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# The Effect of Temperature to CTAB-assisted Solvothermal Synthesis of TiO<sub>2</sub>

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**Abstract.** Surface area has significant impact on the photocatalytic activity of semiconductor material. It was found that templates as structure directing agent played a role in regulating the surface area of materials. The most widely used as template is cetyltrimethylammonium bromide (CTAB) surfactant. In this research, TiO<sub>2</sub> was prepared by solvothermal method used temperature variations of 150, 175, 200, and 225 °C. The X-ray powder diffraction (XRD) data indicated that anatase phase of TiO<sub>2</sub> was successfully obtained with *I4<sub>1</sub>/amd* space group and as the synthesis temperature was increased, the crystallinity increases. The spectra infrared spectroscopy (IR) showed the broad peak situated at wavenumber 400-800 cm<sup>-1</sup> which was assigned to the stretching Ti-O vibration. Raman spectra showed peaks at wavenumber 145, 197, 397, 516, and 639 cm<sup>-1</sup> which were attributed to vibration modes of anatase. The scanning electron microscopy (SEM) image demonstrated the morphology particle has homogeneous distribution and irregular shape. Furthermore, Brunauer-Emmett-Teller (BET) specific surface area showed the CTAB-assisted TiO<sub>2</sub> which was synthesized at 175 °C has the highest surface area of 227.043 m<sup>2</sup>/g in this research among the others.

**Keywords:** TiO<sub>2</sub>, solvothermal, CTAB, surface area

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is an attractive semiconductor with widely advantages in various field due to its good chemical stability, economical cost, stable to light, non-toxic, chemically and biologically inert, thermodynamically stable, and high oxidizing ability [1-3]. As result, TiO<sub>2</sub> has broad applications such as photocatalyst, solar energy conversion, pigment, cosmetics, and medical applications [4-5]. TiO<sub>2</sub> semiconductor has three polymorphic crystal: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The rutile phase is the most stable phase and anatase phase usually exhibit the highest photocatalytic activity [6-7]. Surface area influences the photocatalytic activity of material, as the surface area is increasing the active site will increase, thus causing high rate degradation of organic materials [8]. The Previous researcher reported that TiO<sub>2</sub> has low surface area,



those are 53, 15, 10, and 98.2 m<sup>2</sup>/g for commercial TiO<sub>2</sub> degussa P25, TiO<sub>2</sub> Aldrich, TiO<sub>2</sub> Aldrich anatase, and pure TiO<sub>2</sub> nanopowder, respectively [9]. Thus, TiO<sub>2</sub> needs a modification to increase the surface area.

Template material is a structure directing agent to strike pores with the result is increasing the surface area [10-11]. Generally, templates are categorized into two groups of soft and hard templates. The common hard templates are polymer microspheres, carbon fiber, and anodic aluminium oxide (AAO), while soft templates are surfactant, polymer, and biopolymer. Nevertheless, the hard template has deficiency which is the elimination of template may lead to the collapse of material pore structure. On the other hand, the soft template is easier to remove than the hard template and the most widely used of soft template is surfactant [12-13]. Wei et al. [14] reported that synthesis TiO<sub>2</sub> with assistance of various surfactants, such as cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS), and diethanolamine (DEA) could increase the surface area of TiO<sub>2</sub>. The surface area of TiO<sub>2</sub>-nonmodified, TiO<sub>2</sub>-CTAB, TiO<sub>2</sub>-SDBS, and TiO<sub>2</sub>-DEA were 49.09, 83.45, 67.64, and 76.31 m<sup>2</sup>/g, respectively. The result showed that CTAB had the highest surface area than the other surfactants. Besides, it is well known that CTAB has capability to reduce the particle size and agglomeration of TiO<sub>2</sub> and improve the dispersion of TiO<sub>2</sub> [14-15].

