

SURFACE PROPERTIES OF NANO-TiO₂ SYNTHESIZED FROM TWO DIFFERENT TiO₂ PRECURSOR SOURCES BY AN ALKALINE HYDROTHERMAL PROCESS FOLLOWED WITH A H₂O₂ TREATMENT: EXPERIMENTS COMBINED WITH STATISTICAL ANALYSIS.

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Abstract

Our research aimed to improve the surface properties of TiO₂ for application in dye-sensitized solar cells (DSC) by an alkaline hydrothermal process combined with H₂O₂ treatment. The effect of the TiO₂ sources on the product quality was evaluated further by statistical analysis of the experimental data. The two commercial TiO₂ precursors from Supelco (Merck – Germany) and BA-100 (China) were used to produce nano TiO₂ by the hydrothermal process in NaOH solution with two different concentrations of 5 M and 8 M at 150 °C. The final products were characterized by XRD, FT-IR, FE-SEM, and chemical bonds on the TiO₂ surface were particularly identified by XPS. The XPS data were then analyzed statistically by the K-Means Clustering algorithm based on R software. The results showed that NaOH concentrations were directly involved with the formation of Ti–O; Ti–OH bonds and TiO₂ morphology. The H₂O₂ treatment showed similar effects on TiO₂ surface bonding but with less significant impacts than those of NaOH. In particular, the TiO₂ reactant sources did not influence the structures, morphologies, and especially the surface properties of the products. Hence, a low-cost TiO₂ reactant should be selected in terms of economically effective products. The final TiO₂ products were suitable for applications in DSC.

Keywords: TiO₂, surface properties, hydrothermal synthesis, statistical analysis

1. INTRODUCTION

Titanium dioxide (TiO₂) is well-known as a semiconductor oxide with many outstanding properties such as high stability, low-cost, environmental friendly, and low toxicity, especially TiO₂ also has distinctive physicochemical and optoelectronic properties [1]. Therefore, TiO₂ is widely studied and applied in many disciplines such as pigments [2], energy-conversion [3].... There have been many publications related to the synthesis of TiO₂ for its appropriate uses in different fields. The synthesis process, *e.g.* sol-gel [4], microwave-assisted synthesis [5], hydrothermal [6] *etc.*, affects on the grain-size, morphology, and bonding of the formed product. Amongst them, we found that the hydrothermal method is good to form TiO₂ that was suitable for multi-purpose usages. The

hydrothermal method was easy to conduct under laboratory conditions at low temperatures, additionally, we can control the phase composition, particle size, morphology, and surface bonding of the final product by changing the environment or reaction conditions *e.g.*, temperatures, time, concentration, pH, *etc.*, or even by combining with other treatment processes. Research by T-D. N. Phan *et al.* successfully controlled the morphology, and crystalline phase composition of TiO₂ synthesized by the hydrothermal method, the hanging, the ratio of concentrated HCl [7]. On the other hand, Nian used TiO₂ precursor in tubular form combined with hydrothermal treatment in NaOH solution, followed by filtering and washing steps, and finally adjusted the pH from 2.2 to 8.9 by HNO₃ solution. The results showed that the pH value affected not only the product morphology but also

the crystalline phase composition [8]. Thus, the pH of the hydrothermal environment was proved to be one of the main factors affecting on the final product properties. M. H. Razali *et al.* [9] and A. M. Nor *et al.* [6] also synthesized TiO₂ by the hydrothermal process in 10 M NaOH solution but the products had different phase composition and surface morphology. Furthermore, the alkaline hydrogen peroxide treatment of TiO₂ by using the mixture of NaOH and H₂O₂ was known to lead to the uniform size distribution and increase the surface -OH functional groups [10]. Thus, the effect of individual facts as NaOH and H₂O₂ should be assessed separately to clearly state the impact of each factors on the TiO₂. Furthermore, we also noticed that these authors used different commercial TiO₂ precursor sources, so it might be the reason to explain the differences in the final products. This would lead the difficulties for judging whether the most important factors. Besides, N. Bilgin *et al.* [11] further clarified the role of precursors by using three different types of TiO₂ for hydrothermal processes which showed that the initial precursor had an influence on the morphology of the formed product. Thus, TiO₂ precursor sources should be considered as one of crucial factors affecting on the formation of TiO₂.

