibited the monodispersive particle size and uniform mesoporous shell on the surface of the silica NPs. The C-TiO<sub>2</sub> coated core-shell NPs showed slightly rough surface due to the crystallization of the TiO<sub>2</sub> shell layer. The A- and C-TiO<sub>2</sub> coated core-shell NPs from the results of the TEM images and EDX elemental mapping analysis, as shown in Fig. 1(c-d) and (e-f) were confirmed that the TiO<sub>2</sub> shell layers is well formed on the surface of the silica core templates and have the uniform shell thickness.

Point and line analysis also was investigated to confirm the TiO<sub>2</sub> shell layer formed on the surface of the silica core templates. As shown in Fig. 2, the A- and C-TiO<sub>2</sub> coated core-shell NPs, respectively exhibited the formation of the TiO<sub>2</sub> layer on the external surface of the silica core templates.

The crystal structure of the A- and C-TiO<sub>2</sub> coated core-shell NPs was investigated through a powder XRD analysis (not shown data). Resulting C-TiO<sub>2</sub> coated core-shell NPs showed an anatase phase after the calcination treatment at high temperature, but the A-TiO<sub>2</sub> coated core-shell NPs indicated an amorphous

phase. The crystal size of the C- TiO<sub>2</sub> formed on the surface of the silica core templates was ca. 5.37 nm, when calculated from the Scherrer's equation.

### 3. Conclusions

TiO<sub>2</sub> coated core-shell nanoparticles were fabricated through the sol-gel reaction of the titanium (IV) precursor on the surface of the silica core templates. The formation of the TiO<sub>2</sub> shell layer on the surface of the silica core templates was investigated through the various analyses. TiO<sub>2</sub> shell layer after the calcination treatment at high temperature exhibited the anatase phase with a crystal size of ca. 5.37 nm. Resulting TiO<sub>2</sub> coated core-shell NPs can be utilized as a photocatalyst. Also, the structural stability as well as the separation and recovery of the catalyst materials due to the presence of the silica core templates are expected to be better than hollow capsules.

### REFERENCES

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