It is well known that solvothermal has been widely applied in synthesis various materials such as metals, semiconductors, ceramics, and polymers. The solvothermal method is heterogeneous chemical reaction in isolated system with temperature presence above the boiling temperature of solvent used. The Solvothermal method has many advantages such as using low temperature, controllable particle size distribution and morphology [16-17], high homogeneity and purity, and improving crystallinity of TiO<sub>2</sub> [18]. There are many factors which are influencing the solvothermal synthesis such as temperature, experiment time, solvent type, precursor, and pH [19]. Wahi et al. [20] reported synthesis anatase TiO<sub>2</sub> using solvothermal method with temperature variations of 140-335 °C could decrease the surface area because the average grain size increased with increasing temperature. The increasing grain size occurred via Ostwald ripening, the process leads to dissolution of smaller grain size then diffusion of solute through liquid and reprecipitation into larger grain. TiO<sub>2</sub> material at temperature 140 °C had the highest surface area of 250.6 m<sup>2</sup>/g, otherwise at temperature 330 °C had the lowest surface area of 55 m<sup>2</sup>/g. Therefore, in this work, we investigated the effect of temperature to structure phase, morphology, and surface area of CTAB-assisted TiO<sub>2</sub> which was synthesized by solvothermal method.

## 2. Experimental Section

### 2.1. Materials

Titanium isopropoxide (TTIP) (Sigma –Aldrich 97%), cetyltrimethylammonium bromide (CTAB) [CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N(Br)(CH<sub>3</sub>)] 1 mM, isopropyl alcohol *p.a.*, and aquades.

### 2.2. Catalyst preparations

Material TiO<sub>2</sub> was prepared via solvothermal process with target yield about 2.5 g. Briefly, 0.0182 g of CTAB was added to 50 mL of isopropyl alcohol solvent and stirred for 30 minutes, vigorously. Next, 10 mL of TTIP was added drop by drop to the mixture solution under stirring condition. Acetic acid was added to the mixture until pH 1 and then sonicated for 5 minutes at room temperature. After sonication process, the as-prepared mixture transferred to a 100 mL teflon-lined stainless steel autoclave, sealed, and then heated at temperature variations of 150, 175, 200, and 225°C for 12 hours. After cooling at room temperature, the white precipitates were washed with isopropyl alcohol for 2-3 times, then dried at 100 °C for 12 hours.

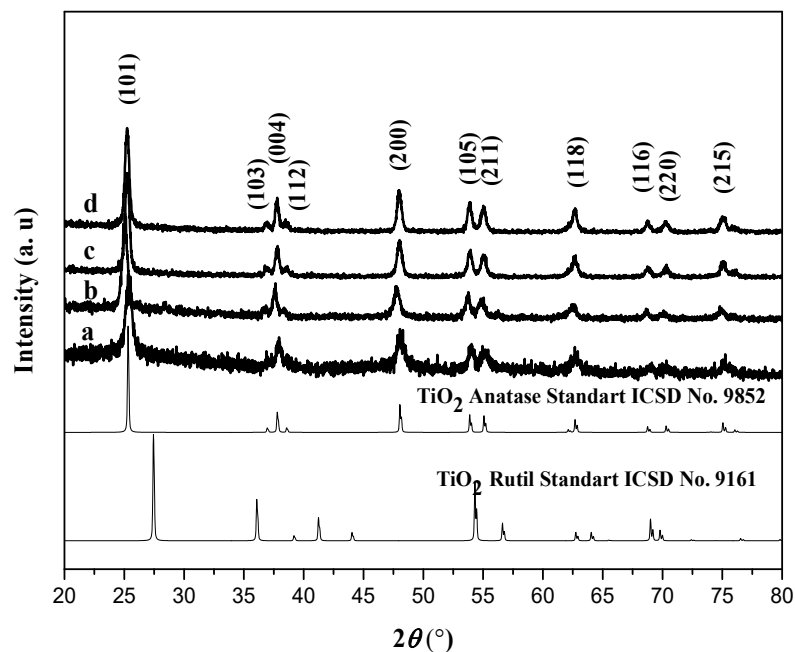
### 2.3. Characterizations

The characteristic structure of sample was studied by XRD Philip E'xpert Pro at range 2 $\theta$  = 20-80°. The XRD data were refined using Le Bail Method at Rietica program. The infrared vibration modes of

sample were measured using Varian 1000 FT-IR at spectral range 400-4000  $\text{cm}^{-1}$ . The Raman vibration modes of sample was measured using Bruker-Senterra Spectrometer at spectral range 50-3600  $\text{cm}^{-1}$  and using laser excitation source of 532 nm. The surface morphology of sample was observed using SEM-EDX FEI, Type: Inspect-S50. The specific surface area was estimated by BET surface area NOVA 1200e, Quantachrome.

