Surface Modification of Nano-TiO₂ with para-Aminobenzoic Acid in Supercritical Carbon Dioxide for Preventing Aggregation of Nanoparticles

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Abstract

Post-modification amino acid modified TiO_2 nanoparticles syntheses were performed by the supercritical CO_2 method to prevent the aggregation of TiO_2 nanoparticles in the solvent systems. The results showed that the modification rate obtained by the supercritical method was 2.24 times higher than the conventional solvent immersion method. From the results of FT-IR analysis and supported by TG-DTA, TEM analysis, it can be concluded that the binding form of PABA molecules on the surface of TiO_2 nanoparticles produced through the chemically bridging reaction. XPS analysis confirmed that the carboxylate group is bound onto the TiO_2 surface and freely lets the amine group. The surface modification by PABA influenced the surface electrical property of TiO_2 nanoparticles to a positive charge and showed better dispersibility in water than unmodified TiO_2 nanoparticles. A supercritical CO_2 method is environmentally friendly and effectively be applied in the surface modification of nanomaterials.

1. Introduction

Modified TiO_2 nanoparticles by organic constituents such as carboxylic acid or amino-based, which combine the properties of inorganic and organic constituents, have an extensive range of uses in the fields of composite materials, catalysis, electrical and optical devices, or in the biomedical area [1]. Many researchers prepared modified TiO_2 NPs by surface modification using carboxylic acid and long-chain alkyl amines to improve their dispersion in the solvent system [2,3]. The control of parameters such as size, shape, crystallinity, phase composition of the oxide nanoparticles, type of bonding and interface between the organic and the inorganic phases, the nature and the amount of the organic component, and finally, the degree of dispersion of the nano-objects are well documented in the literature [3].

They [2,4–6] synthesized and characterized amino-acid-based diacids surface-modified TiO_2 NPs. The modification of TiO_2 NPs carried out by either in situ or post-modification methods. The post-modification of TiO_2 NPs is conventionally recognized by submerging TiO_2 NPs into an organic solution to adsorb the carboxylic modifiers at room temperature (RT) or using ligand exchanging reaction [5,7–9]. However, difficulties in getting well-dispersed nanoparticles and infilling the pores of nano-sized aggregates are encountered efficiently, limiting the control of the

surface coverage [5]. In addition, the pH of the aqueous solution hardly affected the adsorption [10]. Looking for a suitable method to modify the TiO_2 NPs has become challenging work [2,11,12].

We reported surface modification of TiO_2 NPs with terephthalic acid in the supercritical CO_2 method [13]. Along with excellent efficiency in the surface coverage of carboxylic group onto the surface of TiO_2 NPs. These results led us to investigate the "ecofriendly" process and control the properties of modified TiO_2 NPs by changing the modifier used in the modification process as the desire applications. Thomas et al. reported that the adsorption of amino acids on the TiO_2 surface via the carboxyl group is thought to leave the amine group unbound [6,14,15]. The free amine group could graft polymers or biomolecules onto TiO_2 for biosensing or novel biomaterial applications [16]. Para-aminobenzoic acid (PABA) is a good candidate since it is a simple aromatic amino acid which easy to find, inexpensive, biocompatible, and chemically stable.

Therefore, the purposes of the study were to (1) prepare and characterized a modified TiO_2 NPs by PABA obtained by the supercritical CO_2 method. (2) Evaluate whether this new modified TiO_2 NPs surface could enhance the stability and dispersibility of TiO_2 NPs in the solvent systems. The surface morphology, chemical compositions, and dispersibility were evaluated by UV-Vis spectroscopy, Fourier transforms infrared spectra (FT-IR), thermogravimetry-differential thermal analysis (TG-DTA), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and zeta potential analysis.

2. Experimental Section
2.1. Chemicals
Nano-sized TiO_2, rutile (TTO-51A) 76-83 % powder with average particles size around 10 nm - 30 nm, surface area 75 m^2/g - 85 m^2/g from ISHIHARA Chemical Company Ltd. was used as purchased. The modifier used was para-aminobenzoic acid ($C_7H_7NO_2$) >99.0 % purchased from Across Organic. Carbon dioxide (CO_2) 99.9 wt % is used in the process produced by Uno Sanso Co.