In this study, we processed the synthesis of TiO₂ by alkaline hydrothermal in NaOH solution (5 M and 8 M) to analyze the experimental factors affecting surface properties of synthesized TiO₂. Moreover, at 8 M NaOH, the samples were treated with H₂O₂. We investigated the origin of different TiO₂ precursor sources which were proposed to impact the chemical components and surface morphologies. Parallely, we expected that the comparison of different commercial TiO₂ precursor sources might result in a better cost-effective when choosing the starting materials to synthesize the desired products in combining with some post – treatment if necessary.

2. EXPERIMENT

2.1. Materials

TiO₂ particles of Supelco Merck, Germany (99.9 %) and BA-100, China (98.5 %) with code **M-TiO₂** and **C-TiO₂**, respectively, have the same anatase phase, similar morphology–spherical form, particle size 50–250 nm. Sodium hydroxide

(NaOH, 99.9 %) and hydrochloric acid (HCl, 99.9 %) were purchased by Xilong Scientific, China without any further purification previous used. The price of **C-TiO₂** was lower than **M-TiO₂** by a factor of five.

2.2. Synthesis of Titanium dioxide (TiO₂)

Firstly, 2.00 g **M-TiO₂** and NaOH solution with two different concentrations of 5 M and 8 M were dispersed by WUC-DO6H 40HZ ultrasound for 3 hours to form a milky precursor solution. Secondly, the mixtures were carried out by hydrothermal processes in autoclaves at 150 °C. After 12 hours of reaction, the suspensions were further cooled until room temperature and washed with 0.1 M HCl solution, and deionized water respectively until pH~7. Then, the mixtures were dried for 12 hours at 80 °C, pulverized, and further calcined at 500 °C for 2 hours. The synthesized-TiO₂ were coded name **M5** and **M8** corresponding NaOH solution of 5 M and 8 M. The treated products with H₂O₂ were synthesized by a similar hydrothermal process using **M-TiO₂** and **C-TiO₂** applied with 8 M NaOH solution followed by a treating step with 2 mL H₂O₂ (**M8H**; **C8H**) at 60 °C for 12 hours.

2.3. Characterization of the product

The phase components were determined by powder XRD (D8 Advance Bruker) with Cu-K α radiation, 2 θ of 5°–80° and at a size step of 0.020 °.s⁻¹. The crystallite size of the particles has been calculated by the XRD patterns following Debye–Scherrer's equation: $d = (k\lambda) / (\beta \cos\theta)$. Where d is the average crystallite size of the particle, k (= 0.9) is a constant, λ is the X-ray wavelength, β is line broadening in radians, and θ is the maximum Bragg angle. The FT-IR spectra of the samples were recorded using Bruker Vertex 70 FT-IR with analyzed wavenumber from 600 cm⁻¹ to 4000 cm⁻¹. The field-emission scanning electron microscopy (JEOL-7600, JEOL Ltd.) equipped was used to investigate surface morphologies of samples with an accelerating voltage of 15 kV. Chemical bonds on the TiO₂ surface were identified by X-ray photoelectron spectroscopy (JEOL 9010, JEOL Co., Japan) with the calibration of all binding energies to C_{1s} at 285.0 eV. The XPS data were further analyzed statistically by the K-Means Clustering algorithm based on R software to demonstrate the significant

effects of the experimental factors on TiO₂ surface characteristics.

