Effect of pH on the formation of amorphous TiO$_2$ complexes and TiO$_2$ anatase during pyrolysis of aqueous TiCl$_4$ solution

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Abstract: The TiO$_2$ nanostructures resulted by pyrolysis of TiCl$_4$ at low temperature of 80 °C are found to be a mixture of amorphous TiO$_2$ complexes and anatase nanostructure whose ratio depends on the pH of the pyrolysis medium. At low pH level, the resulting TiO$_2$ nanostructure is predominant anatase and gradually shifts to the amorphous TiO$_2$ complexes with pH level increasing. By means of heat treatment, the amorphous TiO$_2$ complexes can be converted back to the anatase nanostructure and then transform to rutile with the elevating temperature. Amongst of the TiO$_2$ nanostructure recovered from amorphous TiO$_2$ complexes, the anatase shows to be the most effective photocatalyst in decomposition of methylene blue.

Keywords: photocatalyst, amorphous TiO$_2$ complexes, TiO$_2$, anatase nanostructure.

1. Introduction

Titanium dioxide (TiO$_2$), a typical metal oxide with high refractive index, chemical stability, long durability, and nontoxicity has been widely used for many applications such as white pigments, textiles, papers, cosmetics, medicines, ceramics, etc. As a $n$-type wide bandgap semiconductor, TiO$_2$ exhibits a unique photoinduced effect that involves photogenerated charge carriers on the material surface that initiate strong redox reaction of adsorbed substances and hydrophilic conversion of itself [1, 2]. The effect offers more potential applications involving photochemical processes such as splitting hydrogen from water, photocatalyst, photoconductor, environment cleaning, antibacterial purpose, chemical sensors, ultraviolet fillers, dye-sensitized solar cells (DSSC) and so forth [3 - 5].

Under normal condition, TiO$_2$ exists in three main structures: stable rutile, metastable anatase, and brookite phase. For pure phase it is generally accepted that anatase exhibits a higher photocatalytic activity compared to that of rutile despite of its larger band gap (3.2 eV for anatase vs. 3.0 eV for rutile). Longer lifetime for photo-excited electrons and holes in the indirect band gap of TiO$_2$ anatase semiconductor is accounted for the feature [6]. On the other hand, TiO$_2$ in the microstructure have been considered as a poor photocatalyst but in the nanostructured form, due to the quantum confinement the material shows stronger photocatalytic activity in comparison to that of the microstructure [7]. The unique photocatalyst of TiO$_2$ is size and structure dependent. Therefore, clarification out the synthesis conditions to achieve desirable nanostructures of TiO$_2$ is of important to diverse photocatalystic applications.
With regard to the synthesis of TiO₂ nanostructure, a variety of techniques based on pyrolysis of Ti precursors such as hydrothermal, solvothermal, sol-gel, direct oxidation, chemical vapor deposition (CVD), electrodeposition, sonochemical, and microwave method has been used [8]. Pyrolysis offers a simple route to synthesize well-crystalline TiO₂ using inexpensive precursors such as titanium (IV) tetrachloride TiCl₄, titanium (IV) butoxide, titanium(IV) isopropanoxide, amorphous TiO₂, P₂₅, etc. In addition, the pyrolysis modest medium of low temperature and adjustable pyrolysis time can provide an effective environment for the synthesis of TiO₂ with high purity, good dispersion and controllable crystalline. From the viewpoint of chemical thermodynamics, before decomposing into TiO₂ either in the form of anatase, brookite or rutile, the titanium precursor undergoes a series of amorphous TiO₂ complexes (or intermediates) such as Ti₂O₃Cl⁴(OH)₂⁺ resulting from pyrolysis of TiCl₄, [Ti(OH)₄·{(H₂O)}₂]ⁿ⁻ from Ti(IV)-butoxide or [Ti₃O₆(UBu)(O═O═O)(Cl)₆−{(OEt)}₄] from alkoxide metal M(OR)₆ [9, 10, 11]. Hence, the amorphous TiO₂ complexes also can be used as a kind of secondary precursor to produce desirable brookite, anatase, or rutile structure [12]. Elucidation out of the formation and conversion of amorphous TiO₂ complexes is assumed to be a critical point to synthesize and bring in desirable TiO₂ nanostructures. With respect to the amorphous Ti₂O₃Cl⁴(OH)₂⁺ complexes resulted from pyrolysis of TiCl₄, the substitution of OH for Cl radicals in the complexes does not lead to much change in the core involving the Ti atoms but a difference in bond lengths and potential energy surfaces [9]. Change relative ratio of the Cl and OH radicals then is considered to be an effective approach to control the complex intermediates and realize the final desirable TiO₂ nanostructures. For example, an increase of the Cl radical in the pyrolysis medium by addition of HCl or higher TiCl₄ concentration has shown to promote the formation of the brookite and rutile structure [13, 14]. In an experiment made on pyrolysis of aqueous TiCl₄ solution with HCl additive, we have found that a nanocrystalline mixture of both the anatase and rutile phase is resulted. The TiO₂ anatase mainly suspends in the aqueous solution while the TiO₂ rutile predominantly deposits in the sedimentation [15, 16]. Higher HCl concentration enables the agglomeration of anatase particles and enhances the anatase to rutile transition due to the compensation of Cl radical for the positive charge of polyhedral complexes [15]. On the other hand, an increase of the OH radical in the TiCl₄ pyrolysis medium by addition of a basic agent such as NH₄OH is expected to give the additional modification on the complexes. Based on those considerations, in this study an experiment is carried on to investigate the effect of pH level (or OH radical) on the formation of amorphous TiO₂ complexes as well as of final anatase nanostructure resulting from pyrolysis of aqueous TiCl₄ solution.

