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Effect of pH on the Formation of Amorphous TiO₂ Complexes and TiO₂ Anatase during the Pyrolysis of an Aqueous TiCl₄ Solution

Huyen Duong Ngoc^{1,*}, Dung Mai Xuan² and Tuan Mai Van^{1,3}

- School of Engineering Physics, Hanoi University of Science and Technology, No. 1, Daicoviet, Hanoi 10000, Vietnam; tuanmvns@gmail.com
- ² Department of Chemistry, Hanoi Pedagogical University 2, 32 Nguyen Van Linh, Phuc Yen, Vinh Phuc 15000, Vietnam; xdmai@hpu2.edu.vn
- ³ Faculty of Natural Sciences, Electric Power University, 235 Hoang Quoc Viet, Hanoi 10000, Vietnam
- * Correspondence: huyen.duongngoc@hust.edu.vn; Tel.: +84-912-153-128

Received: 6 September 2020; Accepted: 12 October 2020; Published: 15 October 2020



Abstract: The titanium dioxide (TiO₂) nanostructures resulted by the pyrolysis of titanium tetrachloride (TiCl₄) at a low temperature of 80 °C were found to be a mixture of amorphous TiO₂ complexes and anatase nanostructures, whose ratio depends on the pH of the pyrolysis medium. At a low pH level, the resulting TiO₂ nanostructures are predominantly anatase and gradually shift to amorphous TiO₂ complexes as the pH level increases. Moreover, the amorphous TiO₂ complexes can convert back to anatase nanostructures by a post-heating treatment, and can then transform to rutile with elevating temperature. Amongst the TiO₂ nanostructures recovered from the amorphous TiO₂ complexes, anatase appears to be the most effective photocatalyst in the decomposition of methylene blue.

Keywords: photocatalyst; amorphous TiO₂ complexes; TiO₂; anatase nanostructures

1. Introduction

Titanium dioxide (TiO₂), a typical metal oxide with a high refractive index, chemical stability, long durability, and nontoxicity, has been widely used for many applications, such as white pigments, textiles, papers, cosmetics, medicines, and ceramics. As an *n*-type wide bandgap semiconductor, TiO₂ exhibits a unique photoinduced effect involving photogenerated charge carriers that initiate a strong redox reaction of adsorbed substances and hydrophilic conversion of itself [1,2]. This effect offers more potential applications involving photochemical processes, such as splitting hydrogen from water, a photocatalyst, a photoconductor, environment cleaning, an antibacterial purpose, chemica sensors, ultraviolet filters, and dye-sensitized solar cells (DSSCs) [3–5].

Under normal conditions, TiO_2 exists in three main structures: stable rutile, metastable anatase, and brookite phases. For the pure phase, it is generally accepted that anatase exhibits a higher photocatalytic activity compared to that of rutile, despite its larger bandgap (3.2 eV for anatase vs. 3.0 eV for rutile). The longer lifetime for photo-excited electrons and holes in the indirect bandgap of TiO_2 anatase semiconductor is explained for this feature [6]. In contrast, TiO_2 in the microstructure is considered a poor photocatalyst, but in a 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 of the effect of synthesis conditions on the resulting TiO_2 nanostructures is of importance to yield effective photocatalysts and diverse photocatalytic applications.

With regard to the synthesis of TiO₂ nanostructures, a variety of techniques based on the pyrolysis of Ti precursors, such as the hydrothermal, solvothermal, sol-gel, direct oxidation, chemical vapor deposition (CVD), electrodeposition, sonochemical, and microwave methods, have 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) isopropoxide, amorphous TiO₂, and P₂₅. In addition, the pyrolysis modest medium of low temperature and adjustable pyrolysis time can provide an effective environment for the synthesis of TiO_2 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 Ti_xO_yCl_z(OH)_w, resulting from the pyrolysis of $TiCl_4$, $[Ti(OH)_{4-n}(H_2O)_{2+n}]^{n+}$ from Ti(IV)-butoxide or $[Ti_{3(y+1)}O_{4y}(OBu)_{4(y+3)-x}(OEt)_x]$ from alkoxide metal $M(OR)_n$ [9–12]. Amorphous TiO₂ complexes in general are metastable phases, so they can evolve into any crystalline phases under special conditions. The heat treatment route with appropriate reactants is usually used to achieve the transformation from amorphous to crystalline TiO₂. For example, pure anatase or rutile and brookite nanoparticles are obtained by hydrothermal treatment of amorphous TiO_2 with a variety of acid additives as reactants at different concentrations [13–15]. Chemical vapor deposition synthesis of pure brookite TiO_2 thin films is also realized by using amorphous TiO_2 as the precursor [16,17]. Hence, the amorphous TiO_2 intermediates can be used as a kind of secondary precursor to produce either brookite, anatase, rutile structures, or their derivatives.