3. RESULTS AND DISCUSSIONS

3.1. Effects of NaOH concentrations on TiO₂ properties after the hydrothermal process.

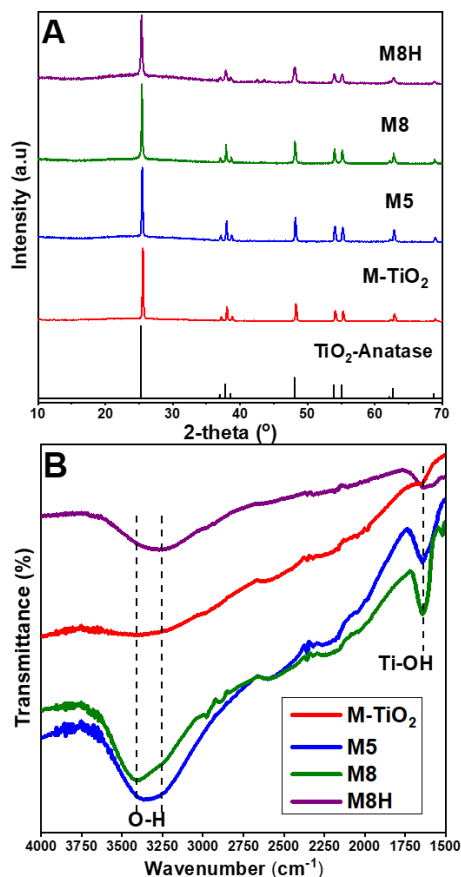


Figure 1. XRD pattern (A) and FT-IR (B) of **M-TiO₂** and TiO₂-synthesized: **M5**; **M8**; and **M8H**.

Fig. 1(A) shows the XRD patterns of **M-TiO₂** precursor and synthesized TiO₂ with different NaOH concentrations of 5 M and 8 M named **M5** and **M8**, respectively. The diffraction peaks were at 2-theta of 25.33°, 37.82°, and 48.08° respectively corresponding to lattice planes of (101), (004), and (200) [12] which characterized for anatase phase (JCPDS files No.21-1272). In comparison with **M-TiO₂**, the products showed rough baselines, and diffraction peaks with broader line widths indicating lower crystallinity. By using Debye-Scherrer's equation (**Table S1**), the average crystal sizes of synthesized TiO₂ decreased compared to the initial TiO₂. Besides, when the concentration of NaOH increased from 5 M to 8 M, sample **M8** exhibited a higher crystallinity and peaks' shifts to higher 2-theta.

This indicated that the increase in NaOH concentration had changed the crystal structure of TiO₂ and reduced the distance of lattice planes.

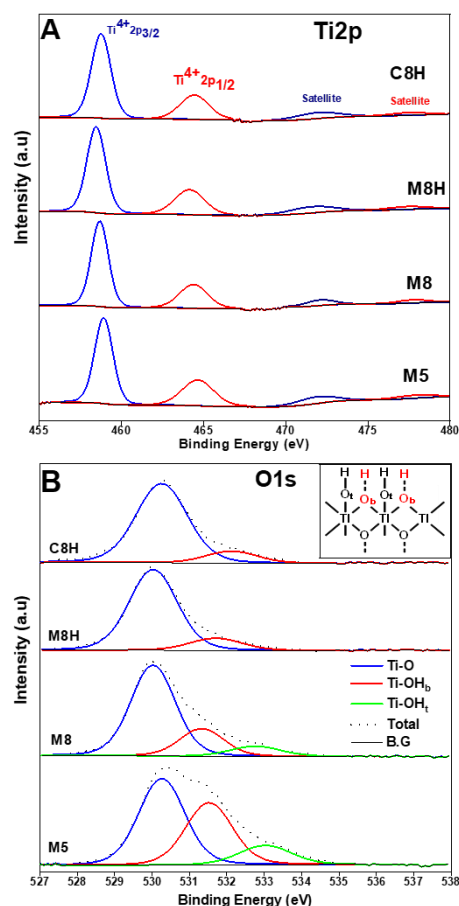


Figure 2. XPS core-level spectra of Ti_{2p} (A) and O_{1s} (B) of TiO₂-synthesized in different reaction conditions with Ti-OH_b: the bridging OH groups and Ti-OH_t: the terminal OH groups. The insert in figure B demonstrates bonding between Ti and OH groups including OH_b, OH_t.

The FT-IR spectra of TiO₂ samples are shown in **Fig. 1(B)**. The absorption bands around 3000–3600 cm⁻¹ was assigned for the stretching vibration of hydroxyl group or of adsorbed water on TiO₂ surface. The vibration peaks at 1640 cm⁻¹ corresponded to the bending vibration of O-H group on the surface [13]. These two signals' intensities of **M5** and **M8** were higher than those of **M-TiO₂**, indicating that the synthesis of TiO₂ by hydrothermal method in alkaline medium had improved the relative quantity of OH group on TiO₂ surface. The vibrational band of OH group in **M5** and **M8** samples was blue shifted that indicated the formation of OH terminal groups [10]. Besides, the intensity of the peak assigned for OH stretching vibration of **M8H** was

decreased significantly compared to the **M5** and **M8** samples.

