

学位請求論文 (Dissertation)

題名 (Title) Surface Modification of TiO₂ Nanoparticles in Supercritical Carbon Dioxide

(邦訳) 超臨界CO₂中での二酸化チタンナノ粒子の表面修飾

専攻 (Division) : Natural System

学籍番号 (Student ID Number) : 1824062006

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ABSTRACT

The surface of TiO₂ nanoparticles needs to be modified to prevent the agglomerations process and ensure they have perfect dispersion in the applied system. This thesis presents a supercritical CO₂ strategy for surface modification of TiO₂ nanoparticles with dicarboxylic acids. To obtain an optimum modification rate, process conditions were examined by changing the process pressure, temperature, and weight ratio of the modifier. A Box-Behnken experimental design and a statistical method of response surface methodology was carried out to determine optimum process conditions. The modified TiO₂ was characterized by FTIR, TG-DTA, FE-SEM, TEM-EDS, and zeta potential analysis and compared to unmodified TiO₂ NPs. The results showed the surface modification of TiO₂ in sc-CO₂ is made of modifier molecules bonding chemically in form of bidentate chelating and bridging mode. The reaction between TiO₂ nanoparticles and dicarboxylic acid molecules in sc-CO₂ provides carboxylic acid-modified TiO₂ nanoparticles with a modification efficiency much higher than the conventional solvent immersion method. Surface modification by terephthalic acid and para-aminobenzoic acid affects the surface electrical property of TiO₂ nanoparticles in water, leading to a positive charge surface. Since this method is ecologically and environmentally friendly, it can be applied in the synthesis of materials for many applications.

Key words: Titanium dioxide nanoparticles, surface modification, carboxylic acids, supercritical carbon dioxide

1. Introduction

Titanium dioxide nanoparticles (TiO_2 NPs) have been widely studied for many important applications in photocatalysis, solar cell, biomedical materials of use, and so on. With the bandgap 3.2 eV [1] TiO_2 NPs can absorb the UV light strongly and excited to form electron-hole pairs and possesses high surface energy. Upon UV radiation, TiO_2 NPs can generate active free radicals (OH^* and O_2^-) that are responsible for decomposing organics on the particle surface [2]. Because of this photocatalytic property, the interest in TiO_2 NPs in biomedical applications has been growing. For the practical purpose in the biomedical application, it has to disperse in an aqueous system. However, these nanoparticles easily agglomerate due to their high surface energy. So, the surface identification of nanoparticles to prevent the agglomerations process was studied and it was ensured they have perfect dispersion in the applied system [3].

The most common used organic modifier is carboxylate groups. By coordinating carboxylic groups (COOH) to the surface of titanium atoms [4], it can improve their dispersion in the applied system [5,6]. In this research, dicarboxylic acid (terephthalic acid) and amino-acid-based diacids (para-aminobenzoic acid) were used to modified TiO_2 NPs. In the present work, a surface modification of TiO_2 NPs in supercritical carbon dioxide (sc-CO_2) was developed in place of organic solvents. Surface modification of nanomaterials in sc-CO_2 is newly applied instead of other processes like the immersion method. CO_2 is non-toxic, harmless, non-flammable, and low price and has the critical temperature ($T_c = 304.4$ K) and the critical pressure ($p_c = 7.38$ MPa), which can be brought into a supercritical state easily [7]. The modification process through the sc-CO_2 method can save a lot of the consumption energy and time for drying process, and waste treatment as no need for organic solvent and additive in the modification reaction process.

Modified TiO_2 NPs were produced by post-modification due to their advantages in adjusting the surface coverage of modifiers easily without changing their original growth features. To discovering optimum conditions (R, p, T) that obtain a maximum modification rate of TiO_2 NPs, the response surface methodology (RSM) designed by Minitab 19 for statistical analysis was studied. In this study, the ratio of modifier to nanoparticles R (mol/mol), T (K), and p (MPa) were independent variables and Y_e (%) was a response of independent variables. In this experiment, all were conducted in triplicate and the average value was taken for statistical analyses.