2. Results and Discussion

Experiments show that the additive NH₄OH significantly affects the appearance and properties of TiO₂ nanostructures in the resulting materials. As clearly seen in Figure 1, the resulting aqueous solution appears transparent at low pH level but gradually changes to slightly opalescent and then separates into transparent and milky parts when the pH level exceeding 2.40. The separated milky column increases with NH₄OH and becomes unchanged as pH level exceeding 7.34. Depending on the transparent or milky state, the surface morphology of the resulting materials transforms from grain to gelation structure as shown in the SEM images in Figure 2. In the sample with pH of 0.98, the resulting material grains are uniform granular with mean size of around 50-70 nm, that in turn has found to be clusters of anatase nanoparticles of 4-5 nm in the mean size [15]. However, when the pH level of the reactive medium increases, the resulting material grain increasingly inflates to coagulated clusters of 150-200 nm in size and gradually become jellylike or amorphous as shown in Fig. 2b to Fig. 2d.
Figure 2. SEM images of TiO$_2$ resulting from pyrolysis of TiCl$_4$ in different pH medium at 80 °C: (a) pH = 0.98; (b) pH = 2.45; (c) pH = 10.0 transparent part; (d) pH = 10.0 milky part.

X-ray diffraction spectra in Figure 3 show the evolution of the resulting materials depending on the pH level, i.e., on NH$_4$OH additive. In the sample with pH level of 0.98, the XRD pattern contains principal peak around 25.29° and the other peaks around 37.80°, 48.05°, 53.89°, 62.68° respectively assigning for the diffraction of anatase structure at (101) and (004), (200), (105), (204) planes (JCPDS no. 00-021-1272). When NH$_4$OH is added, together with the diffraction peaks from anatase the other sharp diffraction peaks at 22.98°, 32.69°, 40.31°, 46.88°, 52.80°, 58.29°, 68.43° standing for the diffractions at (100), (110), (111), (200), (210), (211), and (220) planes, respectively from NH$_4$Cl crystal [17] are emerged. With the increase of pH level as NH$_4$OH additive increasing, the TiO$_2$ diffraction in the XRD pattern is gradually desapeared. The gradual disappearance of TiO$_2$ diffraction in XRD pattern is account for the gradual conversion from TiO$_2$ anatase to amorphous TiO$_2$ complexes. Using Scherrer equation, i.e., $D = \frac{k\lambda}{\beta \cos \theta}$, where $k = 0.94$, $\lambda = 0.154$ nm and $\beta$ is FWHM at diffraction angle $\theta$ according to (101) peak to calculate the mean size $D$ of anatase particles, it has found that the mean sizes of anatase particle is almost unchanged around 4.5 nm as given in Table 1. This value is considered to be the limitation of anatase size in the conversion to amorphous TiO$_2$ complexes.