2.2. Modification apparatus
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 Fig. 1. Firstly, CO_2 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 cm^3 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. An agitator motor with a speed of 1000 rpm (NIDEC-SHIMPO) was used to homogenize the mixture during the process.
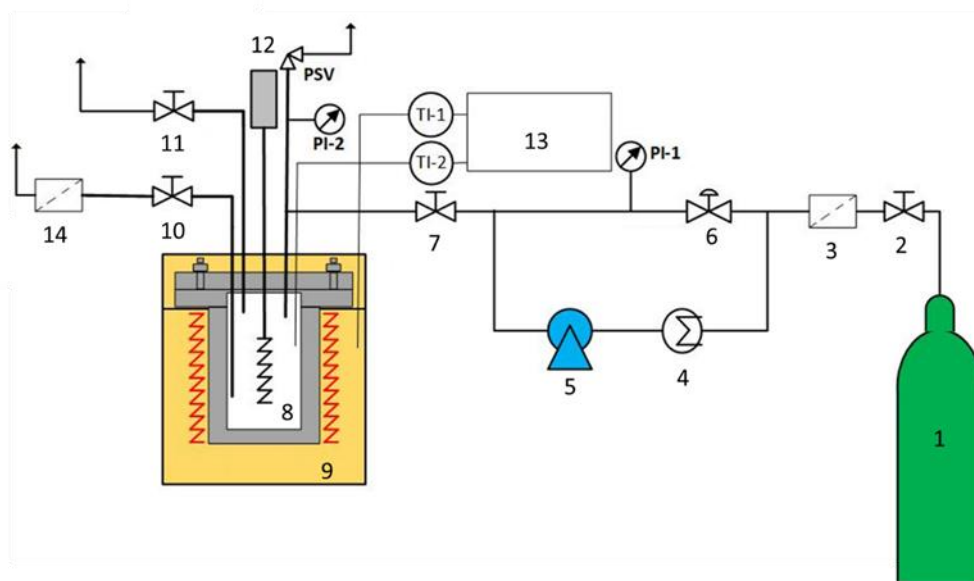
Fig. 1. Apparatus for surface modification of TiO_2 NPs by terephthalic acid under sc-CO_2 in a batch reactor system: 1. CO_2 cylinder, 2. CO_2 valve, 3. Filter, 4. CO_2 cooling circulator, 5. CO_2 pump, 6. Backpressure regulator, 7. Valve, 8. Cell, 9. Heater, 10. Valve, 11. Safety valve, 12. Agitator motor, 13. Temperature controller, 14. Gas filter, PI. Pressure indicator, and TI. Temperature indicator

2.3. Surface modification of TiO_2 in sc-CO_2

Firstly, TiO_2 NPs were dried at 373.1 K for one hour to remove absorbed water. Then TiO_2 NPs 0.1 g $\pm$ 0.001 g and PABA with optimum modifier ratio 2.84 (g/g), obtained from RSM methodology by minitab were loaded into the reaction cell. The mixture was reacted under sc-CO_2 for 1.5 h. The reaction time was set to the shorter time to obtain the maximum modification rate determined from the preliminary experiment. The reaction temperature at 378.3 K and pressure 10.0 MPa were set to the optimum process condition obtained determined by RSM methodology by minitab 19. After the reaction was completed, the mixture was cooling down at room temperature, then washed with ethanol three times to remove unreacted PABA and filtered. In the end, the modified TiO_2 NPs by PABA were dried at 373.1 K before analysis.

2.4. Surface modification of TiO_2 in solvent immersion method

The amount of PABA at optimum ratio obtained by the sc-CO_2 method was used in the modification process of TiO_2 NPs by solvent immersion method. TiO_2 NPs were dried at 373.1 K for one h to remove the adsorbed water. Then TiO_2 NPs 0.1 g $\pm$ 0.001 g in 100.0 mL ethanol was mixed with PABA and magnetically stirred at R.T for 24 h. Finally, the obtained suspension was washed with ethanol three times to remove unreacted TA and filtered. In the end, the modified TiO_2 NPs by PABA were dried at 373.1 K before analysis.