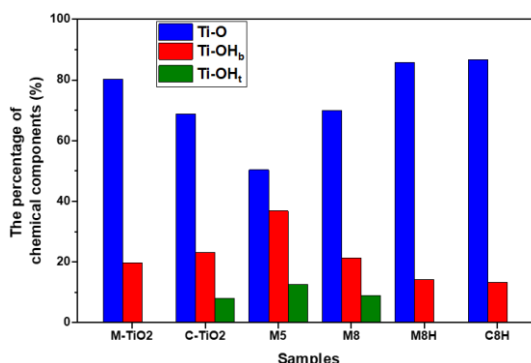


Figure 3. The percentage of chemical components consisting of Ti–O, the bridging OH groups in Ti–OH bond (Ti–OH_b), and H₂O physically adsorbed on TiO₂ surface with terminal OH groups (Ti–OH_t).

XPS Ti_{2p} spectra of **M5** and **M8** (**Fig. 2(A)**) expressed two characteristic peaks at 458.7 and 464.4 eV which were accounted for Ti⁴⁺_{2p3/2}, Ti⁴⁺_{2p1/2} and two satellite peaks appeared at higher binding energies around 472.0 and 478.0 eV. The signals were assigned for Ti⁴⁺ situated at octahedral sites and no peaks of Ti³⁺ were found [14]. For the O_{1s} spectra (**Fig. 2(B)**), all samples exhibited the signals at 530.0 – 530.2, 531.0 – 532.0, and > 532 eV corresponding to the bonding Ti–O in TiO₂ [15], the bridging OH groups denoted by Ti–OH, and H₂O physically adsorbed on TiO₂ surface with terminal OH groups [10], [15], respectively. By using concentrated NaOH solution (5 M & 8 M) during hydrothermal synthesis, the percentage of Ti–O bonding was decreased. Simultaneously, the bridging OH groups increased considerably and the terminal OH groups were newly formed in comparing to **M-TiO₂** precursor (see **Fig. 3** and **Table S2**). Furthermore, both H₂O₂-treated samples (**M8H** & **C8M**) demonstrated the slight decrease of the bridging OH component and without any signs of terminal OH groups. The XPS results were similar to FTIR spectra above. The bridging OH groups were well-known for their ability as hole scavenger which might lead to the improvement in photocatalytic performance [16], [17]. While the terminal OH groups may decrease the TiO₂ particle aggregation and enhance dye sensitization [10]. Depending on particular applications, one can choose the treatment which supports the desirable OH functional groups. In general, the

quantity of OH groups was improved by the action of hydrothermal synthesis and this quantity is favourable the adsorption of more dye for such application in dye-sensitized solar cell [18]. We would not further discuss about the application of these functional groups because it is out of the scope of this study. Moreover, TiO₂ samples did not to have any significant shifts in characteristic peaks (**Fig. 2**).

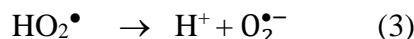
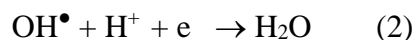
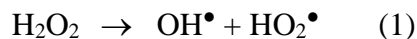
The FE–SEM image of **M–TiO₂** showed that the TiO₂ particles were spherical with rough surface (**Fig. 4(A)**). Additionally, the particle sizes were not uniform, ranging from 50–200 nm. After hydrothermal reaction, TiO₂ existed in tubular and spherical forms. For the sample **M5** (**Fig. 4(C)**) the product existed mainly as spherical particles with the sizes fluctuating around 40–300 nm. The FE–SEM of **M8** sample (**Fig. 4(D)**) also showed that TiO₂ had both spherical and tubular form. The tubular form distributed randomly with the lengths varying from several dozens to 120 nm with the diameter around 20–30 nm. During the hydrothermal process, when the NaOH concentration increased from 5 M to 8 M, the formation of TiO₂ nanotubes was dominant. There have been many studies that successfully synthesized TiO₂ nanotubes by hydrothermal under alkaline environment and the authors have proposed the mechanism of forming these nanotubes based on the breakage of bonding Ti–O–Ti by the reaction of NaOH and TiO₂ precursors from the 3D structure to form 2D TiO₂ nano-sheet then 1D nano-tubes [19]. In the current study, the hydrothermal reaction that used NaOH 5 M might not be adequate to break completely the bonding between Ti and O, so that, the TiO₂ particles existed mainly as spherical form. When the NaOH concentration was high enough (8 M), the reaction between 3D TiO₂ structure and NaOH might occur according to the aforementioned mechanism to form TiO₂ nanotubes. The results showed that the concentration of NaOH solution influenced on the structure and morphology of TiO₂, thus, we could control the TiO₂ shapes for specific purpose of usages by changing NaOH concentration. C.Y. Wu *et.al.* had been successfully synthesized the nanotubes TiO₂ by hydrothermal, also with high NaOH concentration (8 M) to improve the photocatalytic impact [20]. Our results were also in consistent with previous study.