Table 1. The mean size of anatase particle resulted from pyrolysis of TiCl$_4$ in different pH medium at 80 °C.

| pH   | (101) peak FWHM | Size (nm) | Agent addition |
|------|-----------------|-----------|----------------|
| 0.98 | 2.007           | 4.3       | No addition    |
| 1.36 | 1.889           | 4.5       | NH$_4$OH       |
| 3.91 | 1.830           | 4.7       | NH$_4$OH       |
| 7.34 | 1.888           | 4.5       | NH$_4$OH       |
| 10.04| -               | -         | NH$_4$OH       |
Raman spectra also confirm the presence of anatase and NH$_4$Cl in the resulting materials. As shown in Figure 4, in the starting materials, namely, the sample with pH level of 0.98, the spectrum exhibits vibrational mode around 155 cm$^{-1}$, 399 cm$^{-1}$, 513 cm$^{-1}$ and 634 cm$^{-1}$ respectively representing the $E_g$, $B_{3g}$, $A_{1g} + B_{1g}$ and $E_g$ modes of anatase structure [18]. The presence of NH$_4$Cl in the materials gives rise to a broad saddle spectrum consisting of two vibration modes around 168 cm$^{-1}$ and 144 cm$^{-1}$ that is assumed to be the supposition of $E_g$ vibration mode of anatase and $\nu_2$, $\nu_3$ and $\nu_4$ vibration modes of NH$_4$Cl oscillating against Cl along (100) direction and along three orthogonal directions [20].

![Raman spectra](image)

**Figure 4.** Raman spectra of TiO$_2$ resulting from pyrolysis of TiCl$_4$ in different pH medium at 80 °C.

![EDS spectra](image)

**Figure 5.** EDS spectra of sample extracted from the milky part a) and from the transparent part b) that is extracted from pyrolysis of TiCl$_4$ in a medium with pH = 10.04.

The appearance of transparent, opalescent and separable milky part in the solution is believed to be due to the appearance and increase of amorphous TiO$_2$ complexes forming in the pyrolysis medium. At low pH level, in the acidic aqueous medium with higher concentration of hydrogen ions the formation of amorphous TiO$_2$ complexes is negligible, the resulting anatase is crystallized in the form of grain structure with sharp boundary. The presence of NH$_4$OH in the pyrolysis medium will raise the pH level and then the OH radical that promotes the formation of amorphous TiO$_2$ complexes. Consequently, with the increase in NH$_4$OH additive, the separated milky fraction in the medium is gradually increased in agreement with the gradual decrease of anatase diffraction in the XRD spectra. When the pH level exceeding 7.34, the milky column is unchanged even though the NH$_4$OH additive keeps increasing. Furthermore, the EDS spectra show that no trace of Ti presents in the transparent but in the milky part as given in Figure 5. This indirectly indicates that the decomposed TiCl$_4$ precursor is totally converted into...
amorphous TiO$_2$ complexes as the pH level exceeding 7.34. Due to the amorphous nature, no diffraction pattern of amorphous TiO$_2$ complexes is observed in XRD spectra as pH level beyond that point.

![HRTEM image](image.png)

Figure 6. The appearance of anatase nanoparticle scatteringly embedded in the amorphous TiO$_2$ complexes.