With regard to the amorphous $Ti_xO_yCl_z(OH)_w$ complexes resulted from the pyrolysis of TiCl₄, a calculation shows that the substitution of OH for Cl radicals in the complexes does not change much in the core involving the Ti atoms, but there is a difference in the bond lengths and potential energy surfaces [10]. From a thermodynamic point of view, a change in the relative ratio of the Cl and OH radicals modifies the potential surface energy and then the free energy of the complex TiO_2 intermediates, consequently affecting the final TiO_2 nanostructures. As examples, some works have demonstrated that the pyrolysis of aqueous TiCl₄ solutions with high HCl result in rutile and brookite structures [18,19]. However, anatase, which is considered to be the most active photocatalyst, was hardly observed in the resulting materials. From our perspective, the excessive Cl radicals in the reaction medium due to a large amount of HCl additive (pH < 0) resulted in the predominance of rutile and brookite. Moreover, some possible TiO₂ nanostructures in colloidal or amorphous forms left in the reaction solution may have been filtered and washed away. In a series of experiments made on the pyrolysis of an aqueous TiCl₄ solution with lesser HCl concentrations (0.0 < pH < 1.0), we found that the resulting materials were nanocrystalline mixtures of both the anatase and rutile phases. The TiO₂ anatase mainly suspended in the aqueous solution in the colloidal form, while the TiO₂ rutile predominantly precipitated and deposited in the sedimentation [20,21]. It was concluded that a high HCl concentration enabled the agglomeration of anatase particles and enhanced the anatase to rutile transition due to the compensation of a Cl radical for the positive charge of polyhedral complexes. Furthermore, the pyrolysis of $TiCl_4$ in the neutral medium, with a pH level of approximately 6–8, brought in materials of predominantly amorphous TiO_2 , as well as trace amounts of anatase, but no rutile or brookite [14,22]. Then, the pH levels evolving to correlations between H, Cl, and OH radicals in the reaction media were assumed to be the crucial factors to modify and control the resulting TiO_2 nanostructures. Based on these considerations, in this study, an experiment was carried out to further investigate the effect of an elevated pH level (or OH radical) of the reaction media on the formation of amorphous TiO₂ complexes, as well as of the final anatase nanostructures obtained from the pyrolysis of an aqueous TiCl₄ solution.

2. Results and Discussion

The experiments show that the NH_4OH additive, a weak basic agent used to adjust the pH level of the reaction solution, significantly affects the appearance and properties of TiO_2 nanostructures in the resulting materials. As seen in Figure 1, the resulting aqueous solution appears transparent

at a low pH level but gradually changes to slightly opalescent, and then separates into transparent and milky parts when the pH level exceeds 2.40. The separated milky column increases with NH₄OH and becomes unchanged as the pH level exceeds 7.34. Depending on the transparent or milky state, the surface morphology of the resulting materials transforms from a grain to a gelation structure as shown in the Scanning Electron Microscope (SEM) images in Figure 2. In the sample with a pH of 0.98, the resulting material grains are uniformly granular with a mean size of approximately 50–70 nm, which, in turn, shows clusters of anatase nanoparticles of 4–5 nm in mean size [20]. However, when the pH level of the reaction medium increases, the resulting material grains inflate to coagulated clusters of 150–200 nm in size and gradually become jellylike or amorphous structures, as shown in Figure 2b–d.



Figure 1. The appearance of the aqueous titanium tetrachloride (TiCl₄) solution with different pH levels after pyrolysis at 80 °C.