Firstly, optimization has been carried out by monitoring the influence of one factor at a time on experimental response. While only one parameter is changed, others are kept at a constant level. After that, the authors used Box-Behnken as an experimental design and generated second-order polynomial regression model to obtain predicted modification rate. To know the effect of process condition, modified TiO_2 NPs were characterized by several analytical techniques including Fourier transform infrared spectra

(FT-IR), thermogravimetry-differential thermal analysis (TG-DTA), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and zeta potential analysis.

2. Materials and method

2.1. Materials

Nano-sized TiO₂, rutile (TTO-51A) 76-83 % powder with average particles size around 10 nm - 30 nm, surface area 75 m²/g - 85 m²/g from ISHIHARA Chemical Company Ltd. was used as purchased. The modifier used was terephthalic acid (C₈H₆O₄) >99.0 % with melting temperature 700.1 K purchased from Tokyo Chemical Industry, Co, Ltd. Besides that, para-aminobenzoic acid (C₇H₇NO₂) 99% with melting temperature 460.15 K purchased from Acros Organic. Carbon dioxide (CO₂) 99.9 wt % used in the process produced by Uno Sanso Co. Ethanol 99.5 % and methanol purchased from Wako Chemical Ltd.

2.2 Modification apparatus

The apparatus for surface modification of TiO₂ NPs under the sc-CO₂ was constructed in a batch reactor system as schematically presented in Figure 2.1. Firstly, CO₂ in the gas cylinder was liquefied by a cooler circulator (TBG045AE, ADVANTEC) and supplied into the cell by a high-pressure pump (NP-KX-540, Nippon Seimitsu Kagaku, Co. Ltd.). The stainless cell with a capacity of 100 cm³ was placed in an electrical heater and process temperature controlled within ± 0.5 K. The cell was connected to a safety relief valve (SS-4R3A, Swagelok) operated over maximum pressure of 35.0 MPa. The pressure inside the vessel was kept constant by a back pressure regulator (26-1700, TESCOM) within ± 0.1 MPa and an agitator motor with speed 1000 rpm (NIDEC-SHIMPO) used to homogenize the mixture during the process.

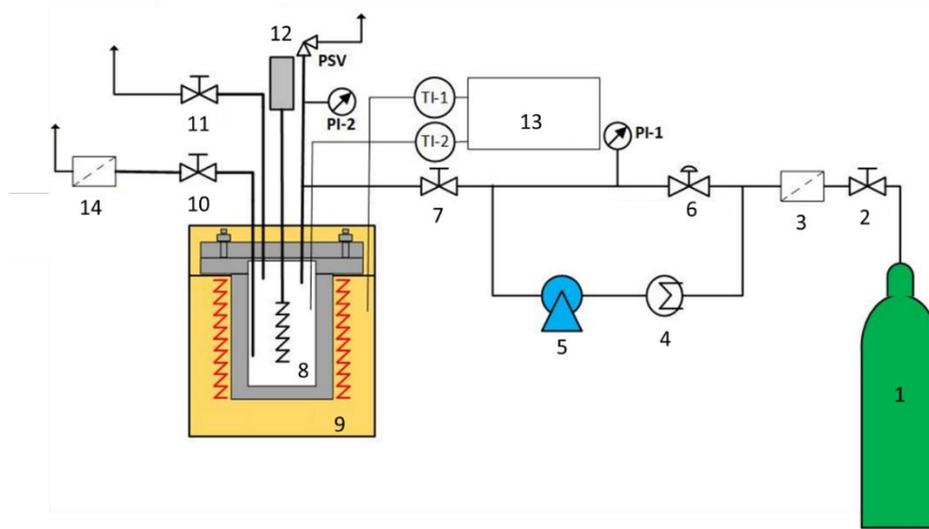


Figure 2.1 Apparatus for surface modification of TiO₂ in sc-CO₂ in a batch reactor system: 1. CO₂ cylinder, 2. CO₂ valve, 3. Filter, 4. CO₂ cooling circulator, 5. CO₂ pump, 6. Back pressure regulator, 7. Valve, 8. Cell, 9. Heater, 10. Valve, 11. Safety valve, 12. Agitator motor, 13. Temperature controller, 14. Gas filter, PI. pressure indicator, and TI. temperature indicator

2.3 Surface modification in sc-CO₂

Firstly, TiO₂ NPs was dried at 373.1 K for 1 h to remove absorbed water. Then TiO₂ NPs 0.1 g ± 0.001 g and modifier with various modifier ratios were loaded into the reaction cell. The mixture was reacted under sc-CO₂ for 1.5 h. The reaction time was set to the shorter time to obtain the maximum modification rate, which determined from the preliminary experiment. To find the highest modification rate of surface TiO₂ NPs, reaction temperature and pressure were varied. After the reaction was completed, the mixture was cooling down at room temperature then unreacted modifier was removed before analysis.