### 3. Results and discussions

Figure 1 showed the X-ray diffractions pattern of CTAB-assisted  $\text{TiO}_2$  and can be seen that all the diffraction peaks were good agreement with pure anatase  $\text{TiO}_2$  (ICSD 9852 with space group  $I4_1/amd$ ). There was no other peak of any impurities or precursors residual. Furthermore, as the solvothermal temperature increased the intensity of XRD diffractions increased, which was indicating that the crystallinity of  $\text{TiO}_2$  was increasing [19, 21]. It indicated that heat treatment had ability to remove organic impurities within  $\text{TiO}_2$  and to promote crystallinity [22]. The results of refinement were showed in Figure 2 and the crystallographic data were summarised in Table 1. The result concluded that the lattice parameters were not different significantly, but the lowest value was obtained by CTAB-assisted  $\text{TiO}_2$  with temperature 175  $^{\circ}\text{C}$ . Furthermore, the agreement between sample and standart was referred to the pattern factor ( $R_p$ ), the weighted pattern factor ( $R_{wp}$ ), and the goodness of fit ( $GoF$ ) value (Table 2). Eddy, et al. [23] reported that the reliable value for both  $R_p$  and  $R_{wp}$  were under 15%, while the  $GoF$  was near or less than 2.



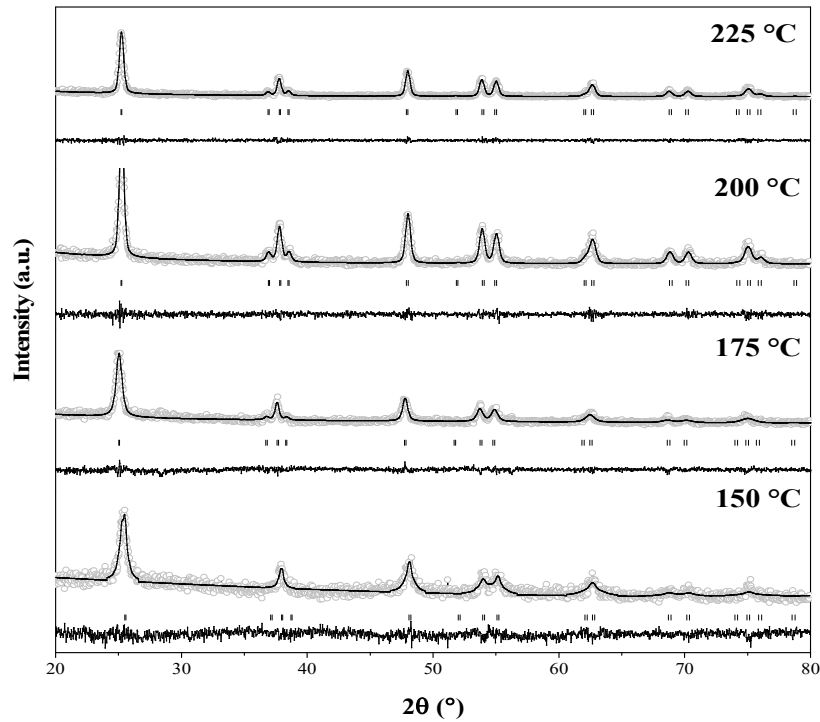
**Figure 1.** X-ray diffractions pattern of CTAB-assisted  $\text{TiO}_2$  at temperature (a) 150, (b) 175, (c) 200, and (d) 225  $^{\circ}\text{C}$  synthesized by solvothermal.

The XRD pattern were used to calculate the crystallite size of CTAB-assisted  $\text{TiO}_2$  materials using Debye-Scherrer equation (equation 1) [11].

$$S_{hkl} = \frac{K\lambda}{B \cos\theta} \quad (1)$$

$S_{hkl}$  is the average crystallite size for hkl peak in Angstrom ( $\text{\AA}$ ),  $K$  is the Scherrer constant (0.89),  $\lambda$  is the X-ray wavelength for Cu- $K\alpha_1$  radiation (1.5406  $\text{\AA}$ ),  $\theta$  is the diffracted angle at maximum intensity,

and  $B$  is the Full Width at Half Maximum (FWHM) in radians. The crystallite size of materials were summarised in Table 2 and showed that CTAB-assisted  $\text{TiO}_2$  with temperature 200 °C had the largest crystallite size in this research.