Figure 2. SEM images of titanium dioxide (TiO₂) resulting from the pyrolysis of TiCl₄ in different pH media at 80 °C: (**a**) pH = 0.98; (**b**) pH = 2.45; (**c**) pH = 10.04 (transparent part); (**d**) pH = 10.0 (milky part).

The X-ray diffraction (XRD) spectra in Figure 3 show the evolution of the resulting materials depending on the pH level, i.e., on NH₄OH additive. In the sample with a pH level of 0.98, the XRD pattern contains a principal peak at approximately 25.29° and the other peaks at approximately 37.80°, 48.05°, 53.89°, and 62.68°, assigned to the diffractions of the anatase structure on the (101) and (004), (200), (105), and (204) planes, respectively (JCPDS no. 00-021-1272). When NH₄OH was added, together with the diffraction peaks from anatase, other sharp diffraction peaks at 22.98°, 32.69°, 40.31°, 46.88°, 52.80°, 58.29°, and 68.43° were observed for the diffractions on the (100), (110), (111), (200), (210), (211), and (220) planes, respectively, with crystals emerging from NH₄Cl [23]. With the increase in pH level, the TiO₂ diffraction in the XRD pattern gradually disappeared, accounting for the gradual conversion from TiO₂ anatase to amorphous TiO₂ complexes. Using the Scherrer equation, i.e., D = $k\lambda/\beta \cos\theta$, where k = 0.94, λ = 0.154 nm, and β is full width at half maximum (FWHM) at diffraction angle θ according to (101) peak, to calculate the mean size D of the anatase particles, it was found that the mean sizes of the anatase particles were almost unchanged at approximately 4.5 nm, as given in Table 1. This value is considered to be the limitation of anatase size in the conversion to amorphous TiO₂ complexes.



Figure 3. X-ray diffraction (XRD) spectra of TiO₂ resulting from the pyrolysis of TiCl₄ in different pH media at 80 $^{\circ}$ C.

Table 1. The mean size of the anatase particles resulting from the pyrolysis of $TiCl_4$ in different pH media at 80 °C. FWHM, full width at half maximum.

pН	(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

The Raman spectra also confirm the presence of anatase and NH₄Cl in the resulting materials. As shown in Figure 4, in the starting materials, namely, the sample with a pH level of 0.98, the spectrum exhibits only vibrational modes at approximately 155 cm⁻¹, 399 cm⁻¹, 513 cm⁻¹, and 634 cm⁻¹, respectively, representing the E_g, B_{1g}, A_{1g} + B_{1g}, and E_g modes of the anatase structure [24,25]. The presence of NH₄Cl in the materials gives rise to a broad saddle spectrum consisting of two vibration modes at approximately 168 cm⁻¹ and 144 cm⁻¹ that are assumed to be the supposition of the E_g vibration mode of anatase and the v_2 , v_3 , and v_4 vibration modes of NH₄Cl oscillating against Cl along the (100) direction and along three orthogonal directions [26].



Figure 4. Raman spectra of TiO₂ resulting from the pyrolysis of TiCl₄ in different pH media at 80 °C.

The appearance of transparent, opalescent, and separable milky parts in the solution is believed to be due to the appearance and increase of amorphous TiO_2 complexes forming in the pyrolysis medium. At a low pH level, in the acidic aqueous medium with a higher concentration of H and Cl radicals, the formation of amorphous TiO_2 complexes is negligible; the resulting anatase is crystallized in the form of grain structures with sharp boundaries. The presence of NH_4OH in the pyrolysis medium raises the pH level and then the OH radicals that promote the formation of amorphous TiO_2 complexes. Consequently, with the increase in NH_4OH 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 exceeds 7.34, the milky column is unchanged, even though the NH_4OH additive keeps increasing. Furthermore, the Energy Dispersive X-ray Spectra (EDS) show that no trace of Ti is present in the transparent part but is in the milky part, as shown in Figure 5. This indirectly indicates

that the decomposed $TiCl_4$ precursor in the pyrolysis solution was totally converted into amorphous TiO_2 complexes and completely separated into the milky part as the pH level exceeded 7.34. Due to the amorphous nature, no crystalline diffraction pattern can be observed in XRD spectra as the materials were synthesized in the medium with the pH level beyond that point.



Figure 5. EDS spectra of the sample extracted from the milky part (**a**) and from the transparent part (**b**), extracted from the pyrolysis of TiCl₄ in a medium with pH = 10.04.