2.4 Modification rate

To evaluate the amount of modifier bound to TiO₂ NPs, total attachment/modification rate of surface modifier (Y_e) is defined as follows.

$$Y_e [\%] = \frac{\text{mass of sample after drying} - \text{mass after thermal decomposition}}{\text{mass of sample after thermal decomposition}} \cdot 100 \quad (1)$$

A single crystal of nano TiO₂ from ISHIHARA Chemical Company Ltd. has 1.9 amount of surface OH or 2.32 × 10⁻³ mol/g TiO₂ (N_{OH}) [8]. Eq. (2) evaluates the surface degree of substitution (DS_{surf}) or number of hydroxyl groups per unit TiO₂ NPs that has been modified by carboxylate on the surface of TiO₂ NPs [9]. N_{mod} is the number of moles of modifier per gram of modified TiO₂ NPs. 1.9 is the number of accessible

hydroxyl groups per unit TiO₂ NPs on the surface [8], X_{TiO₂} is the mass fraction of TiO₂ in the modified TiO₂ NPs, which is calculated by (1 – Y_e) / 100, and N_{OH} is the number of moles of hydroxyl groups per gram on the surface of TiO₂ NPs (N_{OH} in mol/g).

$$DS_{surf} = \frac{1.9N_{mod}}{X_{TiO_2} N_{OH}} \quad (2)$$

3. Results

3.1. Modification of TiO₂ NPs by terephthalic acid

The modification reaction of TiO₂ NPs with TA in sc-CO₂ can be characterized by figure 3.1, where the OH group on the surface of TiO₂ NPs reacts with the COOH group of TA. The reaction is controlled by the reaction temperature, pressure, and the concentration of TA in sc-CO₂.

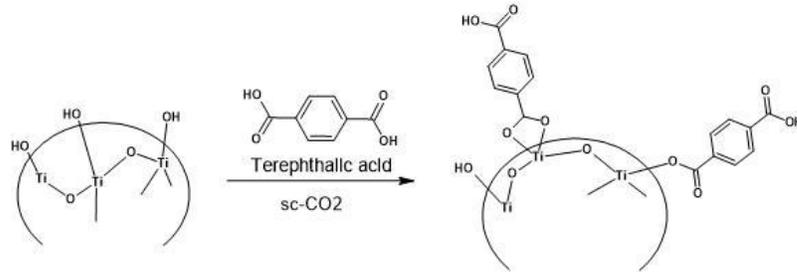


Figure 3.1 Binding form of a carboxylic group on TiO₂ NPs in chemical adsorption (bidentate chelating).

In modification process of TiO₂ NPs with TA, the results showed that the modification rate obtained by the sc-CO₂ method was 55.0 % much higher compared to the conventional solvent immersion method. The analysis variance (ANOVA) provided by the RSM method suggested that the increase of the weight ratio of modifier/TiO₂ up to 4.04 (mol/mol) improved the surface coverage of the modifier molecules on the surface of nanoparticles significantly. The reaction temperature 401.5 K and pressure 14.8 MPa with CO₂ density of 0.26 g/cm³ (5 907.74 mol/m³) resulted in an optimum modification rate about 25.34 %. From the results of FT-IR analysis, it can be concluded that the binding form of TA molecules on the surface of TiO₂ NPs produced through the chemically chelating reaction. TG-DTA analysis also demonstrates that TA was chemically bonded with TiO₂ NPs affected on the thermal behavior of modified TiO₂ NPs. FE-SEM and zeta potential analysis implies that all the TiO₂NPs were in the nano-sized range and enabled to be dispersed in an aqueous solution better than unmodified TiO₂ NPs. TEM and element mapping analysis supported the FT-IR analysis results that TiO₂ NPs have been successfully modified. The surface

modification by TA affects the surface electrical property of TiO₂ NPs in water, leading to a positive charge surface compared to unmodified TiO₂ NPs.

