



## Preparation and photocatalytic activity under visible light irradiation of mesostructured titania particles modified with phthalocyanine in the pores

Hirobumi Shibata<sup>a,\*</sup>, Shin-ichi Ohshika<sup>b</sup>, Taku Ogura<sup>c</sup>, Satoshi Watanabe<sup>b</sup>, Keishi Nishio<sup>b,d</sup>, Hideki Sakai<sup>c,d</sup>, Masahiko Abe<sup>c,d</sup>, Kazuaki Hashimoto<sup>a</sup>, Mutsuyoshi Matsumoto<sup>b,d</sup>

<sup>a</sup> Department of Life and Environmental Sciences, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan

<sup>b</sup> Department of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

<sup>c</sup> Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

<sup>d</sup> Research Institute for Science and Technology, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

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### ABSTRACT

Mesostructured titania particles modified with phthalocyanine (Pc) were prepared by using molecular self-assemblies of cetyltrimethylammonium bromide (CTAB) with solubilized Pc as a template. Low-angle X-ray diffraction pattern and transmission electron microscopy (TEM) image clearly show the formation of Pc/titania particles with hexagonal mesopore structures. Diffuse reflectance UV–vis spectrum and fluorescence spectrum of Pc/titania indicate that Pc molecules in the pores are in a monomeric state. In addition, Pc/titania particles have photocatalytic activity under visible light irradiation (>610 nm) due to the reduction reaction by the electrons transferred from Pc to titania.

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### 1. Introduction

Titania (TiO<sub>2</sub>) is well known as an n-type semiconductor applied for the photocatalyst to remove toxic organic compounds and for the electrode of the solar cell due to holes and electrons generated by UV irradiation [1–6]. Titania can work only when it is excited by the irradiation of UV light with energy higher than the band gap energy. The introduction of transition-metal ions into titania [7] or doping titania with nitrogen [8–10] or sulfur atoms [11–13] has been investigated to synthesize visible light responsive titania. We recently succeeded in the fabrication of visible light responsive titania through sol–gel processes using cationic surfactants having nitrogen atoms and titania precursors having sulfur atoms [14]. To use titania as the electrode of a solar cell, the surface of the titania is modified with dye which can act as a visible light absorber. Electric energy can be produced by the transfer of the electron from the dye to the titania electrode [4–6]. In recent years, it was reported that when titania particles in aqueous dispersion containing dyes were irradiated with visible light, the dyes were reduced and decomposed by the electrons transferred from the sensitizers located in the pores of the titania particles [15–18]. This suggests that novel

photocatalysts can be prepared using the working principle of dye-sensitized solar cells. The fabrication and photocatalytic activity of titania whose surface is modified with dyes have been investigated [19–21]. The problem is the photolysis of the dye that acts as a visible light absorber by the reduction reaction.

Mesoporous materials [22–27] synthesized using molecular self-assemblies of amphiphilic molecules are applicable to catalysts, separatory materials and adsorbents due to their high surface area, uniform pore size and highly ordered pore structure. To use mesoporous materials as catalysts and catalyst supports, silica [23,24], titania [28,29] and zirconia [30,31] have been used as the frameworks of the mesoporous materials. In particular, mesoporous titania has gathered considerable attention because it works as photocatalyst with high adsorbability and photocatalytic activity. Mesostructured titania containing dyes in the pores shown in Fig. 1 will be a novel visible light responsive photocatalyst with photocatalytic activity due to the photo-induced reduction reaction by the electrons transferred from the dyes to the titania. This reaction scheme promises that the photo-induced decomposition of the reaction substrates occurs only at the outer surfaces of the mesostructured titania particles and that the dye used as a visible light absorber situated in the pores will not be decomposed. However, uniform introduction of dyes into the pores is difficult after the formation of the frameworks of mesoporous titania due to the low dispersibility of the dyes in the pores. In this study, we prepared mesostructured titania particles modified with dye in the

\* Corresponding author. Tel.: +81 47 478 0410; fax: +81 47 478 0410.  
E-mail address: [hirobumi.shibata@it-chiba.ac.jp](mailto:hirobumi.shibata@it-chiba.ac.jp) (H. Shibata).