A High-resolution Transmission Electron Microscope (HRTEM) image taken from a milky sample with a 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 the materials is considered to be the TiO_2 complexes. The lattice spacing of the tiny nanocrystallites at approximately 0.346 nm is identical to the lattice spacing of the (101) plane of TiO_2 anatase. The estimated size of the TiO_2 anatase particles is comparable to that calculated from the XRD pattern, approximately 4.5 nm, which 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 the appearance of the E_g vibration mode of anatase in the Raman spectra in Figure 4.

In order to further characterize the evolution of the amorphous TiO_2 complexes into the other crystalline forms, a post-heating treatment was made at an elevated temperature of up to 600 °C. The experiments reveal that the materials underwent a conversion back to anatase and then from anatase to rutile. At a heating temperature below 200 °C, the XRD pattern in Figure 7 shows only the presence of NH₄Cl but no trace of TiO₂ structures. However, when the heating temperature exceeds 200 °C, anatase diffraction gradually emerges while NH₄Cl diffraction gradually disappears in the XRD patterns. The disappearance of NH₄Cl is accounted for by the decomposition of the materials, while the appearance of TiO₂ anatase explains the decomposition and recrystallization of amorphous TiO₂ complexes at an elevated temperature. When the heating temperature exceeds 300 °C, the NH₄Cl is converted into TiO₂ nanostructures that are predominantly anatase. Brookite and rutile structures 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 the XRD patterns was found to grow from approximately 4.5 nm at a heating temperature of 200 °C to 8.9 nm at a heating temperature of 600 °C, as given in Table 2. For the sample with a pH level of 0.98, anatase is predominant over amorphous TiO₂ complexes; the heat treatment is merely a means to enable the separation of anatase nanoparticles from the cluster.



Figure 6. The appearance of anatase nanoparticles scatteringly embedded in the amorphous TiO_2 complexes.



Figure 7. XRD spectra of TiO_2 resulting from the pyrolysis of $TiCl_4$ in a medium with pH = 10.04 at 80 °C and then treated at different elevated temperatures. A, anatase; B, brookite; R, rutile; N, ammonium chloride.

Baking Temp.	Crystallite Size (nm)	E _g Mode Peak (cm ⁻¹)	FWHM of Eg Mode (cm ⁻¹)
200 °C	4.5	154	31
300 °C	6.2	150	25.8
450 °C	6.8	148	18.9
500 °C	6.8	148	18.1
550 °C	8.3	147	15.9
600 °C	8.9	145	14.5

Table 2. The mean size and E_g vibration mode of anatase resulting from annealing amorphous TiO₂ complexes.

The Raman spectra also verify the conversion of anatase from the amorphous TiO_2 complexes (the milky part) when heated up, as given in Figure 8. With a heating temperature below 200 °C, the Raman spectrum is a composition of the NH₄Cl vibration mode centered at approximately 168 cm⁻¹ and 144 cm⁻¹ and the E_g vibration mode of TiO₂ anatase at 147 cm⁻¹. As the heating temperature increases from 200 to 600 °C, the E_g vibration mode shows a shift in frequency from 154 to 145 cm⁻¹ and a shrinkage in FWHM (see Table 2). This feature accounts for the size growth from 4.5 to 8.9 nm of the TiO₂ anatase nanocrystallites [27].



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

The formation of TiO₂ nanostructures by the pyrolysis of TiCl₄ in an elevated pH medium can be explained by two mechanisms; one is the decomposition, dissolution, and recrystallization and the other is the in-situ transition [20,28]. At an elevated temperature exceeding 80 °C, TiCl₄ is decomposed and hydrolyzed into HCl and amorphous $Ti_XO_yCl_z$ (or $Ti_xO_yCl_z(OH)_w$) complexes and then converted into TiO₂ anatase nanostructures [10]. The component ratio of the amorphous TiO₂ complexes and TiO₂ anatase is established by an equilibrium balance between the H, OH, Cl, and NH₃ radical concentrations in the medium. At a low pH level of 0.98 to 2.40, excessive H and Cl radicals promote the formation of anatase nanocrystallites, which likely follows the first mechanism. In this medium, the mean size of the anatase particles is approximately 4.5 nm below the limitation for the anatase to rutile transition [29–31]. Consequently, no rutile trace can be observed in the XRD diffraction pattern. In contrast, at a high pH level, the presence of OH and NH₃ radicals reduces and eliminates the activity of the Cl radical and brings in OH-dominant amorphous $Ti_XO_y(OH)_w$ or $[Ti(OH)_{4-n}(H_2O)_{2+n}]^{n+}$ complexes with a consumption of the anatase. As a result, at a low pH level (–1.0 to 2.40), the anatase fraction is dominant, while the amorphous TiO₂ complexes are dominant at a high pH level (>7.34). The amorphous TiO₂ complexes can be converted back to TiO₂ anatase nanoparticles by a post-heat treatment at a temperature of

