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学　位　論　文　概　要
Dissertation Summary

学位請求論文（Dissertation）
題名（Title）Surface Modification of TiO_2 Nanoparticles in Supercritical Carbon Dioxide
*（邦訳又は英訳）*超臨界 CO_2 中での二酸化チタンナノ粒子の表面修飾

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学位論文概要（Dissertation Summary）

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 [7].

The most common used organic modifier is carboxylate groups. By coordinating carboxylic groups (COOH) to the surface of titanium atoms [8], it can improve their dispersion in the applied system [9,10]. 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 [22]. 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.

The apparatus for surface modification of TiO_2 NPs under the sc-CO_2 was constructed in a batch reactor system as schematically presented in Figure 1.

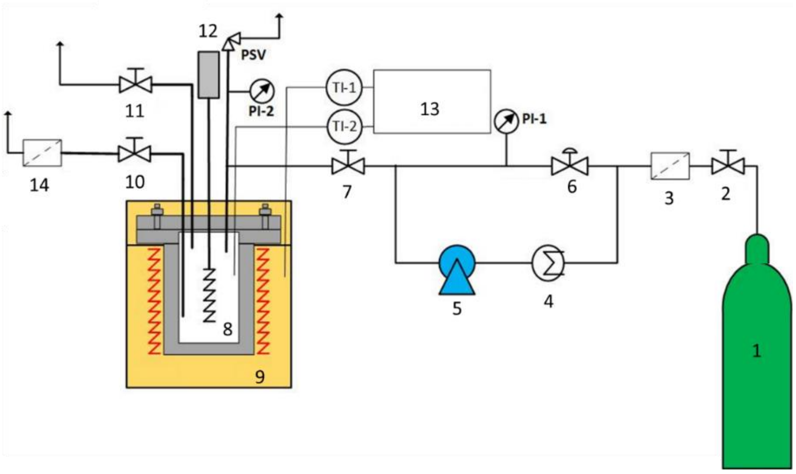

Figure 1. Apparatus for surface modification of TiO_2 in sc-CO_2 in a batch reactor system: 1. CO_2 cylinder, 2. CO_2 valve, 3. Filter, 4. CO_2 cooling circulator, 5. CO_2 pump, 6. Back pressure regulator, 7. Valve, 8. Cell, 9. Heater, 10. Valve, 11. Safety valve, 12. Agitator motor, 13. Temperature controller, 14. Gas filter, PI. pressure indicator, and TI. temperature indicator

To evaluate the amount of modifier bound to TiO_2 NPs, total attachment/modification rate of surface modifier (Y_e) is defined as follows.

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

A single crystal of nano TiO_2 from ISHIHARA Chemical Company Ltd. has 1.9 amount of surface OH or 2.32×10^{-3} mol/g TiO_2 (N_{OH}) [32] . Eq. (2) evaluates the surface degree of substitution (DS_{surf}) or number of hydroxyl groups per unit TiO_2 NPs that has been modified by carboxylate on the surface of TiO_2 NPs [33]. N_{mod} is the number of moles of modifier per gram of modified TiO_2 NPs. 1.9 is the number of accessible hydroxyl groups per unit TiO_2 NPs on the surface [32], X_{TiO2} is the mass fraction of TiO_2 in the modified TiO_2 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 TiO_2 NPs (N_{OH} in mol/g).

$$DS_{surf} = \frac{1.9 N_{mod}}{X_{TiO2}\ N_{OH}} \qquad (2)$$

In modification process of TiO_2 NPs with TA, the results showed that the modification rate obtained by the sc-CO_2 method was 55.0 % much higher compared to the conventional solvent immersion method. The surface modification by TA affects the surface electrical property of TiO_2 NPs in water, leading to a positive charge surface. The analysis variance (ANOVA) provided by the RSM method suggested that the increase of the weight ratio of modifier/TiO_2 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 CO_2 density of 0.26 g/cm^3 (5 907.74 mol/m^3) 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 TiO_2 NPs produced through the chemically chelating reaction. TG-DTA analysis also demonstrates that TA was chemically bonded with TiO_2 NPs affected on the thermal behavior of modified TiO_2 NPs. FE-SEM and zeta potential analysis implies that all the TiO_2NPs were in the nano-sized range and enabled to be dispersed in an aqueous solution better than unmodified TiO_2 NPs. TEM and element mapping analysis supported the FT-IR analysis results that TiO_2 NPs have been successfully modified by TA.