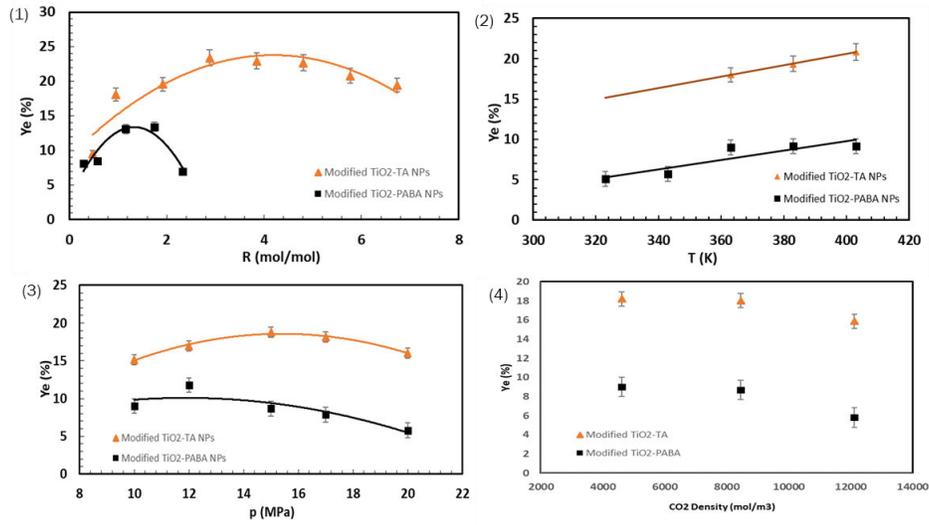


Figure 3.2. Influence of surface coverage of modifier on TiO₂ NPs. (1) weight ratio of modifier to TiO₂ NPs, (2) temperature, (3) pressure, and (4) CO₂ density on surface coverage of modifier on TiO₂ NPs.

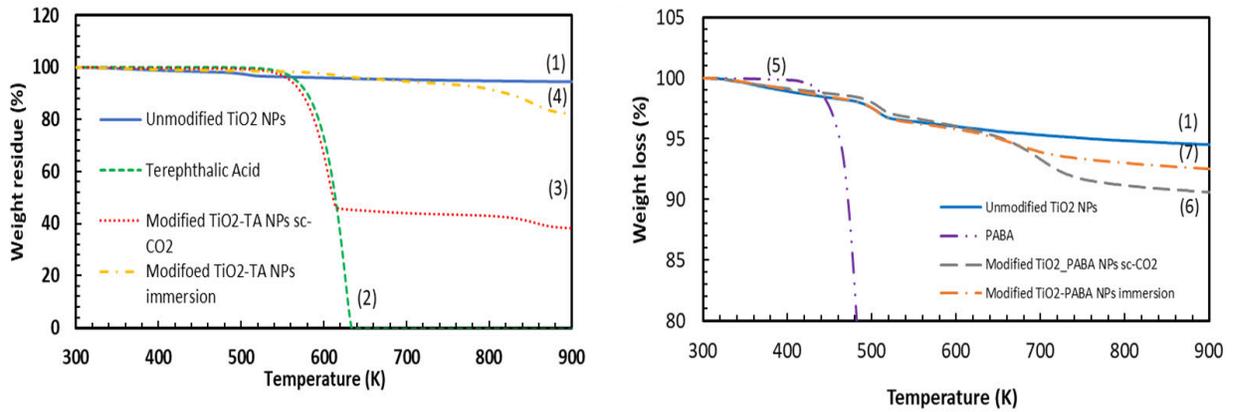


Figure 3.3 TG-DTA thermograph of unmodified and modified TiO₂ NPs by dicarboxylic acids. of (1) ———, bare-TiO₂ NPs, (2) — — —, terephthalic acid, (3) ·····, modified TiO₂-TA NPs obtained by sc-CO₂ method with modification rate 24.62 %, and (4) — · — ·, modified TiO₂-TA NPs via immersion method with modification rate 16.25 %, (5) — · · —, para-aminobenzoic acid, (6) — — —, modified TiO₂-PABA NPs obtained by sc-CO₂ method with modification rate 13.84 %, and (7) — · — ·, modified TiO₂-PABA NPs via immersion method with modification rate 4.26 %.