HRTEM image taken from milky sample with pH level of 10.04 as given in Figure 6 shows the appearance of tiny nanocrystallites scatteringly embedded in an amorphous medium. The amorphous medium surrounding materials is considered to be the amorphous TiO$_2$ complexes. A lattice spacing of the tiny nanocrystallite around 0.346 nm is identical as the lattice spacing of the (101) plane of TiO$_2$ anatase. The estimated size of TiO$_2$: anatase particle is comparable to those calculated from XRD pattern, around 4.5 nm that is considered to be the size limitation of anatase in equilibrium with amorphous TiO$_2$ complexes. The presence of anatase nanoparticles embedded in the amorphous TiO$_2$ complexes elucidates for the appearance of $E_g$ vibration mode of anatase in Raman spectra in Figure 4.

![XRD spectra](image.png)

Figure 7. XRD spectra of TiO$_2$: that resulted from pyrolysis of TiCl$_4$ in the medium with pH =10.04 at 80 °C and then are treated in different elevated temperature, A (anatase), B (brookite), R (rutile), N (ammonium chloride).
Under heat treatment at elevated temperature, the XRD and Raman spectra demonstrate the conversion from amorphous TiO₂ complexes back to anatase and then from anatase to rutile. At heating temperature below 200 °C, the XRD pattern in Figure 7 shows only the trace of NH₄Cl but not anatase nor brookite nor rutile. However, when heating temperature exceeds 200 °C the anatase diffraction is gradually emerging while NH₄Cl diffraction is gradually disappearing in the XRD patterns. The disappearance of NH₄Cl is accounted for the decomposition of the materials into NH₃ and HCl gases while the appearance of TiO₂ anatase is explained from the decomposition and recrystallization of amorphous TiO₂ complexes at elevated temperature. When the heating temperature exceeds 300 °C, the NH₄Cl is completely decomposed and the complexes is totally converted into TiO₂ nanostructure with predominant anatase. The brookite and rutile structure are hardly observed in the XRD patterns and can be neglected in the conversion process. When the heating temperature exceeds 450 °C the appearance of rutile diffraction in the XRD patterns indicates the onset of the anatase-rutile transition. The mean size of anatase calculated from XRD patterns is found to grow from around 4.5 nm at heating temperature of 200 °C to 8.9 nm at heating temperature of 600 °C as given in Table 2. For the sample with pH level of 0.98, the anatase is predominant over amorphous TiO₂ complexes, the heat treatment is merely the mean to enable the separation of the anatase nanoparticle from the cluster.

![Raman spectra of TiO₂](image)

**Figure 8.** (a) Raman spectra of TiO₂ that resulted from pyrolysis of TiCl₄ in the medium with pH = 10.04 at 80 °C and then are treated in different temperature; (b) blue shift of E₈ vibration mode as the heating temperature increases from 200 °C to 600 °C.

The Raman spectra also verify the conversion of anatase from the amorphous TiO₂ complexes (the milky part) when it is heat up as given in Figure 8. With baking temperature below 200 °C the Raman spectrum is a composition of NH₄Cl vibration mode centered around 168 cm⁻¹ and 144 cm⁻¹ and the Eg vibration mode of TiO₂ anatase at 147 cm⁻¹. As the heating temperature increases from 200 °C to 600 °C the E₈ vibration mode shows a shift in frequency from 154 cm⁻¹ to 145 cm⁻¹ and a shrinkage in FWHM (see in Table 2). The feature accounts for the size growth from 4.5 nm to 8.9 nm of the TiO₂ anatase nanocrystallites [18].