2.5. Determination of surface coverage

The percentage of modification rate by gravimetric analysis was calculated at thermal decomposition at 873.1 K for 1.5 hours. The total attachment/modification rate of the surface modifier (Y_e) is defined as follows.

$$Y_e \, [\%] \; = \frac{mass\ of\ sample\ after\ drying - mass\ after\ thermal\ decomposition}{mass\ of\ sample\ after\ thermal\ decomposition} \cdot 100 \tag{1}$$

2.6. Sample characterization

UV-spectrophotometer (UV-1900i, Shimadzu) was used to measure the UV-absorption spectra of the samples. FT-IR spectra data for the sample were obtained by spectrophotometer (Agilent-carry 660+620) at resolutions of 4 cm^{-1}. They were scanned at wave number range 400 to 4000 cm^{-1}. TG-DTA (STA 2500, NET2SCH) was used to measure the weight losses of the sample in a nitrogen (N_2) atmosphere from 298.1 K to 973.1 K at 10.0 K/min of heating rate. The (TEM, JEM-ARM 200 F, JEOL) was used to obtain a high-resolution image of TiO_2 NPs, before and after the modification process. The stability of modified TiO_2 NPs' dispersion was estimated in aqueous solutions and ethanol at pH 7.0 and concentration of 100 ppm through the zeta potential analyser (MT3000 II UPA-UZ152) to characterize their dispersibility improvement after modification.

3. Results and discussion
3.1. UV spectra analysis and FTIR analysis

UV-Vis absorbance spectra of TiO_2, para-aminobenzoic acid, modified TiO_2-PABA in sc-CO_2, and modified TiO_2-PABA through the solvent immersion method are given in Fig. 2. Measurements on the sample of modified TiO_2-PABA showed that the bandgap absorption redshifted from 220 to 500 nm relative to TiO_2 with efficient and attractive protection in the UV-A (320 – 400 nm) and UV-B (290 – 320 nm) domain [17]. The significant change in the PABA absorption spectrum in the presence of TiO_2 NPs implied strong binding of the PABA onto the TiO_2 NPs surface. When the UV-absorbance intensity of modified TiO_2-PABA NPs obtained by immersion method (4) was compared to the sc-CO_2 method (3), modified TiO_2-PABA NPs obtained by the sc-CO_2 method had a higher PABA UV-absorption intensity than the immersion method (4). The UV-absorption results agreed well with the modification rate calculated by Eq. (1), whereas the sc-CO_2 method produced modified TiO_2-PABA NPs with a higher modification rate (13.84 %) than the immersion method (4.26 %). These findings indicated that the solvent immersion method of modification has a much slower reaction rate than the sc-CO_2 modification method. Although the solvent immersion method required a 24-hour reaction time while the sc-CO_2 method required only 1.5 hours, the reaction rate of the modification process in sc-CO_2 was much faster.
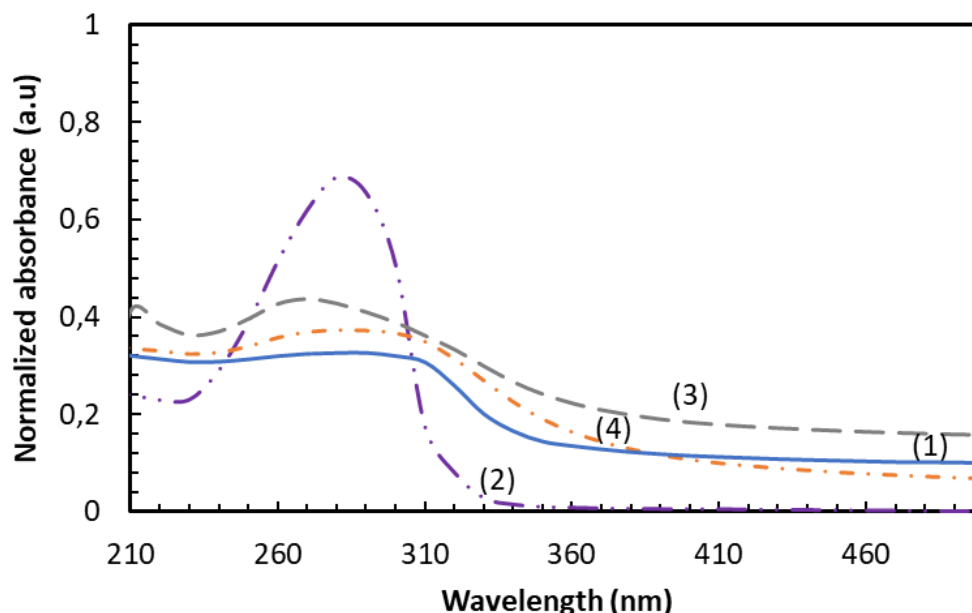
Fig.2. UV-absorption spectra of (1) ——— , bare-TiO_2 NPs, (2) — ·· ·· „para-aminobenzoic acid, (3) — — , modified TiO_2-PABA NPs obtained by sc-CO_2 method with modification rate 13.84 %, and (4) — · - , modified TiO_2-PABA NPs via immersion method with modification rate 4.26 %