approximately 300 °C. The amorphous–anatase transition here likely follows the in-situ transition mechanism. The relatively low transition temperature (approximately 300 °C) from amorphous TiO_2 to anatase nanoparticles is explained for the nucleation seeding effect that is due to the embedded anatase nanoparticles in the amorphous TiO_2 medium [14].

The experiments show that the amorphous TiO_2 complexes exhibit strong photocatalytic activity upon exposure to UV light radiation. By comparison of the relative intensity of the methylene blue (MB) principal adsorption peak in the UV–Vis spectrum, the percentage of oxidated MB in the solution was deduced and then the photocatalytic activity of the materials was calculated.

With regard to the photocatalysis of amorphous TiO_2 complexes, the rates of photocatalytic oxidation of MB show an exponential reduction that is well fitted to the Langmuir-Hinshelwood (L–H) kinetics model [32]. As illuminated in Figure 9a, when the MB concentration is small, the L–H equation can be simplified to an apparent first-order: $\ln(C_0/C_t) = \text{kt or } C_t = C_0 \exp(-\text{kt})$, where C_0 is the initial concentration of MB, Ct is the concentration of the MB at UV illumination time t, and k is a constant standing for the photocatalytic redox or reaction rate. By fitting the MB decomposition curve (in Figure 9a) to the L-H equation, the dependence of the photocatalysis of amorphous TiO_2 complexes in terms of reaction rate on the heating temperature can be observed (Figure 9b). At a heating temperature bellow 200 °C, the photocatalysis (reaction rate) of the materials is weak but rapidly increases with increasing temperature, then reaches the maximum reaction rate at a heating temperature of approximately 300 °C. By further increasing the heating temperature, the photocatalysis of the materials declines. When NH₄Cl is evaporated and eliminated, the appearance of anatase nanostructures due to the decomposition and recrystallization of amorphous TiO₂ complexes in the materials accounts for such behavior. At a heating temperature of approximately 300 °C, the NH₄Cl and amorphous TiO_2 complexes are assumed to be totally decomposed, and the materials completely convert into pure anatase and exhibit the maximum photocatalysis. By further increasing the heat temperature, the photocatalysis is reduced due to the growth of anatase particles and the appearance of a rutile fraction resulting from the anatase-rutile transition.



Figure 9. (a) Rates of photocatalytic oxidation of methylene blue (MB) as a function of TiO_2 complexes treated at different heating temperatures; (b) the photocatalytic activity of amorphous TiO_2 complexes depends on the heating temperature.

3. Materials and Methods

Titanium tetrachloride (TiCl₄) of 99.9% purity (Sigma-Aldrich Chemical Co., USA) as Ti precursor was used as received. An ammonium hydroxide solution (NH₄OH) of 28% NH₃ (Merck Corp., USA) was used as a basic agent to adjust the pH of the pyrolysis medium. The TiO₂ synthesis process was straightforward, as follows: TiCl₄ was added dropwise into deionized water at 5 °C to a concentration of 0.04 M. The pH level of the solution was then dropped to approximately 0.98 (starting point).