The formation of TiO₂ nanostructures by pyrolysis of TiCl₄ in elevated pH medium can be explained by the decomposition, dissolution mechanism [20]. At elevated temperature exceeding 80 °C, TiCl₄ is decomposed into HCl and amorphous TiO₂Cl₂ or TiO₂Cl₂(OH)ₙ complexes and then converted into TiO₂ anatase nanostructure. The component ratio of the amorphous TiO₂ complexes and TiO₂ anatase is established by an equilibrium balance between H, OH and Cl radical concentration in the medium. At low pH level, the Cl radical promote the formation of anatase nanocrystallites whose mean size bellow the limitation for the anatase to rutile transition [15, 16]. On the other hand, at high pH level the presence of OH and NH₄ radical eliminates the activity of Cl radical and brings in a consequent materials of OH dominant amorphous TiO₂(OH)ₙ or [Ti(OH)₂(n(H₂O)₂)]⁺⁺ complexes. As a result, at low pH level the anatase fraction is dominant while the amorphous TiO₂ complexes is
dominant at high pH level. The amorphous TiO$_2$ complexes can be converted back to the TiO$_2$ anatase nanoparticles by heat treatment at elevated temperature around 300 °C.

Experiments show that amorphous TiO$_2$ complexes and TiO$_2$ anatase nanoparticles exhibit strong photocatalytic activity upon exposure to UV light radiation. Quatitatively, a mixture of 50 ml of 0.25 μmol methylene blue (MB) aqueous solution and 50.0 mg of amorphous TiO$_2$ complexes or TiO$_2$ anatase nanoparticles is stirred magnetically under dark conditions for 30 min before exposed upon a UV mercury vapor lamp. After a fixed UV exposure duration, 1.0 ml of the aqueous solution is taken out for UV-Vis characterization. By comparison of the relative intensity of MB principal adsorption peak in the UV-Vis spectrum, the percentage of oxidated MB in the solution is deduced and then the photocatalytic activity of the materials is calculated.

With respect to the amorphous TiO$_2$ complexes, the photocatalytic activity of the materials is shown to be dependent to the heating temperature. As illuminated in Figure 9a, the rates of photocatalytic oxidation of MB show to be exponential reduction that is well fitted to the Langmuir–Hinshelwood (L-H) kinetics model [22]. When MB concentration is small the L-H equation can be simplified to an apparent first-order: \( \ln(C_0/C) = kt \) or \( C = C_0 \exp(-kt) \), where \( C_0 \) is the initial concentration of MB, \( C \) is the concentration of the MB at illumination time \( t \), \( k \) is a constant standing for the photocatalitic redox or reaction rate. By fitting the MB decomposition curve in Figure 9 a) to the L-H equation the dependence of the photocatalytic activity of amorphous TiO$_2$ complexes on the heating temperature is shown in Figure 9 b). As can be seen from Fig. 9b, the photocatalytic activity (reaction rate) of the materials is weak as heating temperature bellow ~200 °C but rapid increases with elevated temperature then has the maximum at the heating temperature of around 300 °C. Further increasing
the heating temperature, the photocatalytic activity of the materials is declined. The evaporation then elimination of NH$_4$Cl and the decomposition of amorphous TiO$_2$ complexes with the following recrystallization into anatase nanostructure in the materials is accounted for the behavior. At heating temperature around 300 °C, NH$_4$Cl and amorphous TiO$_2$ complexes are assumed to be totally decomposed the materials completely turn into pure anatase the materials exhibits the maximum photocatalytic activity. Further increasing the heat temperature, the photocatalytic activity is reduced due to the growth in size of anatase particle and the appearance rutile fraction from the anatase-rutile transition.

