Effect of Morphology of Titanium Dioxide Nanoparticles on Photocatalytic Activity

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Abstract. Dispersing nanoparticles into the matrix is a simple but effective method to improve properties of coating layer. Titanium dioxide (TiO₂), known for its photocatalytic activity (PCA) to degrade organic substances and to protect microbial infection, is considered to be potential candidate. However, intense light is required to achieve high PCA. Scattering layer composing of hollow TiO₂ nanoparticles, known as light harvester in solar cell devices, may be suitable for photocatalysis at lower light intensity. In this work, we studied the effect of hollow morphology to the PCA of TiO₂ nanoparticles. Hollow TiO₂ nanoparticles were successfully synthesized using hard-template-assisted sol-gel method. Transmission Electron Microscope (TEM) images show hollow TiO₂ nanoparticles possessing 125-nm hollow core and 50-nm TiO₂ shell. X-ray Diffraction (XRD) results revealed no crystalline peak for both calcined and non-calcined samples, but difference for each sample was reported by Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-DRS). UV-DRS spectrum showed the higher diffuse reflectance for both hollow TiO₂ samples than the dense counterpart, suggesting multiple light scattering and high reflection. However, energy bandgaps of amorphous and calcined hollow TiO₂ samples are higher than dense counterparts.

1. Introduction
Incorporating dispersed nanoparticles into the polymer matrix have been used to improve or to introduce new properties to coating layer. [1] Focusing on the dispersed nanoparticles possessing multifunctionalities is considered to be an interesting choice. Titanium dioxide (TiO₂) is one of widely-used additives in coatings and photocatalyst industries due to its expedient advantages e.g. low-toxicity, photoactive as well as chemical and thermal stability. [2] Extensive studies have been focused on its photocatalytic activity (PCA), such as dyes-sensitized solar cell (DSSCs), hydrogen production, self-cleaning surface, medical devices, and antimicrobial properties. [2-6] However, this property is photo-intensive. Its PCA might be limited to only environment that possesses high intensity of light. Hence, the improvement of light intensifying properties of TiO₂ is necessary.

Since the functions of coating stem from integrated components, its efficiency could be enhanced through modification of TiO₂ particles by manipulating particle size, surface chemistry, crystallinity and morphology. [7-9] With the concept of light intensification, hollow morphology is of great interest due to its unique optical properties. Hollow cavity inside the shell can perform internal multiple light scattering and reflection, which results in the enhancement of light harvesting ability comparing with their dense counterpart. In addition, the hollow particle possesses large number of active sites due to high specific surface area and short electron diffusion pathway. This high surface area to volume ratio also increases the possibility of contact between reactants and active sites. [9-13] There are reports on
the improvement of mechanical, electrical and chemical properties of hollow nanoparticles of silica (SiO$_2$), polystyrene and zinc oxide as well as their applications. [10,11]

Similarly, studies of hollow TiO$_2$ has been focused on green energy aspects. Only a few have been examined on their advantages in terms of PCA for photodegradation or antimicrobial applications. Moreover, most of the available literatures involved composite hollow particles. [12,13] Yamaguchi et al. reported the comparative studies of inactivating chemical and biological substances using hollow and solid TiO$_2$ nanoparticles. However, the representative of hollow morphologies in their work was actually an opened-hole, cup-like structure. [14] More precise understanding in structural effects could allow us to improve the photocatalytic activity characteristic of TiO$_2$.

Herein, we studied the effects of hollow structure of TiO$_2$ particles on photocatalytic activity in term of bandgap energy, with respect to dense particles. Facile sol-gel approach was employed for syntheses of hollow TiO$_2$ particles with the aid of SiO$_2$ nanoparticle template. After the formation of TiO$_2$ shell, silica core was removed using chemical etching. [15] Resulting particles were then calcined to form anatase phase. Particle size and morphology were investigated using transmission electron microscope (TEM). X-ray diffraction spectroscopy (XRD) was used for characterization of crystallinity. Finally, Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-DRS) was employed to evaluate optical properties of the samples as diffuse reflectance and bandgap. Comparison of photocatalytic activity was done according to the bandgap values.

2. Materials and Methods

2.1. Chemicals and Materials
Tetraethyl orthosilicate (TEOS, 99%, Aldrich), Titanium tetraisopropoxide (TTIP, 99%, Aldrich), Titanium tetrabutoxide (TBT, Aldrich), Methanol (MeOH, 95%, Fluka), Ethanol (EtOH, 95%, Aldrich), Ammonium hydroxide (28%, Acros) Sulfuric acid (H$_2$SO$_4$, 18 M, Aldrich), Sodium hydroxide (NaOH, 99%, Fluka) and Calcium chloride (CaCl$_2$, Fluka) were used as received. Deionized (DI) water was used throughout the work.