As presented in Fig. 3, FT-IR analyses were performed to study the binding reaction between the modifier molecules and TiO_2 NPs. FTIR transmittance spectra (3), modified TiO_2-PABA obtained by the sc-CO_2 method showed absorption peaks for the ν_{OH}, $\nu_{CO2,}$ and ν_{TiO} vibrations. The broad feature between 3700 and 2500 cm^{-1} was due to the hydroxy groups' O–H stretching vibrations and adsorbed water and ethanol molecules. In contrast, the band at 1602 cm^{-1} was ascribed to the bending vibrations of the adsorbed molecules. Due to the lower hydrolytic susceptibility of carboxylate ligands than alkoxides, new sharp bands at 1602 cm^{-1} and 1423 cm^{-1} were attributed to asymmetric ν_{as} (COO), and ν_s symmetric (COO) stretches. It demonstrates that para-aminobenzoic acid is chemisorbed onto the surface of TiO_2. The value $\Delta\nu =[\nu_{as}(COO) - \nu_s(COO)]$ of around 179 cm^{-1} implies bidentate bridging coordination. This value agrees well with that found by Finnie et al. [18] and Raed et al. [5]. They concluded that benzoic acid and para-aminobenzoic acid are attached to TiO_2 films through bridging or bidentate coordination. The low wavenumber region exhibited a strong vibration between 880 and 500 cm^{-1}, assigned to $\nu_{Ti–O–Ti}$ of the titanium oxide framework. From FTIR spectra (3) and (4), it can be concluded that TA modified tiO2 NPs under the sc-CO_2 more effective than by immersion method.
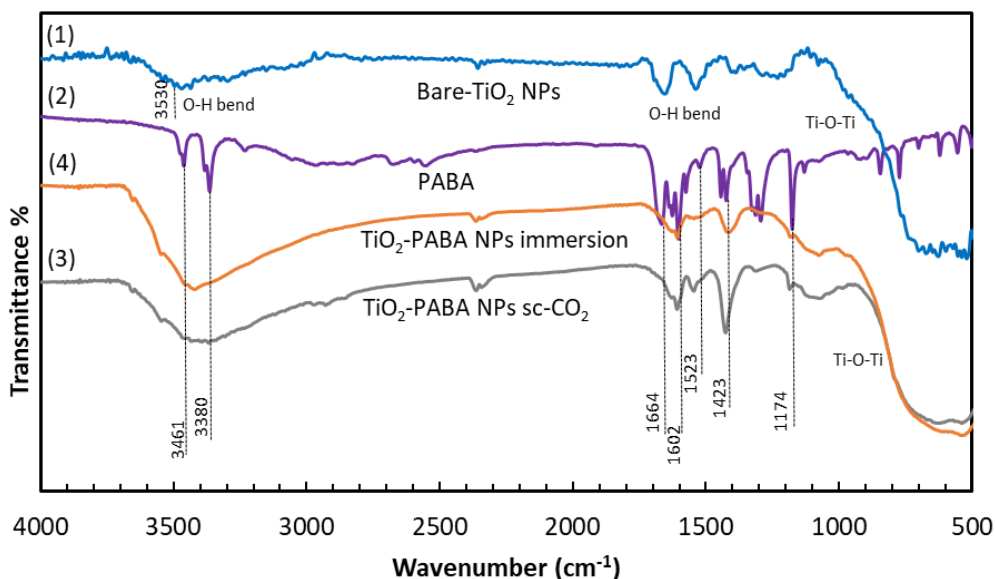
Fig. 3. FTIR transmittance spectra along with photographs of (1) ——— ,bare-TiO_2 NPs, (2) ———, terephthalic acid, (3) ——— , modified TiO_2-PABA NPs by sc-CO_2, and (4) ——— , modified TiO_2-PABA NPs by immersion