**Figure 2.** Refinement result of CTAB-assisted  $\text{TiO}_2$  obtained in different synthesis temperatures.

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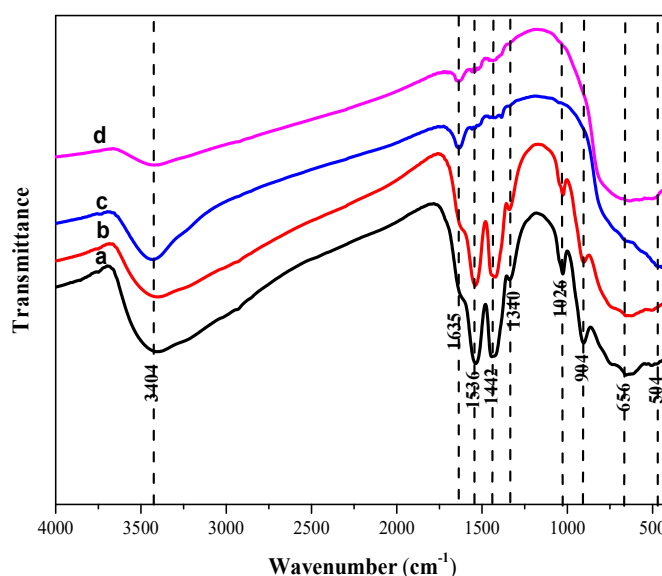
**Table 1.** Crystallographic data of CTAB-assisted  $\text{TiO}_2$  with different synthesis temperature

Materials	a=b (Å)	c (Å)	Rp (%)	Rwp (%)	GoF
$\text{TiO}_2$ -CTAB 150 °C	3.890(4)	9.769(5)	14.70	13.88	0.04
$\text{TiO}_2$ -CTAB 175 °C	3.786(2)	9.484(9)	12.30	8.93	0.49
$\text{TiO}_2$ -CTAB 200 °C	3.7888(5)	9.488(1)	14.04	9.92	0.03
$\text{TiO}_2$ -CTAB 225 °C	3.7902(4)	9.494(1)	13.95	9.84	0.03

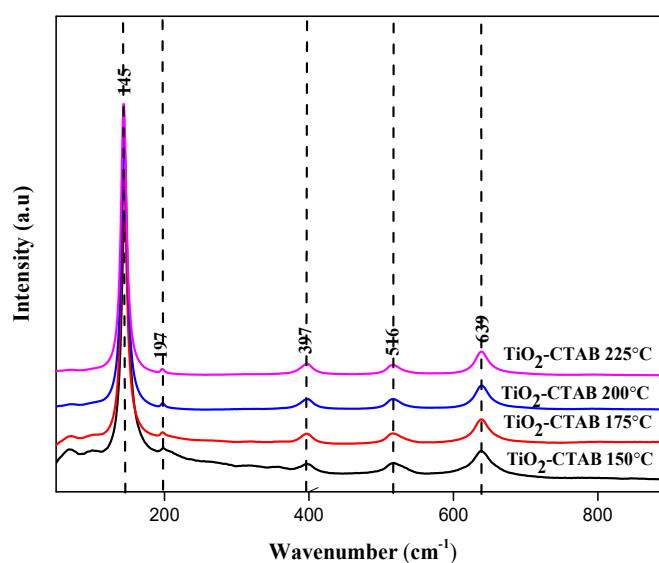
**Table 2.** Crystallite size of CTAB-assisted  $\text{TiO}_2$  obtained in different synthesis temperature.

Materials	Crystallite size (nm)
$\text{TiO}_2$ -CTAB 150 °C	14.40
$\text{TiO}_2$ -CTAB 175 °C	58.74
$\text{TiO}_2$ -CTAB 200 °C	78.15
$\text{TiO}_2$ -CTAB 225 °C	23.42