2.2. Preparation of SiO$_2$ Nanoparticle Template
Ammonium hydroxide, DI water and EtOH were first mixed in a round-bottom flask for 10 minutes. TEOS was slowly added into the prepared mixture and stir for 4 hours. Unreacted chemicals were removed by centrifugation. Re-disperse the resulting particles in ethanol and repeat the washing step twice.

2.3. Preparation of Hollow TiO$_2$ Nanoparticles [15]
Known weight of prepared SiO$_2$ particle was dispersed in the mixture of EtOH and DI water and refluxed at 85 °C. Prepare the solution of TBT in EtOH at volume ratio of 1:4.5 (TBT: EtOH) before slowly adding titania precursor into the refluxed solution. After 12 h, remove unreacted chemicals by centrifugation and re-disperse the resulting particles in DI water. Add NaOH solution (2.5 M) into the particle mixture and stir for 6 hours before cleaning with DI water. Dry the sample at 80 °C overnight before eliminating the remaining Na atoms on the particle surface by dispersing the prepared particles in diluted H$_2$SO$_4$ solution for 30 minutes. Centrifuge to remove undesired chemicals. Calcine dried samples at the desired temperature and time.

2.4. Preparation of Dense TiO$_2$ Nanoparticles [16]
Prepare 50 ml of MeOH in round-bottom flask. Add CaCl$_2$ solution with the desired concentration as a size regulator and stir for 10 minutes. Gradually add 850 μl TTIP. Age resulting solution for 24 hours while gently stirring and then remove the unreacted chemicals using centrifugation. Re-disperse the particles in EtOH and repeat the centrifugation twice. Dry particles at 80 °C. Calcine dried sample at the desired temperature and time.
2.5. **Characterization**

Transmission Electron Microscopy (TEM) images were investigated with TEM (Philips Tecnai 12) microscope. X-ray Diffraction (XRD) patterns of dense and hollow TiO$_2$ particles before and after calcination were obtained on XRD Rigaku Smartlab. Optical properties were measured by Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-DRS) (Shimadzu UV-2600).

3. **Results and Discussion**

Figure 1 shows TEM images of dense and hollow TiO$_2$ particles before (a, c) and after calcination (b, d), respectively. Before calcination, particle size distribution of dense TiO$_2$ particles was approx. 150 nm with relatively uniform contrast throughout particle. As-made hollow TiO$_2$ particles in Figure 1c showed well-defined hollow structure with 50-nm thick shell and approx. 150 nm hollow core. The shells were the assemblage of much smaller TiO$_2$ nanoparticles. The inner shell surrounded the hollow core was denser than the outer part. To transform the as-made amorphous TiO$_2$ to crystalline anatase structure, the samples were calcined at different temperatures (400-950 °C) and times. It was found that, regardless of morphologies, TiO$_2$ particles were severely aggregated when calcination temperatures were higher than 500 °C and longer than 5 h (data not shown). Calcination temperature at 400 °C for 3 h was then selected. After calcination, slightly shrinkage in size were observed in both calcined dense and hollow samples. The intensity contrast of calcined dense TiO$_2$ particles were less uniform. In the case of calcined hollow TiO$_2$, the hollow morphology still remained, but particle size became smaller (approx. 140 nm) with denser shell due to further condensation of titania. In addition, their particle shape and hollow core became slightly irregular.

![Figure 1](image1.png)

**Figure 1.** TEM images of dense TiO$_2$ before (a) and after (b) calcination and hollow TiO$_2$ before (c) and after (d) calcination, respectively.

Figure 2 shows the XRD patterns of dense and hollow TiO$_2$ before and after calcination at 400 °C. Compared to the reference anatase, only the diffraction pattern of calcined dense TiO$_2$ (DTC) showed peaks that corresponded to anatase phase. Diffraction pattern of the calcined hollow TiO$_2$ exhibited non-
resolved peaks, suggesting incomplete phase transformation. This might be due to the loosely assemblage of TiO$_2$ nanoparticles in the shell layer around the hollow core. However, the difference in optical properties between calcined and amorphous hollow TiO$_2$ samples was observed in UV-DRS analysis.

**Figure 2.** XRD patterns of anatase (reference) as well as dense and hollow TiO$_2$ particles before and after calcination (denoted as amorphous dense TiO$_2$ (DTA), amorphous hollow TiO$_2$ (HTA), calcined dense TiO$_2$ (DTC) and calcined hollow TiO$_2$ (HTC), respectively).