3.2. TG-DTA analysis

The thermal degradation behavior was studied by TG-DTA analysis. Fig. 4 presented TGA curves of unmodified and modified TiO_2 NPs got under an inert environment. As presented in Fig. 4, the thermal studies analysis has shown that the unmodified TiO_2 NPs have a slight weight loss attributed to dehydration of water absorbed by NPs [11,19]. At the same time, the grafted one displayed noticeable weight loss. It is attributed to the composition of the grafted diacid on the TiO_2 NPs. Samples of modified TiO_2-PABA NPs showed two-weight losses. TGA experiments confirmed that the first step (300.1 K – 450.1 K) corresponds to the loss of residual solvent (H_2O, Ethanol), and the further steps (450.1 K – 800.1 K) result from the release and combustion of the organic groups (–OH, $-O_2CC_6H_4NH_2$). It can be seen that the most significant weight loss appeared around 670 K. The modified TiO_2-PABA NPs represented by the sc-CO_2 method in TG-DTA thermograph (3) have better thermal stability than the unmodified TiO_2 NPs in TG-DTA thermograph (1). The findings established that the presence of PABA on the surface of TiO_2 NPs also supports the FT-IR results.
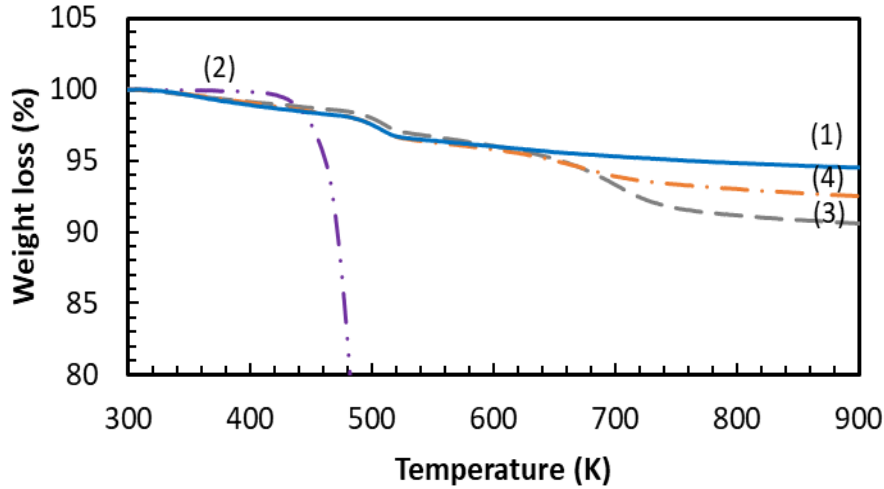
Fig. 4. TG-DTA thermographs of (1) ——— , bare-TiO$_2$ NPs, (2) — · · — „para-aminobenzoic acid, (3) — — , modified TiO$_2$-PABA NPs obtained by sc-CO$_2$ method with modification rate 13.84 % and (4) — · - , modified TiO$_2$-PABA NPs via immersion method with modification rate 4.26 %