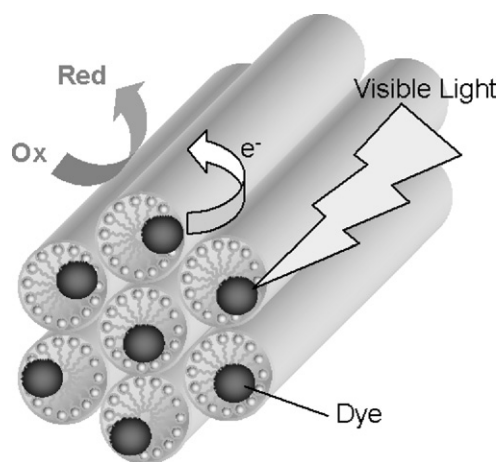


Fig. 1. Schematic illustration of the mesostructured titania with dye in the pores.

pores by using molecular self-assemblies of surfactants containing dye and investigated its photocatalytic activity under visible light irradiation.

## 2. Experimental

### 2.1. Materials

Titanium oxysulfate sulfuric acid hydrate ( $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ ; Aldrich) and cetyltrimethylammonium bromide (CTAB; Aldrich) were used as a titania precursor and a template material for mesopore formation, respectively. Phthalocyanine (Pc; Tokyo Chemical Industry Co. Ltd.) shown in Fig. 2 was used for the modification in the pores. Methyl orange (MO; Aldrich) was used as a reaction substrate to investigate the photocatalytic activity. We chose this dye because the absorption band of MO is different from that of Pc.

### 2.2. Preparation of mesostructured titania particles modified with phthalocyanine

Pc-modified mesostructured titania particles (Pc/titania) were obtained according to the following way:  $1.0 \times 10^{-2}$  mmol of Pc was added to 25 ml of 60 mM CTAB aqueous solution and stirred at room temperature for 24 h. The obtained Pc/CTAB aqueous solution and 25 ml of 720 mM  $\text{TiOSO}_4$  aqueous solution were mixed and stirred at room temperature for 24 h. Then, the obtained particles were filtrated, washed with pure water and dried at 393 K for 10 h (Pc/titania). As a control, we also prepared mesostructured titania particles as described above in the absence of Pc. The mesostructural properties of the obtained particles were investigated using X-ray diffraction (XRD; Philips, X'pert-MPD Cu  $K\alpha$  radiation) measurements and transmission electron microscope (TEM; Hitachi model H-7650; W filament) observations.

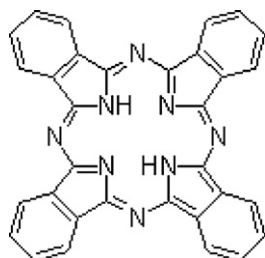


Fig. 2. Molecular structure of phthalocyanine (Pc).

To investigate the adsorption state of Pc, diffuse reflectance UV–vis spectroscopic measurements (JASCO, V-650) and fluorescence spectroscopic measurement at the excitation wavelength of 660 nm (HITACHI, F-4500) were carried out. In addition, we investigated the photoabsorption properties of Pc/CTAB aqueous solution and Pc ethanol solution using UV–vis absorption spectroscopic measurements (SHIMADZU, UV-2450).

### 2.3. Evaluation of photocatalytic activity under visible light irradiation of the obtained Pc/titania particles

0.2 g of Pc/titania particles or mesostructured titania particles were added to 40 ml of  $3.0 \times 10^{-2}$  mM MO aqueous solution and stirred at room temperature for 15 min in the dark. Then, the particles were filtrated and dried at 373 K for 1 h. The samples for the investigation of photocatalytic activity were obtained by mixing 0.1 g of the dried particles with 1.0 g of KBr. The samples were irradiated with visible light ( $>610$  nm) obtained by passing the light from a xenon lamp (TOKINA, Super Bright 152S) through a light cutting filter. To investigate the photocatalytic activity, the decoloration of MO with light irradiation was monitored by diffuse reflectance UV–vis spectroscopic measurements. The spectra were obtained after visible light irradiation for 24, 48, 72, 96, and 120 h.