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By adding a small amount of NH_4OH into the solution, the pH level was adjusted and preserved at a point in the range of 0.98 to 10.04. The solution was then poured into test tubes and placed in an oven at 80 °C, the onset point of TiCl₄ decomposition. The solution was gradually changed to an opalescent suspension, indicating that the TiCl₄ was thermally decomposed and converted into TiO₂ complexes, and then TiO₂ nanostructures accompanied the formation of HCl and NH₄Cl [12]. The pyrolysis was carried out for approximately 3 h; then, the power was shut down and the solution was slowly cooled to room temperature. Depending on the pH level, the appearance of the resulting solution showed either transparent, opalescent, or a clear split into transparent and milky parts, as seen in Figure 1. For characterization, these parts were separated and dried by vacuum evaporation, then thermally post-treated in an oven with a heating temperature up to 600 °C.

The structure of the resulting materials was determined by a D8 Advance Bruker diffractometer using CuK_{α} radiation of a 0.154 nm wavelength. The mean size, D, of the TiO₂ crystallites was calculated using the Scherrer equation, i.e., $D = k\lambda/\beta\cos\theta$, where k = 0.94, $\lambda = 0.154$ nm, and β is full width at half maximum (FWHM) according to the principal diffracted angle θ , i.e., (101) peak for anatase. The Raman spectra were obtained on a LabRAM HR800 (Horiba) using a 632.8 nm excitation laser at a resolution of 1.0 cm^{-1} . High-resolution Transmission Electron Microscope (HRTEM) images were obtained using a JEOL JEM-2100 TEM. Scanning Electron Microscope (SEM) images were conducted on a JEOL JEM-7600F Field Emission SEM. The photocatalytic activity of the TiO₂ nanostructures was determined by measuring the degradation rate of methylene blue (MB) under UV light radiation. Normally, a mixture of 50 mL of 0.25 μ mol MB aqueous solution and 50 mg of amorphous TiO₂ complexes was stirred magnetically under dark conditions for 30 min before being exposed under a UV mercury vapor lamp. After a fixed UV exposure duration, 1 mL of the aqueous solution was taken out for UV–Vis characterization. In a diluted MB solution, the MB absorbance in the UV–Vis spectra is linearly proportional to the MB concentration according to the Lambert–Beer law. The degradation rate of MB in the solution under UV light radiation was then deduced by comparing the intensity of the MB absorbance at the maximum absorption peak of 661 nm in the UV–Vis spectrum. The experiment was replicated several times with different samples under different exposure doses to obtain the relevant results. The UV–Vis was carried out using a Cary 100 UV–Visible Spectrophotometer (Agilent).

4. Conclusions

The pyrolysis of an aqueous TiCl₄ solution generally results in a mixture of anatase nanostructures and amorphous TiO₂ complexes. The ratio of TiO₂ anatase nanostructures to amorphous TiO₂ complexes can be controlled by changing the pH of the pyrolysis medium. The anatase fraction is predominant at a low pH level and gradually declines and completely converts to the amorphous TiO₂ complexes at a high pH level. The pyrolysis of a 0.04 M aqueous TiCl₄ solution brings about a mixture of TiO₂ anatase nanostructures and amorphous TiO₂ complexes at a pH below 7.34 and yields predominantly amorphous TiO₂ beyond that point.

The amorphous TiO_2 complexes are found to be converted to TiO_2 nanostructures by heat treatment. With an annealing temperature of approximately 300 °C, the amorphous TiO_2 is completely converted into anatase nanostructures and gradually transforms into rutile at a high temperature. Amongst the TiO_2 nanostructures recovered from the amorphous TiO_2 complexes, the anatase nanostructure is the most effective photocatalyst in the decomposition of methylene blue.