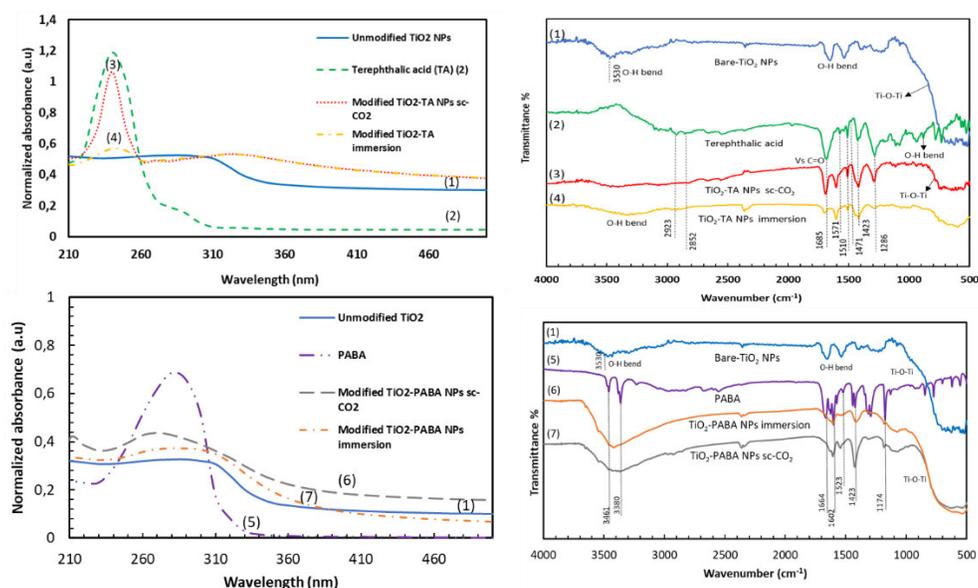


Figure 3.4. UV-absorption and FTIR spectra of (1) ———, bare-TiO₂ NPs, (2) - - -, terephthalic acid, (3) ·····, modified TiO₂-TA NPs obtained by sc-CO₂ method with modification rate 24.62 %, and (4) — · —, modified TiO₂-TA NPs via immersion method with modification rate 16.25 %, (5) — · · —, para-aminobenzoic acid, (6) — — —, modified TiO₂-PABA NPs obtained by sc-CO₂ method with modification rate 13.84 %, and (7) — · · —, modified TiO₂-PABA NPs via immersion method with modification rate 4.26 %.

3.2. Modification of TiO₂ NPs by para-aminobenzoic acid

The modification reaction of TiO₂ NPs with PABA in sc-CO₂ can be characterized by Figure 3.5, where the adsorption of amino acids on TiO₂ NPs surface via carboxyl group is through to leave the amine group unbound.

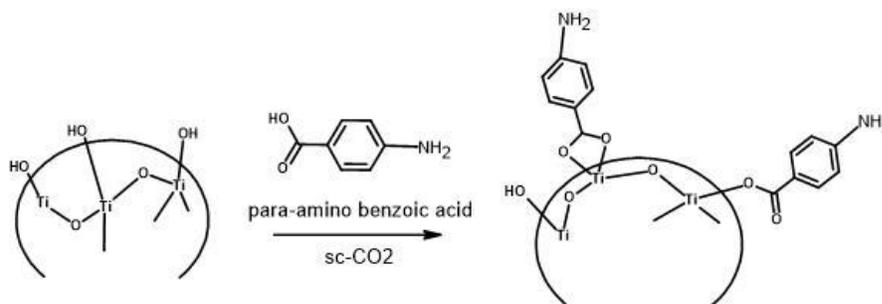


Figure 3.5. Binding form of a carboxylic group on TiO₂ NPs in chemical adsorption.