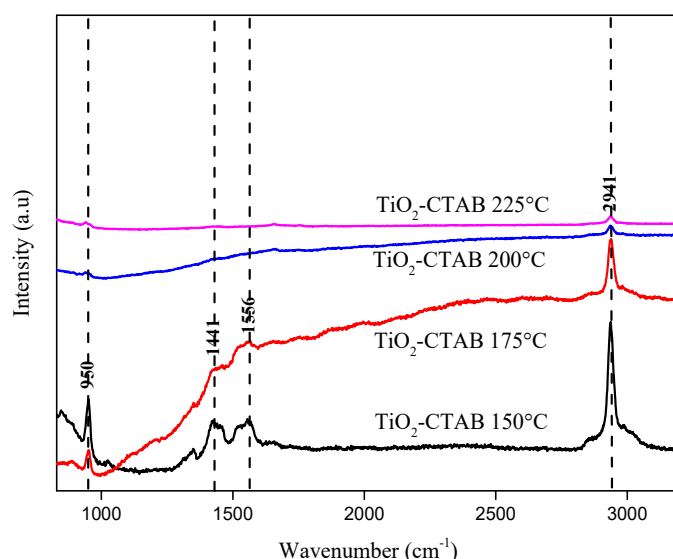
The IR spectra of sample were showed in Figure 3. The band in range  $400\text{--}800\text{ cm}^{-1}$  was assigned to vibration mode of Ti-O bonds in crystalline anatase phase [24-27]. The impurities bands were identified, the absorption peaks at  $3404$  and  $1635\text{ cm}^{-1}$  were attributed to hydroxyl functional group of absorbed water and Ti-OH, respectively [14, 25]. The bands at  $1536$  and  $904\text{ cm}^{-1}$  were the characteristics bands of CTAB, while the bands at  $1442$  and  $1340\text{ cm}^{-1}$  were C-H stretching and C-H bending of CTAB [28], and band at  $1026\text{ cm}^{-1}$  was C-O bending of acetic acid [29]. The spectra showed that the impurities peaks were decreasing with increasing solvothermal temperature, which was indicating that impurities functional group were diminished in the materials [21].



**Figure 3.** IR spectra of CTAB-assisted  $\text{TiO}_2$  synthesized by solvothermal with temperature variations.



**Figure 4.** Raman spectra of CTAB-assisted  $\text{TiO}_2$  synthesized by solvothermal with temperature variations.



**Figure 5.** Raman spectra of CTAB-assisted  $\text{TiO}_2$  at wavenumbers 800-3200  $\text{cm}^{-1}$  synthesized by solvothermal with temperature variations.

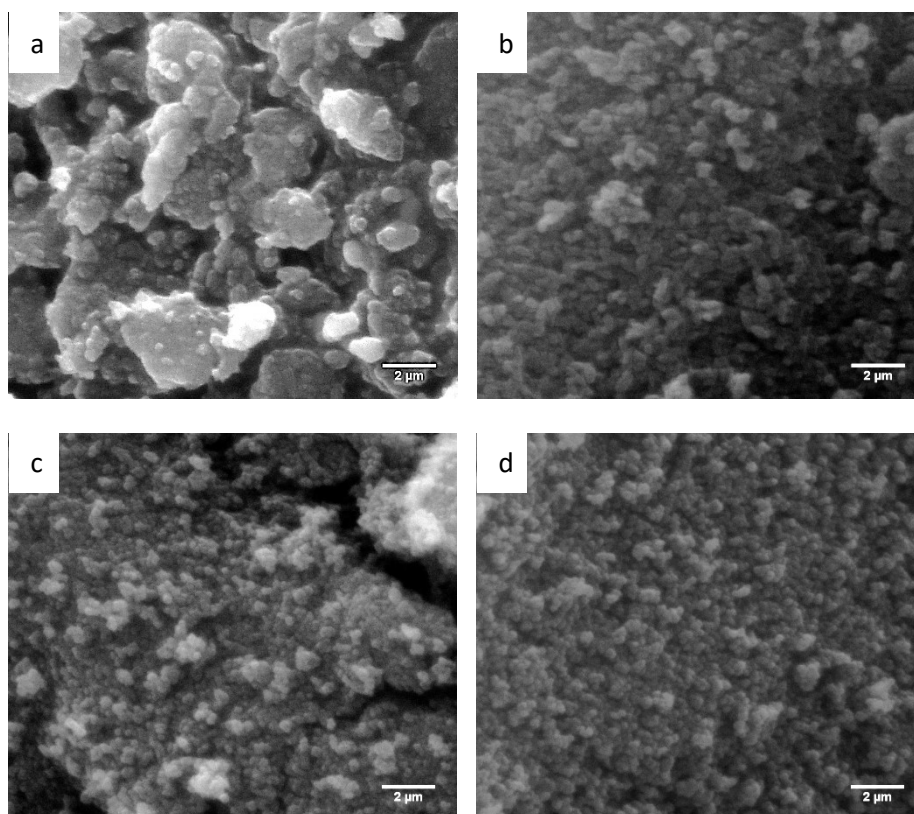
Figure 4 showed the Raman vibration of  $\text{TiO}_2$  and found the five Raman active modes at 145, 197, 397, 516, and 639  $\text{cm}^{-1}$  which were assigned to  $E_g$ ,  $B_{1g}$ ,  $A_{1g}$ ,  $E_g$ , and  $E_g$ , respectively [30-31]. The observed peaks at spectral range of 800-3200  $\text{cm}^{-1}$  related to the impurities peaks of precursors residual which was depicted in Figure 5. The peaks at 950 and 1441  $\text{cm}^{-1}$  were correspond to  $\text{CH}_2$  rocking mode and bending of CTAB [32-33], while peaks at 1556 and 2941  $\text{cm}^{-1}$  were correspond to  $\text{C}=\text{N}$  and  $\text{CH}_3$  from  $-\text{N}^+(\text{CH}_3)_3$  symmetric stretching vibrations of CTAB [34]. The intensity of CTAB Raman vibration mode decreased at synthesis temperature of 200 and 225  $^\circ\text{C}$  which were indicating that the concentration of CTAB in samples decreased. The decreasing in intensity occurred because CTAB evaporated at higher synthesis temperature.