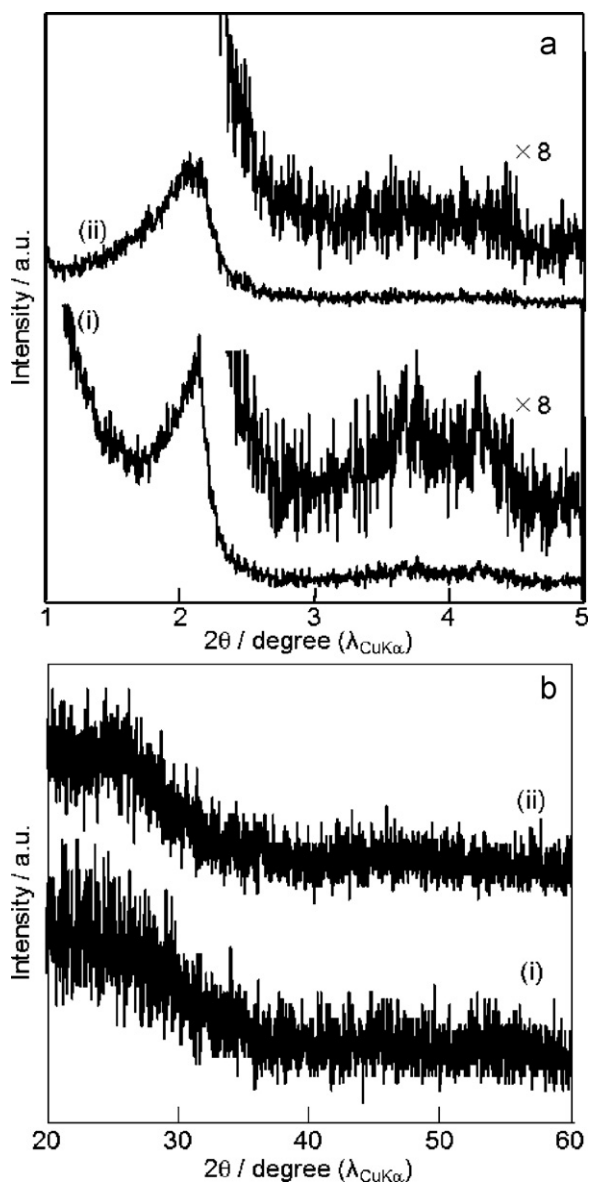
## 3. Results and discussion

### 3.1. Synthesis and structural properties of the Pc/titania particles

Fig. 3a shows the low-angle XRD patterns of the Pc/titania and mesostructured titania particles. The low-angle XRD pattern of the mesostructured titania particles shows three diffraction peaks at around  $2.1$ ,  $3.7$  and  $4.2^\circ$  due to the (100), (110) and (200) reflections, respectively, indicating the formation of highly ordered mesostructures. Our previous reports clearly demonstrate that the mesostructured titania particles form highly ordered hexagonal mesostructures [14,28,29]. The three diffraction peaks assigned to hexagonal structures are also present at the same positions in the low-angle XRD pattern of Pc/titania particles. The interplanar spacing calculated using Bragg's equation on the basis of the (100) reflection is about 4 nm. This distance almost coincides with that of mesoporous titania having hexagonal structures [14,28,29]. The diffraction peak assigned to the (100) reflection is broadened in the presence of Pc probably because of the increased breadth of the micelle size distribution caused by the incorporation of Pc. The wide-angle XRD patterns exhibit no peaks assigned to titania crystal irrespective of the presence or absence of Pc (Fig. 3b). These results indicate that the titania framework is amorphous.

Fig. 4 shows a typical TEM image of the obtained Pc/titania particles. This TEM image reveals that the Pc/titania particles have highly ordered mesopore structures. The periodic distance of the pores estimated from the TEM image coincides with the value of about 4 nm calculated from the low-angle XRD pattern shown in Fig. 3. These results indicate that the molecular self-assemblies of CTAB can act as the template even in the presence of Pc and that Pc/titania particles synthesized using a Pc/CTAB mixed template system as well as mesostructured titania particles form highly ordered hexagonal mesostructures.