3.2. Post-hydrothermal TiO₂ with H₂O₂ treatment

XRD pattern of **M8H** sample (**Fig. 1(A)**) showed that the H₂O₂ treatment of post-hydrothermal TiO₂ caused the low crystallinity of TiO₂. **M8H** sample also showed a rougher baseline and smaller crystal size while comparing to **M8** sample without H₂O₂ treatment. The FT-IR (**Fig. 1(B)**) exhibited the signal involved with the surface hydroxyl groups and adsorbed water but at lower intensities. From these results, we supposed that the H₂O₂ treatment of TiO₂ reduced the TiO₂ crystal size, –OH surface functional group and contributed to remove water on the surface of TiO₂. Hence, we processed the synthesis of TiO₂ under the same condition as in **M8H** sample but with a different TiO₂ precursor BA-100 to evaluate the impact of H₂O₂ on different precursors.

Similar to **M8** sample, **M8H** sample exhibited the characteristic signals of Ti⁴⁺ as Ti⁴⁺_{2p3/2}, Ti⁴⁺_{2p1/2} and satellite peaks without any shifts in binding energies (**Fig. 2(A)**) [15]. Nevertheless, in XPS O_{1s} spectra, the H₂O₂ treated samples showed only characteristic signals as Ti–O and Ti–O–H_b situated 530.0 – 530.2, 531.0 – 532.0, lacking of H₂O physically adsorbed on TiO₂ surface with terminal OH groups signal which was supposed to locate at > 533.0 eV (**Fig. 2(B), 3(B)**). The XPS results were in agreement with FT-IR spectra. The quantitative analysis of XPS peaks showed that the relative amount of Ti–O bonding increased while Ti–OH bonding reduced. C. Y. Wu *et al.* treated TiO₂ by H₂O₂, but TiO₂ particles were obtained in the shape of spheres sizing around 5 nm [20]. While C.Y. Wu *et al.* used H₂O₂ treatment prior to the hydrothermal reactions, we combined the H₂O₂ treatment for post-hydrothermal TiO₂ to ensure the safety during the experiment. These results proved that both factors H₂O₂ and the hierarchy of introducing the H₂O₂ treatment during the synthesis influenced on the final product. The effects of H₂O₂ on –OH surface functional group could be explained by the formation of H₂O between H⁺ and OH[•] radical decomposed from H₂O₂ [21] described in the equations (1) – (3). Besides that, a weak acid as H₂O₂, in the presence of metal oxide, could easily create radicals adsorbed, stabilized on the surface of TiO₂ and filled the oxygen vacancy [22]. The bonding composition analyzed from the O_{1s} peak of both

M8 and **C8H** samples were comparable despite different precursor sources.



Moreover, observation of FE-SEM of TiO₂-synthesized with assisted-H₂O₂ treatment using two different TiO₂ precursor sources was shown in **Fig. 4 (E, F)**. The products formed mainly nanotubes with 10-20 nm diameter around 80–400 nm and 50-300 nm length corresponding to **M8H** and **C8H**, respectively.

The results of XPS and FE-SEM demonstrated the impact of assisted-H₂O₂ on the chemical components, surface functional groups, shape-sized of TiO₂-synthesized with declining the –OH surface functional group. This could be suitable for application in the reflector titania layer in DSC which must use TiO₂ with lacked –OH groups to prevent the adsorption of the dye.