**Table 3.** BET surface area of CTAB-assisted  $\text{TiO}_2$  synthesized by solvothermal with temperature variations.

Materials	Surface area ( $\text{m}^2/\text{g}$ )
$\text{TiO}_2$ -CTAB 150 $^\circ\text{C}$	132.892
$\text{TiO}_2$ -CTAB 175 $^\circ\text{C}$	227.043
$\text{TiO}_2$ -CTAB 200 $^\circ\text{C}$	60.104
$\text{TiO}_2$ -CTAB 225 $^\circ\text{C}$	62.896

The BET measurement results were summarised in Table 3 and showed that CTAB-assisted  $\text{TiO}_2$  at 175  $^\circ\text{C}$  had the highest surface area. The high surface area could provide more active sites which is beneficial to the photocatalytic activity. Besides, the results also indicated that high temperature at 200 and 225  $^\circ\text{C}$  in solvothermal system could reduce the surface area. The low surface area could probably occur because of particle agglomeration through Ostwald ripening process. Researchers reported that agglomerated particle was undesirable because reduce the surface area [36-38].

The SEM images in Figure 6 showed that the shapes of CTAB-assisted  $\text{TiO}_2$  materials were still irregular, but generally they were in spherical shape. Material CTAB-assisted  $\text{TiO}_2$  at 175 °C has the most homogeneous surface distribution, while CTAB-assisted  $\text{TiO}_2$  at 200 °C and 225 °C were agglomerated. Agglomeration is a process of particles dispersed in liquid phase stick to each other and spontaneously forms irregular particle cluster or aggregate. Agglomeration occurred as the effect of high solvothermal temperature which were increasing the surface energy, so to minimize this energy the particles tend to agglomerate [35].



**Figure 6.** SEM images of CTAB-assisted  $\text{TiO}_2$  at temperature (a) 150, (b) 175, (c) 200, and (d) 225 °C synthesized by solvothermal.

#### 4. Conclusions

The anatase phase of  $\text{TiO}_2$  was successfully prepared by solvothermal method using TTIP as titanium source and CTAB surfactant in isopropanol solvent. The surface area of  $\text{TiO}_2$  was modified by assistance of CTAB surfactant and temperature variation during preparation. The highest surface area was obtained for the sample synthesized at 175 °C. However, further temperature at 200 and 225 °C caused an agglomeration of particles and consequently diminishing the surface area of CTAB-assisted  $\text{TiO}_2$  material.

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#### References

- [1] Linsebigler A L, Lu G, and Yates J T 1995 *Chem. Rev.* **95** 735-758
- [2] Pookmanee P, Phiwichai I, Yoriya S, Puntharod R, Sangrichan S and Phanichphant S 2013