Next, we carried out the visual observations of the solutions and UV–vis absorption spectroscopic measurements to investigate the location of Pc molecules adsorbed in Pc/titania particles. Fig. 5 shows the photographs of the Pc/CTAB solutions (a) as-synthesized and (b) mixed with  $\text{TiOSO}_4$  aqueous solution after stirring at room temperature for 24 h. The as-synthesized Pc/CTAB solution is uniformly blue (Fig. 5a), whereas the Pc/CTAB solution mixed with  $\text{TiOSO}_4$  is colorless and transparent (Fig. 5b). Fig. 6 shows the UV–vis

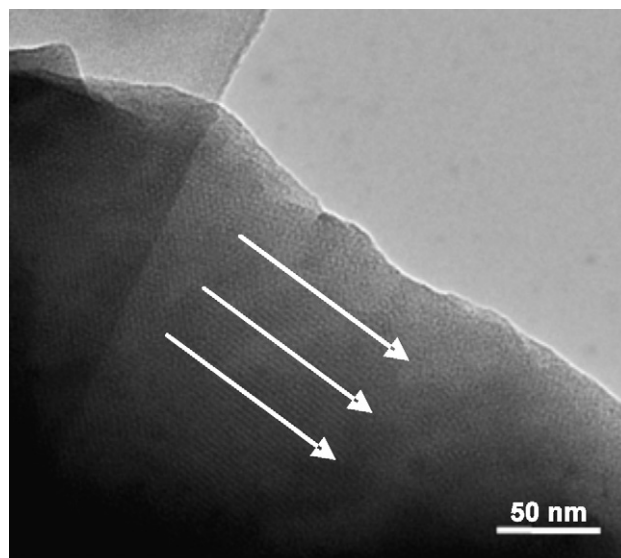


**Fig. 3.** (a) Low- and (b) wide-angle XRD patterns of (i) mesostructured titania particles synthesized without Pc and (ii) Pc/titania particles.

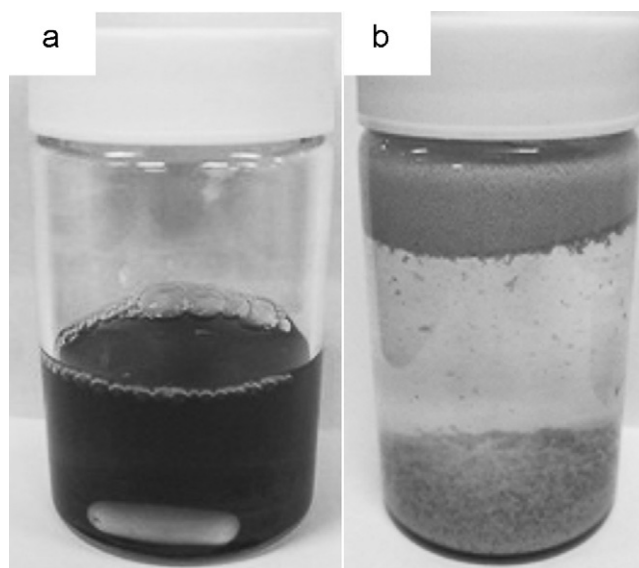
absorption spectra of the filtrate obtained from Pc/CTAB solution mixed with  $\text{TiOSO}_4$  and Pc ethanol solution. The absorption bands assignable to Pc molecules are present at around 340, 380, 600 and 700 nm in the UV–vis spectrum of Pc ethanol solution. On the other hand, the UV–vis spectrum of the filtrate shows an absorption threshold due to titania at around 400 nm and no peaks assignable to Pc. This result indicates that Pc is absent in the filtrate. The solubility of Pc in water is extremely low. However, Pc is solubilized by CTAB molecules used as templates. This strongly suggests that Pc molecules are located in the pores of the mesostructured titania particles. These results show that the obtained Pc/titania particles are mesostructured titania particles modified with Pc molecules in the pores.