3. Materials and Methods

Titanium tetrachloride (TiCl$_4$) of 99.9 % purity (Sigma Aldrich Chemical Co.) as Ti precursor was used as received. Ammonium hydroxide solution (NH$_4$OH) of 28 % NH$_4$ (Merck Corp.,) was used as basic agent to change the pH of pyrolysis medium. The TiO$_2$ synthesis process was straightforward as follows: TiCl$_4$ was added dropwise into DI water at 5 °C to a concentration of 0.04 M, the pH level of the solution then was dropped to around 0.98 (starting point). By adding a small amount of NH$_4$OH into the solution the pH level was adjusted and preserved at a point in range of 0.98 to 10.04. The solution then was poured into test tubes and placed in an oven at 80 °C, the onset point of TiCl$_4$ decomposition. The solution was gradually changed to opalescent suspension indicating that the TiCl$_4$ was thermally decomposed and converted into Ti complexes and then TiO$_2$ accompanying with the formation of HCl and NH$_4$Cl [11]. The pyrolysis was carried on about 3.0 h then the power was shut down, the solution was slowly cooled to room temperature. Depending on pH level, the appearance of resulting solution shows either transparent, opalescent or clearly splits into transparent and milky part as seen in Figure 1. For characterization, these parts were separated and dried by vacuum evaporation then were thermally treated in an oven with baking temperature up to 600 °C. The structure of the resulting materials was determined by D8 Advance Bruker diffractometer using CuK$_{α}$ radiation of 0.154 nm wavelength. The mean size, D of TiO$_2$ crystallites was calculated using Scherrer equation, i.e., $D = \frac{k\lambda}{βcosθ}$, where $k = 0.94$, $λ = 0.154$ nm and $β$ is full width at half maximum (FWHM) according to the principal diffracted angle $θ$, i.e., (101) peak for anatase. Raman spectra were obtained on a LabRAM HR800 (Horiba) using a 632.8 nm excitation laser at a resolution of 1.0 cm$^{-1}$. TEM images were obtained using a JEOL JEM-2100 Transmission Electron Microscope. SEM images were conducted on a JEOL JEM-7600F Field Emission Scanning Electron Microscope. The photocatalytic activity of TiO$_2$ nanostructures was determined by measuring the degradation rate of methylene blue (MB) under UV light radiation.

4. Conclusion

The pyrolysis of aqueous TiCl$_4$ solution generally results in a mixture of anatase nanostructure and amorphous TiO$_2$ complexes. The ratio of TiO$_2$: anatase nanostructure and amorphous TiO$_2$ complexes can be controlled by changing the pH of the pyrolysis medium. The anatase fraction is predominant at low pH level and gradually declines and completely converts to the amorphous TiO$_2$ complexes at high pH level. By addition of NH$_4$OH to adjust the pH, the pyrolysis of a 0.04M aqueous TiCl$_4$ solution results in a mixture of TiO$_2$: anatase nanostructure and amorphous TiO$_2$ complexes at pH below 7.34 and predominant amorphous TiO$_2$ beyond that point.

The amorphous TiO$_2$ complexes is found to be converted to TiO$_2$ nanostructure by heat treatment. With annealing temperature around 300 °C, the amorphous TiO$_2$ is completely converted into anatase nanostructure and gradually transform into rutile at high temperature. Amongst of the TiO$_2$ nanostructures recovered from amorphous TiO$_2$ complexes, the anatase nanostructure shows to be the most effective photocatalyst in decomposition of methylene blue.
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References