**Figure 3.** UV-DRS spectra of (a) %reflectance (%R) and (b) absorbance (Abs) of amorphous dense TiO$_2$ (DTA), amorphous hollow TiO$_2$ (HTA), calcined dense TiO$_2$ (DTC) and calcined hollow TiO$_2$ (HTC), respectively.
Optical properties were characterized by UV-DRS and the resulting spectra are illustrated in Figure 3(a-b). The diffuse reflectance results (%R) in Figure 3a were directly measured as raw data with the instrument while the results shown in Figure 3b were obtained using Kubelka-Munk function. Amorphous hollow TiO$_2$ nanoparticles exhibited higher %R and border range of wavenumber compared to dense TiO$_2$. Similar trend was also observed in calcined samples. These results suggested that the presence of hollow cavity, regardless on crystallinity, can enhance light scattering and reflection, as reflected in reflection enhancement. [14] From absorbance analysis (Figure 3b), the first wavenumber of response (cut-off wavelength) is related to the energy that particle can absorb (bandgap). Using data from Figure 3b, bandgap energies were reported in Table 1. According to the results, both calcined and non-calcined hollow TiO$_2$ started to response at higher wavenumber, indicating that they involved the higher bandgap energy with respect to dense TiO$_2$ samples. In the case of crystalline phase, the calcined samples exhibited lower bandgap energy.

Table 1. Cut-off wavelengths ($\lambda_{\text{cut off}}$) and calculated bandgaps at $\lambda_{\text{cut off}}$ of dense and hollow TiO$_2$ particles before and after calcination.

| Sample | $\lambda_{\text{cut off}}$ (nm) | Bandgap (eV) |
|--------|---------------------------------|--------------|
| DTA    | 352                             | 3.53         |
| DTC    | 370                             | 3.36         |
| HTA    | 333                             | 3.73         |
| HTC    | 347                             | 3.58         |

From Table 1, both hollow TiO$_2$ samples possessed higher bandgap energy compared with dense TiO$_2$ counterparts. Note that the bandgap energy of calcined dense TiO$_2$ sample is close to those reported generally in bulk anatase TiO$_2$ (3.2 eV). [2-6, 17] While the bandgap of hollow TiO$_2$ became smaller after thermal treatment, implying that there was partial polymorph transition. Based on absorbance spectra and calculated band gap energy, it could be said that in term of PCA, dense TiO$_2$ samples required lower energy to activate the photocatalysis. This made them response to lower energy spectrum of light, which provide good trait for PCA. However, as mention earlier, the concept of multiple light scattering and reflection was proved by the reflectance spectra, consistence with studies in the field of DSSC applications. [12] Moreover, the results reported by Yamaguchi and co-workers also support that PCA can be enhanced through multiple light scattering. [14]

To further confirm the effect of morphology on PCA, photodegradation test was performed by coating a thin layer of palmitic acid (organic model) on TiO$_2$ particle-incorporated polyurethane films prior to UV irradiation at 365 nm for 10 h. FTIR spectra of coated films before and after irradiation are presented in Figure 4(a-b). Before irradiation, intensities of peaks attributed to C-H stretching vibration at 2828-2916 cm$^{-1}$ and C=O stretching vibration at around 1700 cm$^{-1}$ of palmitic acid were sharp and strong. After irradiation, intensities of these characteristic peaks at 2828-2916 and 1700 cm$^{-1}$ became lower, which indicated the photodegradation of palmitic acid on the surface of both TiO$_2$ particle-incorporated polyurethane films upon UV irradiation. Higher reduction of C-H and C=O vibrations was observed in the irradiated polyurethane films incorporated with crystalline dense TiO$_2$, which could be attributed to crystallinity-dependent PCA. [17] Despite being amorphous, FTIR spectra of hollow TiO$_2$ particle-incorporated polyurethane film (Figure 4b) also showed significant depletion of C-H and C=O stretching of palmitic acid. This result supported the UV-DRS analysis and suggested that hollow structure took part in the enhancement of light scattering and hence photodegradation of palmitic acid.
Figure 4. FTIR spectra of palmitic acid-coated polyurethane films incorporated with (a) crystalline dense and (b) hollow TiO$_2$ particles before and after UV irradiation at 365 nm for 10 h.

4. Conclusions
Dense and hollow TiO$_2$ particles were successfully synthesized using sol-gel method. After calcined at 400 °C for 3 h, particle shapes of both dense and hollow TiO$_2$ particles remained but their particle sizes became smaller. Although there was no crystalline peak observed in the XRD patterns, %R of calcined hollow TiO$_2$ particles was higher than that of non-calcined hollow TiO$_2$. All hollow TiO$_2$ exhibited higher reflectance than dense counterparts, indicating that hollow cavity can enhance the light scattering. However, band gap energy of all hollow TiO$_2$ was slightly higher than dense samples. Photodegradation results indicated the degradation of palmitic acid on the surface of amorphous hollow TiO$_2$-incorporated polyurethane films.

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