### 3.2. Adsorption state of Pc in the pores of mesostructured titania particles

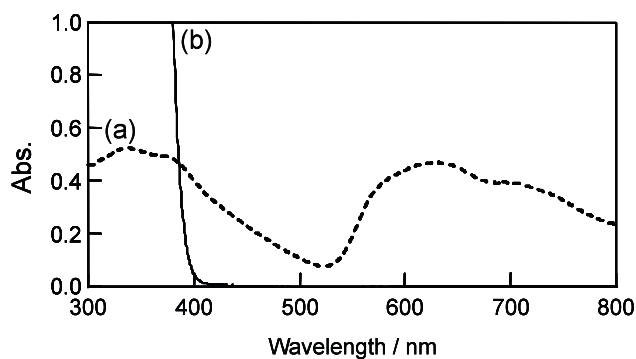
Diffuse reflectance UV–vis spectroscopic measurements of the PC/titania particles were carried out to investigate the adsorption state of Pc molecules in detail. UV–vis spectra of the Pc/titania



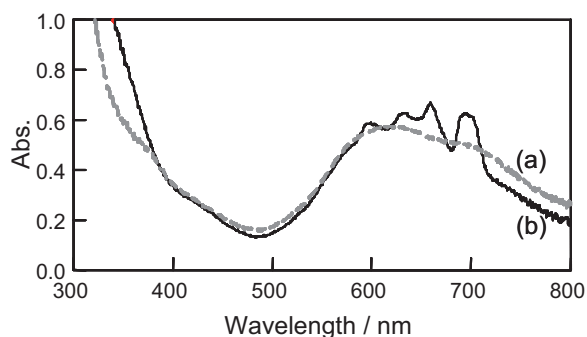
**Fig. 4.** Typical TEM image of Pc/titania particles.



**Fig. 5.** Photographs of the Pc/CTAB solutions (a) as-synthesized and (b) mixed with  $\text{TiOSO}_4$  aqueous solution after stirring at room temperature for 24 h.



**Fig. 6.** UV–vis absorption spectra of (a) Pc ethanol solution (broken line) and (b) filtrate after the formation of mesostructured titania particles (solid line).



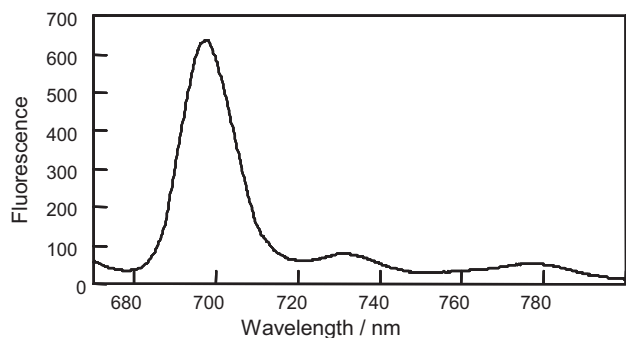
**Fig. 7.** Diffuse reflectance UV-vis spectra of (a) solid-state Pc (gray broken line) and (b) Pc/titania particles (black solid line).

particles and the Pc powder are shown in Fig. 7. The spectrum of Pc has two broad absorption bands at around 600 and 700 nm. The broad band at 700 nm is due to the aggregation of Pc. Four absorption bands are present at around 600, 640, 680 and 700 nm in the spectrum of Pc/titania particles. The bands at around 680 and 700 nm originate from Q-band of the monomeric Pc [32–34]. The splitting in the Q-band region reflects the unsymmetric nature of Pc moiety, due to the fact that Pc is located in the pores and/or the fact that Pc is buried in the molecular self-assemblies of CTAB. Two vibrational satellites of the monomeric species are present at 600 and 640 nm [32].