*Ferroelectrics* **457** 30-38

- [3] Sayed M, Pingfeng F, Khan H M and Zhang P 2014 *Int. J. Photoenergy* 1-11
- [4] Lusvardi G, Barani C, Giubertoni F and Paganelli G 2017 *Materials* **10** 1-11
- [5] Ge M, Cao C, Huang J, Li S, Chen Z, Zhang K Q, Al-Deyab S S and Lai Y 2016 *J. Mater. Chem. A* **4** 6772–6801
- [6] Yang L, Wang C, Liu Z, Liu X, Song Y, Feng X and Zhang B 2017 *Ceram. Int.* 1-25
- [7] Pookmanee P, Phiwichai I, Yoriya S, Puntharod R, Sangsrirachan S, Kittikul J and Phanichphant S 2015 *Mater. Sci. Forum* **804** 209–212
- [8] Wen J, Li X, Liu W, Fang Y, Xie J and Xu Y 2015 *Chinese J. Catal.* **36** 2049–2070
- [9] Hussain M, Ceccarelli R, Marchisio D L, Fino D, Russo N and Geobaldo F 2010 *Chem. Eng. J.* **157** 45–51
- [10] Wu S H, Mou C Y and Lin H P 2013 *Chem. Soc. Rev.* 1-14
- [11] Marien C B D, Marchal C, Koch A, Robert D and Drogui P 2016 *Environ. Sci. Pollut. Res.* 1-7
- [12] Xie Y, Kocaefe D, Chen C and Kocaefe Y 2016 *J. Nanomater.* 1-10
- [13] Ramimoghaddam D, Bagheri S and Hamid S B A 2014 *BioMed. Res. Int.* 1-7
- [14] Wei J, Wen X and Zhu F 2018 *J. Nanomater.* 1-7
- [15] Vishwanath A D, Shankar J S, Eknath N M, Eknath A A and Haribhau K N 2017 *Orient. J. Chem.* **33** 104-112
- [16] Canu G and Buscaglia V 2017 *Cryst Eng Comm.* **19** 3867–3891
- [17] Wang Y, Sun J, Fan X and Yu X 2011 *Ceram. Int.* **37** 3431–3436
- [18] Li J, Wu Q and Wu J 2015 *Handbook of Nanoparticle* 1-28
- [19] Khaksar E, Afarani M S and Samimi A 2016 *J. Metall. Mater. Eng.* **27** 1-2
- [20] Wahi R K, Liu Y, Falkner J C and Colvin V L 2006 *J. Colloid Interface Sci.* **302** 530–536
- [21] Perumal S 2015 *Int. J. Eng. Res. Appl.* **5** 115–118
- [22] Othman S H, Rashid S A, Ghazi T I M and Abdullah N 2010 *J. Nanomater.* 1-11
- [23] Eddya M, Tbib B and El-Hami K 2018 *J. Mater. Environ. Sci.* **9** 3087–3093
- [24] Sridevi D V, Ramesh V, Sakthivel T, Geetha K, Ratchagar V, Jagannathan K, Rajarajan K and Ramachadran K 2017 *Mechanics, MMSE* 4-9
- [25] Wu W, Zhang L, Zhai X, Liang C and Yu K 2018 *Nanomater. Nanotechno.* **8** 1-8
- [26] Ramalingam R J, Arunachalam P, Radhika T, Anju K R, Nimitha K C and al-Lohedan H A 2017 *Int. J. Electrochem. Sci.* **12** 797–811
- [27] Gardy J, Hassanpour A, Lai X and Ahmed M H 2016 *Applied Catal. A* **527** 81–95
- [28] Nithiyanantham U, Ramadoss A and Kundu S 2014 *RSC Adv.* **4** 35659–35672,
- [29] Dong K, Choi J, Lee Y D, Kang B H, Yu Y, Choi H H and Ju B K 2013 *Nanoscale. Res. Lett.* **8** 12
- [30] Syzrantsev V, Paukshtis E, Larina T, Chesalov Y, Bardakhanov S and Nomoev A 2018 *J. Nanomater.* 1-11
- [31] Ohsaka T, Izumi F and Fujiki Y 1978 *J. Raman Spectrosc.* **7** 321–324
- [32] Foucault R, Birke R L and Lombardi J R 2003 *Langmuir* **19** 8818–8827
- [33] Duan H, Jia L, Chen M, Ge S and Guo X 2016 *Mater. Express* **6** 77–82
- [34] Joseph D, Rodriguez R D, Verma A, Pousaneh E, Zahn D R T, Lang H and Chandra S 2017 *RSC Adv.* **7** 3628–3634
- [35] Liu X, Ye L, Liu S, Li Y and Ji X 2016 *Sci. Rep.* 1-9
- [36] Yunus N N, Hamzah F, So'aib M S and Krishnan J 2017 *J. Mater. Sci. Eng.* **206** 1-7
- [37] Lin Y, Bai H, Lin C and Wu J 2013 *Aerosol Air Qual. Res.* **13** 1512–1520
- [38] Sieland F, Schneider J and Bahnemann D W 2018 *Phys. Chem. Chem. Phys.* **20** 8118-8132