1. U. Diebold, The surface science of titanium dioxide, Surf. Sci. Rep. 2003, 48, pp.33-229.
2. K. Hashimoto, H. Irie, and A. Fujishima, TiO2 photocatalysis: a historical overview and future prospects, Jpn. J. Appl. Phys. 2005, vol. 44 (12), pp. 8269–8285.
3. K. Nakata and A. Fujishima, TiO2 photocatalysis: design and applications, J. Photochem. Photobiol. C 2012, vol. 13 (3), pp. 169–189.
4. M. Montazer, S. Seifollahzadeh, Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO2 treated textile through enzymatic pretreatment. Photochem Photobiol. 2011, 87, pp. 877–883.
5. A. Fujishima and K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 1972, vol. 238 (5358), pp. 37–38.
6. L. Liu, H. Zhao, J. M. Andino & Y. Li, Photocatalytic CO2 reduction with H2O on TiO2 nanocrystals: Comparison of anatase, rutile, and brookite polymorphs and exploration of surface chemistry. ACS Catal. 2012, 2, pp. 1817–1828.
7. S. M. Gupta and M. Tripathi, A review of TiO2 nanoparticles, Chinese Sci. Bull. 2011, vol. 56 (16), pp. 1639–1657.
8. M. M. Byranvand, A. Nemati Kharat, L. Fatholahi, and Z. Malekshahi Beiranvand, A review on synthesis of nano-TiO2 via different methods, J. Nanostruct., 2013, vol. 3, pp. 1–9.
9. T. H. Wang, A. M. Navarrete-López, S. Li, and D. A. Dixon, Hydrolysis of TiCl4 Initial Steps in the Production of TiO2, J. Phys. Chem. A 2010, 114, 7561–7570.
10. M. A. Vargas, J. E. Rodríguez-Páez, Amorphous TiO2 nanoparticles: Synthesis and antibacterial capacity, J. Non-Cryst Solids 2017, 459, pp. 192–205.
11. V. Jordan, U. Javornik, J. Plavec, et al. Self-assembly of multilevel branched rutile-type TiO2 structures via oriented lateral and twin attachment. Sci Rep 2016, 6, 24216.
12. Abdullah M. Alobaibi, Sanjayan Sathasivam, et al, Chemical Vapor Deposition of Photocatalytically Active Pure Brookite TiO2 Thin Films, Chem. Mater. 2018, 30, 1353–1361.
13. J. H. Lee, and Y. S. Yang, Effect of HCl concentration and reaction time on the change in the crystalline state of TiO2 prepared from aqueous TiCl4 solution by precipitation, J. Eur. Ceram., 2005, 25, 3573–3578.
14. S. W. Lee, K. S. Ahn, K. Zhu, N. R. Neale, and A. J. Frank, Effects of TiCl4 Treatment of Nanoporous TiO2 Films on Morphology, Light Harvesting, and Charge-Carrier Dynamics in Dye-Sensitized Solar Cells, J. Phys. Chem. C 2012, 116, 21285–21292.
15. N. T. Tung, D. Ng. Huyen, Effect of HCl on the Formation of TiO2 Nanocrystallites, J. Nanomater. 2016, vol. 2016, Article ID 6547271.
16. N. T. Tung, M. X. Dung and D. Ng. Huyen, Simultaneous Synthesis of Anatase Colloidal and Multiple-branched Rutile TiO2 Nanocrystals, B. Korean Chem. Soc., 2017, 38(3); p. 401–405.
17. Downs, R. T., Bartelmehs, K. L., Gibbs, G. V., & Boisen, M. B., Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. Am. Mineral., 1993, 78(9-10), pp. 1104-1107.
18. W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin and Q. Chen, Raman scattering study on anatase TiO2 nanocrystals, J. Phys. D: Appl. Phys. 2000, 33, pp. 912–916.
19. M.N. Iliev, V.G. Hadjiev, A.P. Litvinchuk, Raman and infrared spectra of brookite (TiO2): Experiment and theory, Vib. Spectrosc., 2013, 64, pp. 148–152.
20. R. S. Krishnan, Raman spectra of ammonium chloride and its variation with temperature, Proc. Indian Acad. Sci., 1947, A, 26 (6), pp. 432-449.
21. S. Dai, Y. Wu, T. Sakai, Z. Du, H. Sakai, and M. Abe, Preparation of highly crystalline TiO2 nanostructures by acid-assisted hydrothermal treatment of hexagonal-structured nanocrystalline titania/cetyltrimethylammonium bromide nanoskeleton, Nanoscale Res. Lett. 2010, vol. 5(11), pp. 1829–1835.
22. G. W. Roberts and C. N. Satterfield, Effectiveness Factor for Porous Catalysts. Langmuir-Hinshelwood Kinetic Expressions, Ind. Eng. Chem. Fundamen., 1965, 4, 3, pp. 288–293.