The modified TiO₂-PABA NPs were produced from the reaction between TiO₂ NPs and para-aminobenzoic acid through the sc-CO₂ method. The results showed that the modification rate obtained by the sc-CO₂ method was 2.24 times higher compared to the conventional solvent immersion method. The surface modification by PABA affects the surface electrical property of TiO₂ NPs in water, leading to a

positive charge surface better than terephthalic acid. The analysis variance (ANOVA) provided by the RSM method suggested that the increase of the weight ratio of modifier/TiO₂ up to 1.65 (mol/mol) improved the surface coverage of the modifier molecules on the surface of nanoparticles significantly. The reaction temperature 378.3 K and pressure 10 resulted in an optimum modification rate about 13.84 %. From the results of FT-IR analysis, it can be concluded that the binding form of TA molecules on the surface of TiO₂ NPs produced through the chemically bridging reaction. TEM and element mapping analysis supported the FT-IR analysis results that TiO₂ NPs have been successfully modified by PABA. XPS analysis confirmed that carboxylate group is bound symmetrically through its two oxygen atoms onto the TiO₂ surface and let the amine group freely. Since this method is ecologically and environmentally friendly, it can be applied in precursor composites for the synthesis materials of biomedical application. Also, modified TiO₂-PABA NPs showed better dispersibility in aqueous system compared to unmodified TiO₂ NPs, the supercritical CO₂ method can be applied in other surface modification of nanomaterials.

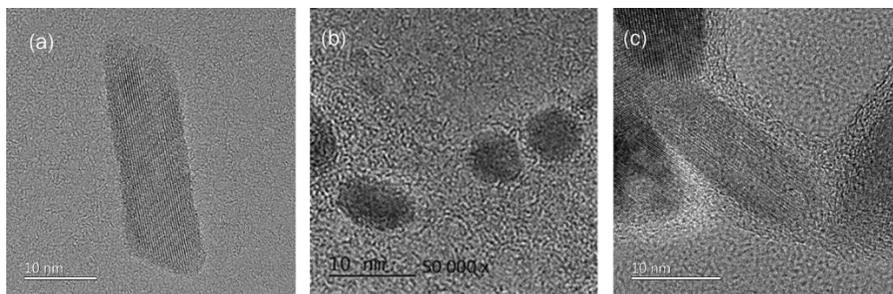


Figure 3.6. HRTEM image of (a) unmodified TiO₂ NPs, (b) modified TiO₂ NPs by TA, (c) modified TiO₂ NPs by PABA obtained by sc-CO₂ method.

Table 3.1. Comparison of zeta potential of unmodified TiO₂ with modified TiO₂ NPs obtained from sc-CO₂ method.

Zeta Potential [mV]	TiO₂ NPs	TiO₂-PABA NPs in sc- CO₂	TiO₂-TA NPs in sc- CO₂
Water	-21.4	50.26	-11.4
Ethanol	2.10	23.84	2.11

4. Conclusion

In this dissertation, the surface modification of TiO₂ NPs with terephthalic acid and para-aminobenzoic acid in supercritical CO₂ has been studied. We discovered an optimum process conditions (reaction temperature, pressure, and the ratio of modifier to TiO₂ NPs) that obtain a maximum modification rate of modified TiO₂ NPs. Also, the modification reaction of TiO₂ NPs in supercritical carbon dioxide and the effect of surface modification in supercritical carbon dioxide to the properties of modified TiO₂ NPs through several analytical techniques were evaluated. We conclude that supercritical CO₂ method can be applied in surface modification process of TiO₂ NPs since it is more efficient compared to the conventional solvent immersion method. Moreover, amino-acid-based diacids (para-aminobenzoic acid) is a better modifier in decreasing the agglomeration of TiO₂ NPs in water system compared to dicarboxylic acids (terephthalic acid) since modification process leave the amine group unbound on the surface of TiO₂ NPs and affected on the surface electrical property of TiO₂ NPs in water, leading to a positive charge surface.