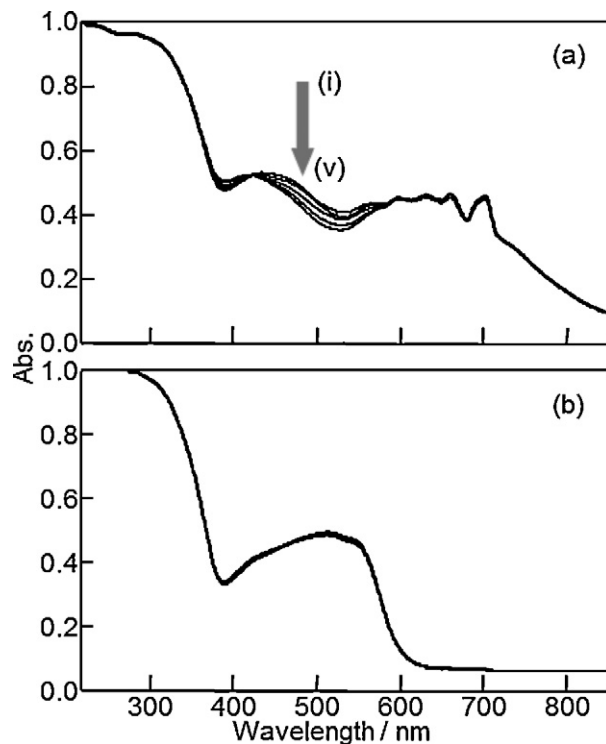
The fluorescence spectrum of Pc/titania particles is shown in Fig. 8. An intense fluorescence band at 700 nm and weak bands at 730 and 780 nm are present. The intense band corresponds to the excitation to the first excited electronic level of Pc. The other bands are interpreted as vibrational levels characteristic of the molecular ground state. This fluorescence spectrum is the same as that of a typical monomeric Pc molecule [35–37]. These results clearly demonstrate that Pc molecules are adsorbed in the pores as a monomeric state.

### 3.3. Photocatalytic properties of Pc/titania particles

Finally, the photocatalytic activity of the obtained Pc/titania particles under visible light irradiation was investigated. Fig. 9a shows a change in diffuse reflectance UV-vis spectrum of MO-adsorbed Pc/titania particles with the irradiation time up to 96 h. The absorption band of MO (400–600 nm) and those of Pc (600–700 nm) are evident. The absorption of MO decreases with increasing irradiation time whereas the absorption of Pc remains unchanged. Fig. 9b shows a change in diffuse reflectance UV-vis spectrum of MO-adsorbed mesostructured titania particles during the irradiation. It is clear that the irradiation does not cause any significant change in the absorption of MO in MO-adsorbed mesostructured titania



**Fig. 8.** Fluorescence spectrum of Pc/titania particles. The excitation wavelength is 660 nm.



**Fig. 9.** Changes in diffuse reflectance UV-vis spectra of (a) Pc/titania and (b) mesostructured titania particles under visible light irradiation (>610 nm). The irradiation times were (i) 0 h, (ii) 24 h, (iii) 48 h, (iv) 72 h, and (v) 96 h.

particles. This indicates the absence of the photolysis of MO by the electrons transferred from MO to titania during the visible light irradiation. This means that the decrease of absorption of MO shown in Fig. 9a is due to the reduction reaction by the electrons transferred from Pc to titania. In addition, the fact that the absorption of Pc remains unchanged clearly demonstrates that Pc is not decomposed by the reduction, suggesting that the photolysis of CTAB occurs prior to that of Pc and that CTAB works as a photo-protective material. These results show that mesostructured titania modified with Pc in the pores is a novel visible light responsive photocatalyst which allows for the selective photolysis of MO by the electrons transferred from Pc.

## 4. Conclusion

In this study, mesostructured titania particles modified with Pc in the pores (Pc/titania) were prepared and the photocatalytic activity was investigated under visible light irradiation. We succeeded in the synthesis of Pc/titania particles using molecular self-assemblies of CTAB containing Pc. Pc molecules in the pores were in a monomeric state. The obtained Pc/titania particles served as a photocatalyst that decomposed methyl orange under visible light irradiation. In addition, Pc which acted as a visible light absorber was not decomposed by this reduction reaction. This is the first paper on the novel dye-sensitized photocatalyst endowed with the ability of the photosensitization and the charge separation. This material can be also applied to the electrode of a dye-sensitized solar cell. The method and concept for this material design will be important in the synthesis of photo-functional materials.

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