3.3. TEM-EDS analysis

TEM-EDS was used to obtain a high-resolution image and element mapping of modified TiO2. Fig. 5. (a) visualized unmodified TiO$_2$ nano seeds in the form of nanotubes around 10 nm in size, confirming that these seeds are generally polycrystalline and have lattice distances and angular relationships compatible with rutile. Fig. 5. (b) described modified TiO$_2$-PABA NPs produced by the sc-CO$_2$ method. The patched crystallization of PABA was observed outside the seeds, and the particle size of TiO$_2$ (10 nm - 30 nm) was successfully coated by small particles of PABA to form a core/shell structure. Compared to the particle size of bare TiO$_2$ NPs used in this experiment (10 nm – 30 nm), the TEM image of modified TiO$_2$ NPs revealed that the surface modification did not significantly change the particle size of nanomaterials which is a good point for application purposes.
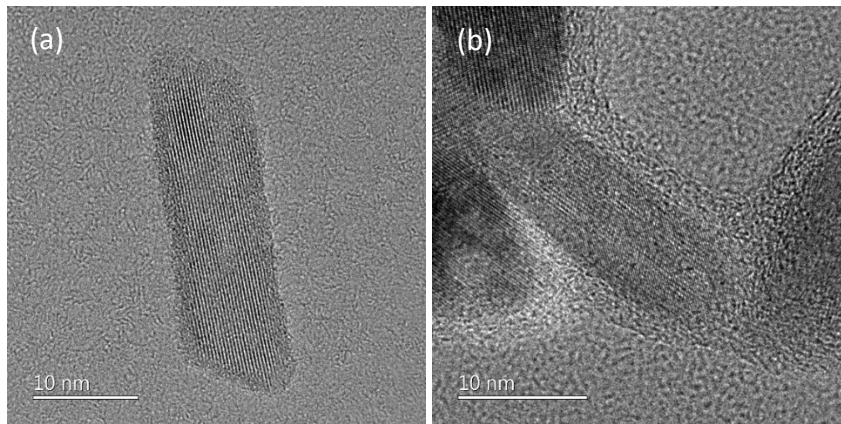

Fig. 5. HRTEM image of (a) unmodified TiO$_2$ NPs, (b) modified TiO$_2$-PABA NPs obtained by the sc-CO$_2$ method

3.4. XPS Analysis

In this experiment, XPS analysis is used to investigate the orientation of the PABA molecule on the TiO_2 NPs surface to confirm that the amine group does not bond to the surface and is thus free. The Ti 2p, N1s, O 1s, and C 1s XPS spectra of unmodified and PABA-modified TiO_2 NPs were shown in Fig. 6. The spectrum of N 1s modified TiO_2 NPs consists of a single peak at a binding energy of 395.8 eV consistent with the presence of NH_2 (8, 18, 41). It suggests that the molecule does not form the zwitterion upon adsorption, in agreement with the adsorption of PABA on anatase TiO_2 [4]; therefore, it appears that the amine group is present as R–NH2. It may suggest that the proton lost from the carboxylate group is adsorbed on the surface to form a surface hydroxyl species, as observed in other carboxylic acids upon adsorption on TiO_2 surfaces.

Fig. 6. (b) shows the O 1s spectrum recorded from unmodified TiO_2 NPs fitted with two peaks at binding energies of 526.5 and 528.7 eV, assigned to the oxide and surface oxygen close to O-vacancy sites, respectively [20,21]. After PABA adsorption on the TiO_2 surface, the intensity of the shoulder on the high-binding-energy side of the "oxide peak" increases. Following PABA adsorption on the TiO_2 surface, there is only one O 1s peak associated with the molecule, strongly indicating adsorption through both oxygen atoms in the carboxyl group following proton loss from the carboxylic acid group. If the carboxyl group had remained intact, one would expect to see a second adsorbate-derived peak with higher binding energy due to the chemically shifted C-OH group. The dissociation of the carboxylic group implies that the molecule adsorbs dissociatively on TiO_2 NPs in a bidentate configuration via the carboxylic group [22]. The data here make it impossible to determine whether this is a chelating or bridge-bonding mode. Previous research on the adsorption of carboxylic acids on anatase and rutile TiO_2 surfaces, on the other hand, appears to favor the bidentate bridging mode. The results of the FT-IR analysis also demonstrated that the reaction on the surface is a bidentate bridging mode.
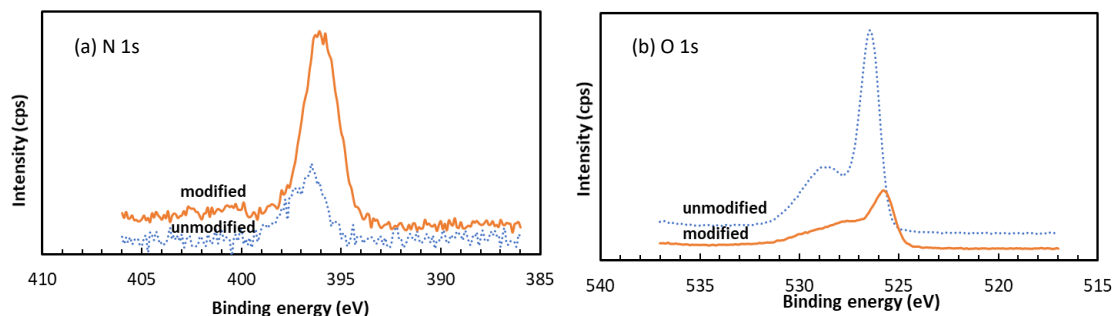