References

- [1] K.M. Reddy, S. V. Manorama, A.R. Reddy, Bandgap studies on anatase titanium dioxide nanoparticles, *Mater. Chem. Phys.* 78 (2003) 239–245. [https://doi.org/10.1016/S0254-0584\(02\)00343-7](https://doi.org/10.1016/S0254-0584(02)00343-7).
- [2] T. Lai, W. Lee, *Journal of Photochemistry and Photobiology A : Chemistry* Killing of cancer cell line by photoexcitation of folic acid-modified titanium dioxide nanoparticles, 204 (2009) 148–153. <https://doi.org/10.1016/j.jphotochem.2009.03.009>.
- [3] N. Nakayama, T. Hayashi, Preparation of TiO₂ nanoparticles surface-modified by both carboxylic acid and amine: Dispersibility and stabilization in organic solvents, *Colloids Surfaces A Physicochem. Eng. Asp.* 317 (2008) 543–550. <https://doi.org/10.1016/j.colsurfa.2007.11.036>.
- [4] M.A. Neouze, U. Schubert, Surface modification and functionalization of metal and metal oxide nanoparticles by organic ligands, *Monatshefte Fur Chemie.* 139 (2008) 183–195. <https://doi.org/10.1007/s00706-007-0775-2>.
- [5] S. Mallakpour, E. Nikkhoo, Surface modification of nano-TiO₂ with trimellitylimido-amino acid-based diacids for preventing aggregation of nanoparticles, *Adv. Powder Technol.* 25 (2014) 348–353. <https://doi.org/10.1016/j.appt.2013.05.017>.
- [6] F. Chang, H. Kim, B. Joo, K. Park, H. Kim, Novel CO₂-soluble pyridine derivatives and the extraction of heavy metals into Sc-CO₂, *J. Supercrit. Fluids.* 45 (2008) 43–50.

<https://doi.org/10.1016/j.supflu.2007.11.014>.

- [7] T. Bai, K. Kobayashi, K. Tamura, Y. Jun, L. Zheng, Supercritical CO₂ dyeing for nylon, acrylic, polyester, and casein buttons and their optimum dyeing conditions by design of experiments, *J. CO₂ Util.* 33 (2019) 253–261. <https://doi.org/10.1016/j.jcou.2019.05.013>.
- [8] C. Wu, Markedly Enhanced Surface Hydroxyl Groups of TiO₂ Nanoparticles with Superior, (2017). <https://doi.org/10.3390/ma10050566>.
- [9] V.A. Online, Surface modification of cellulose nanocrystals, (2014) 7764–7779. <https://doi.org/10.1039/c4nr01756k>.

学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

Surface Modification of TiO₂ Nanoparticles in Supercritical Carbon Dioxide

（超臨界 CO₂ 中での二酸化チタンナノ粒子の表面修飾）

2. 論文提出者 (1) 所 属 自然システム学専攻

(2) ^{ふり}氏 ^{がな}名 Anggi Regiana Agustin

3. 審査結果の要旨（600～650字）

提出された学位論文に対し、各審査員による個別審査と指導を行うとともに、令和3年8月2日開催の口頭発表の結果をふまえ、同日開催の論文審査委員会にて協議し、以下のとおり判定した。ナノ粒子の分散性向上並びに環境調和型のナノ粒子表面処理プロセス開発の必要性から、本論文では、従来の有機溶媒を超臨界二酸化炭素に代替し、二酸化チタンナノ粒子表面上の水酸基と修飾剤として分子内にカルボキシル基及びアミノ基を有するテレフタル酸及びパラアミノ安息香酸を化学修飾する手法を新たに開発した。修飾ナノ粒子表面上の修飾率と超臨界域での実験条件（温度・圧力・修飾剤の添加割合）の関係を、実験計画法に基づいて得られた測定結果を応答曲面法により解析し、最大修飾率を与える実験条件を明らかにした。さらに、修飾二酸化チタンナノ粒子のTEM-EDSによる形態観察結果から粒子表面上に均一に修飾分子が存在していることを示し、FT-IR、UV、XPSを用いた分光学的分析により、修飾ナノ粒子表面上の水酸基と修飾分子のカルボキシル基による結合状態がナノ粒子表面上でキレート結合している可能性を示した。また、TG、DSCなどの熱分析結果から、有機溶媒中で表面修飾した場合に比べて、より強い結合を形成していることを明らかにした。さらに、修飾ナノ粒子の各溶媒中でのゼータ電位の測定結果から、分散性の著しい向上が見られることを明らかにした。以上の成果は、ナノ粒子表面処理プロセスの開発に関して、新たな知見を与えるものであり、本論文は博士（学術）の学位に値するものと判定した。

4. 審査結果 (1) 判 定（いずれかに○印） 合 格 ・ 不合格

(2) 授与学位 博 士（学術）