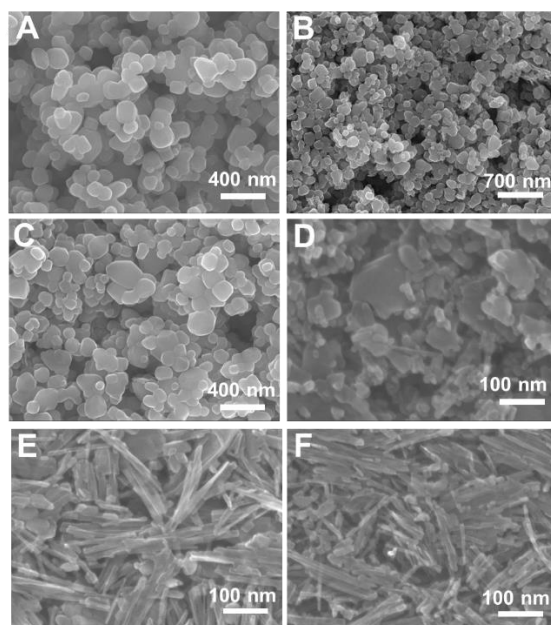


Figure 4. FE-SEM images of (A) M-TiO₂ (B) C-TiO₂ (C) M5 (D) M8 (E) M8H, and (F) C8H.

3.3. K-Means Clustering Algorithm calculations

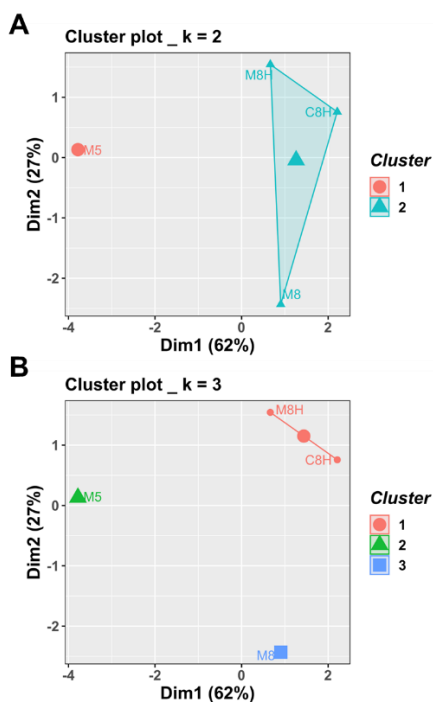


Figure 5. Scatter plot with grouping by k-mean algorithm

The XPS data were used as data input analyzed by the K-Means Clustering Algorithm on R software. **Fig. 5(A)** showed the dispersion diagrams of samples **M5**, **M8**, **M8H** and **C8H** which were analyzed by K-Means with $k = 2$, meaning that we divided the samples into two groups. The results confirmed a clear cluster of concentration group with group 1 – sample with NaOH 8 M and group 2 – sample with NaOH 5 M. This means the NaOH concentration affected strongly on the product properties. **Fig. 5(B)** showed the dispersion diagrams of the samples in three different groups ($k = 3$). The results showed that except for NaOH concentration, the H_2O_2 treatment also had the impact on the product characteristic. Despite the ways in grouping samples were into 2 or 3 groups, the **M8H** and **C8H** samples always belonged to the same group regardless the origin or the purity of the precursors. The results of statistical analysis were in consistent with the FE-SEM and FT-IR data. We supposed that both NaOH concentration and H_2O_2 treatment had major influences on the properties of TiO_2 products prepared by hydrothermal process. These valuable points should be notified in the experimental design to obtain appropriate TiO_2 product for different specific applications.

4. Conclusion

The chemical bonding composition and morphology of the TiO_2 surface can be controlled by NaOH-based hydrothermal processing followed by H_2O_2 treatment. Increasing NaOH concentration from 5 M to 8 M improved the relative quantity of Ti–O bonding at the expense of Ti–OH bonding and resulted in more nanotubes instead of spherical particles in TiO_2 structure. In addition, H_2O_2 treatment also increased the relative number of Ti–O bonding while reducing the size of TiO_2 nanotubes. Notably, starting TiO_2 precursors appear to have no discernable influence on the final TiO_2 products. Overall, we demonstrated that customized products can be achieved by adjusting the hydrothermal processing with NaOH and subsequent H_2O_2 treatment using relatively low-cost materials such as BA-100 TiO_2 in this study.

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