Fig. 6. XPS spectra of unmodified and modified TiO_2 NPs by PABA

The modification reaction of TiO_2 NPs with PABA in sc-CO_2 can be characterized by Fig. 7. The adsorption of amino acids on TiO_2 NPs surface via carboxyl group leaves the amine group unbound. These results are similar to previous research about the adsorption of carboxylic acids on anatase TiO_2 surfaces [4].
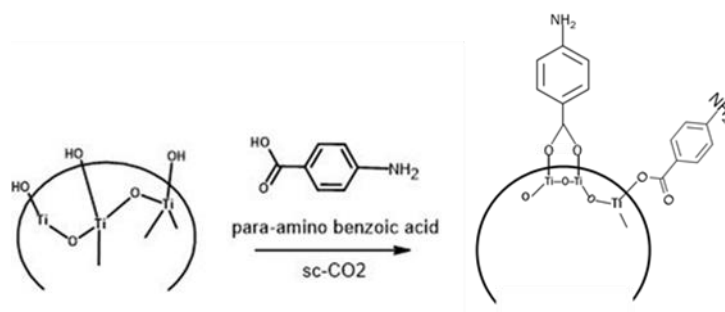
Fig. 7. Binding form of a carboxylic group on TiO_2 NPs in chemical adsorption

3.5. Dispersion analysis

It was investigated how the modification process affected their dispersibility. Zeta potential analysis was used to compare the stability of modified TiO_2-PABA NPs dispersion in water and ethanol to unmodified TiO_2 NPs. The findings demonstrated that the modifier molecules on TiO_2 NPs affect their surface electrical property, resulting in a positive charge surface [23,24]. As shown in Table 4.4, the zeta potential of unmodified TiO_2 NPs in an aqueous solution at pH 7 is about – 21.44 mV, implying poor dispersibility [25]. The zeta potential increased to 50.62 mV after PABA modification, indicating a significant improvement in their stability in an aqueous solution. Because agglomeration can be restrained when the electrostatic repulsive interaction between the surface of TiO2 is greater than the Van der Waals force and the zeta potential value approaches 30 mV, and above, the modified TiO_2-PABA NPs became more stable in the water system than unmodified TiO_2 NPs. Even though PABA is more soluble in ethanol, the modified TiO_2-PABA NPs are less stable in ethanol solution. The sc-CO_2 modification method was successful in modifying the surface of nanomaterials, according to this study. It can be used for future research on the surface modification process of nanomaterials using modifiers that dissolve in sc-CO_2.

Table 1. Comparison of zeta potential of unmodified TiO_2 with modified TiO_2-PABA NPs obtained from the sc-CO_2 method

Zeta Potential [mV]	TiO_2 NPs	TiO_2-PABA NPs in sc-CO_2
Water	-21.4	50.26
Ethanol	2.10	23.84

4. Conclusion

The modified TiO_2-PABA NPs were invented by reacting TiO_2 NPs with para-aminobenzoic acid using the sc-CO_2 method. The results showed that the sc-CO_2 method obtained a 2.24 times higher modification rate than the conventional solvent immersion method. PABA surface modification influences the surface electrical property of TiO_2 NPs in water, resulting in a more positive charge surface than terephthalic acid. FT-IR analysis that the binding form of PABA molecules on the surface of TiO_2 NPs is bidentate bridging. TEM and element mapping analysis supported the FT-IR analysis results. XPS analysis confirmed that the carboxylate group is bound

symmetrically through its two oxygen atoms onto the TiO_2 surface and freely lets the amine group. Since modified TiO_2-PABA NPs showed better dispersibility in an aqueous system compared to unmodified TiO_2 NPs, the supercritical CO_2 method can be applied in other surface modifications of nanomaterials.

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