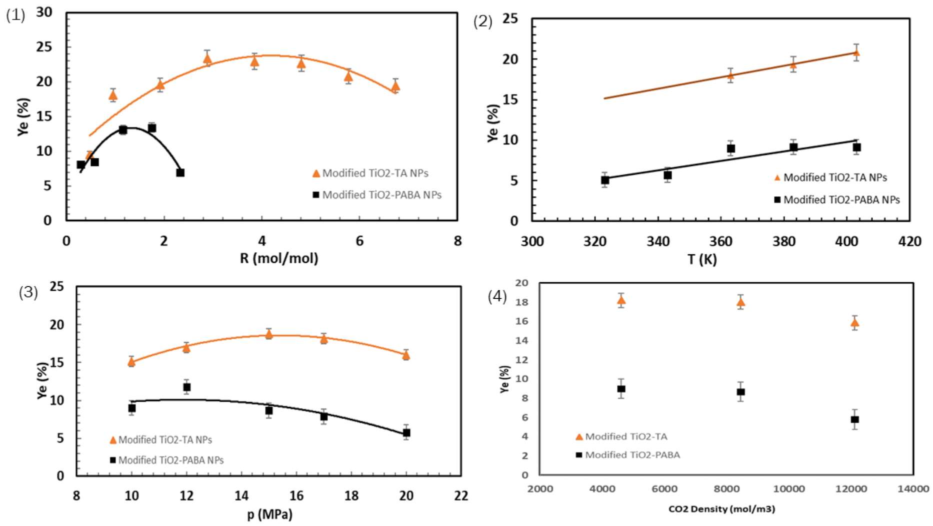

Figure 2. Influence of surface coverage of modifier on TiO_2 NPs. (1) weight ratio of modifier to TiO_2 NPs, (2) temperature, (3) pressure, and (4) CO_2 density on surface coverage of modifier on TiO_2 NPs.

The modified TiO_2-PABA NPs were produced from the reaction between TiO_2 NPs and para-aminobenzoic acid through the sc-CO_2 method. The results showed that the modification rate obtained by the sc-CO_2 method was 2.24 times higher compared to the conventional solvent immersion method. The surface modification by PABA affects the surface electrical property of TiO_2 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/TiO_2 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 TiO_2 NPs produced through the chemically bridging reaction. TEM and element mapping analysis supported the FT-IR analysis results that TiO_2 NPs have been successfully modified by PABA. XPS analysis confirmed that carboxylate group is bound symmetrically through its two oxygen atoms onto the TiO_2 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 TiO_2-PABA NPs showed better dispersibility in aqueous system compared to unmodified TiO_2 NPs, the supercritical CO_2 method can be applied in other surface modification of nanomaterials.

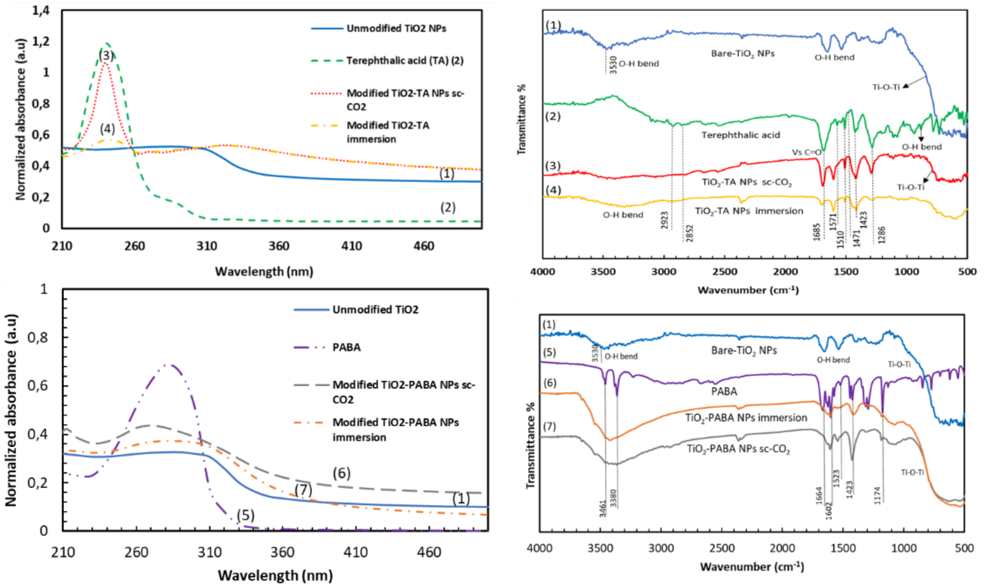

Figure 3. UV-absorption and FTIR spectra of (1) ———, bare-TiO_2 NPs, (2) – – –,terephthalic acid, (3) ………, modified TiO_2-TA NPs obtained by sc-CO_2 method with modification rate 24.62 %, and (4) — · -, modified TiO_2-TA NPs via immersion method with modification rate 16.25 %, (5) — · · ,,para-aminobenzoic acid, (6) — —, modified TiO_2-PABA NPs obtained by sc-CO_2 method with modification rate 13.84 %, and (7) — · -, modified TiO_2-PABA NPs via immersion method with modification rate 4.26 %.

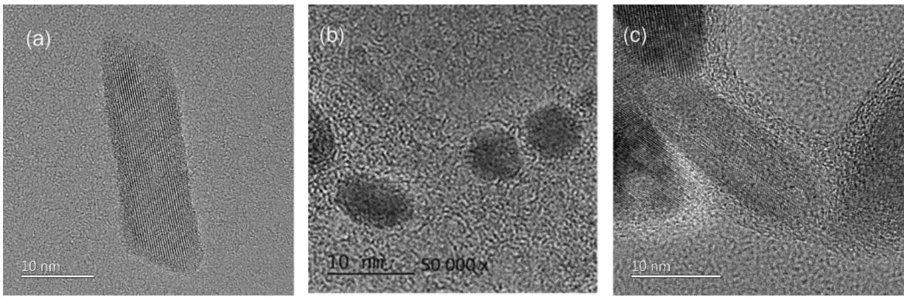

Figure 4. HRTEM image of (a) unmodified TiO_2 NPs, (b) modified TiO_2 NPs by TA, (c) modified TiO_2 NPs by PABA obtained by sc-CO_2 method.