Author Contributions: Conceptualization, H.D.N. and T.M.V.; Methodology, H.D.N.; Formal Analysis, H.D.N., D.M.X. and T.M.V.; Investigation, H.D.N. and T.M.V.; Resource, H.D.N. and T.M.V.; Writing-Original Draft Preparation, H.D.N. and T.M.V.; Writing-Review and Editing, H.D.N. and D.M.X.; Supervision, H.D.N. and D.M.X. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support received in the form of a Basic Research Project Grant in Aid (T2008-PC-123) provided by Hanoi University of Science and Technology (HUST), Vietnam.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Diebold, U. The surface science of titanium dioxide. Surf. Sci. Rep. 2003, 48, 53–229. [CrossRef]
- Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ photocatalysis: A historical overview and future prospects. *Jpn. J. Appl. Phys.* 2005, 44, 8269–8285. [CrossRef]
- Nakata, K.; Fujishima, A. TiO₂ photocatalysis: Design and applications. J. Photochem. Photobiol. C 2012, 13, 169–189. [CrossRef]
- Montazer, M.; Seifollahzadeh, S. Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO₂ treated textile through enzymatic pretreatment. *Photochem. Photobiol.* 2011, *87*, 877–883. [CrossRef] [PubMed]
- 5. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, 238, 37–38. [CrossRef] [PubMed]
- Liu, L.; Zhao, H.; Andino, J.M.; Li, Y. Photocatalytic CO₂ reduction with H₂O on TiO₂ nanocrystals: Comparison of anatase, rutile, and brookite polymorphs and exploration of surface chemistry. *ACS Catal.* 2012, 2, 1817–1828. [CrossRef]
- 7. Gupta, S.M.; Tripathi, M. A review of TiO₂ nanoparticles. *Chin. Sci. Bull.* **2011**, *56*, 1639–1657. [CrossRef]
- 8. Byranvand, M.M.; Kharat, A.N.; Fatholahi, L.; Beiranvand, Z.M. A review on synthesis of nano-TiO₂ via different methods. *J. Nanostruct.* **2013**, *3*, 1–9.
- 9. Sun, S.; Song, P.; Cui, J.; Liang, S. Amorphous TiO₂ nanostructures: Synthesis, Fundamental Properties and Photocatalytic Application. *Catal. Sci. Technol.* **2019**, *9*, 4198–4215. [CrossRef]
- Wang, T.H.; Navarrete-López, A.M.; Li, S.; Dixon, D.A. Hydrolysis of TiCl₄: Initial Steps in the Production of TiO₂. J. Phys. Chem. A 2010, 114, 7561–7570. [CrossRef]
- 11. Vargas, M.A.; Rodríguez-Páez, J.E. Amorphous TiO₂ nanoparticles: Synthesis and antibacterial capacity. *J. Non-Cryst. Solids* **2017**, *459*, 192–205. [CrossRef]
- 12. Jordan, V.; Javornik, U.; Plavec, J.; Podgornik, A.; Rečnik, A. Self-assembly of multilevel branched rutile-type TiO₂ structures via oriented lateral and twin attachment. *Sci. Rep.* **2016**, *6*, 24216. [CrossRef] [PubMed]
- Reyes-Coronado, D.; Rodríguez-Gattorno, G.; Espinosa Pesqueira, M.E.; Cab, C.; de Coss, R.; Oskam, G. Phase-pure TiO₂ nanoparticles: Anatase, brookite and rutile. *Nanotechnology* 2008, *19*, 145605–145615. [CrossRef] [PubMed]
- 14. Xie, H.; Xi, T.; Zhang, Q.; Wu, Q. Study on the Phase Transformation Behavior of Nanosized Amorphous TiO₂. *J. Mater. Sci. Technol.* **2003**, *19*, 463–466.
- Yin, H.B.; Wada, Y.; Kitamura, T.; Kambe, S.; Murasawa, S.; Mori, H.; Sakata, T.; Yanagida, S. Hydrothermal Synthesis of Nanosized Anatase and Rutile TiO₂ Using Amorphous Phase TiO₂. *J. Mater. Chem.* 2001, 11, 1694–1703. [CrossRef]
- Haggerty, J.E.S.; Schelhas, L.T.; Kitchaev, D.A.; Mangum, J.S.; Garten, L.M.; Sun, W.; Stone, K.H.; Perkins, J.D.; Toney, M.F.; Ceder, G.; et al. High Fraction Brookite Film from Amorphous Precursors. *Sci. Rep.* 2017, 7, 15232. [CrossRef] [PubMed]
- Alotaibi, A.M.; Sathasivam, S.; Williamson, B.A.D.; Kafizas, A.; Sotelo-Vazquez, C.; Taylor, A.; Scanlon, D.O.; Parkin, I.P. Chemical Vapor Deposition of Photocatalytically Active Pure Brookite TiO₂ Thin Films. *Chem. Mater.* 2018, *30*, 1353–1361. [CrossRef]
- 18. Lee, J.H.; Yang, Y.S. 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. [CrossRef]
- Lee, J.H.; Yang, Y.S. Effect of hydrolysis conditions on morphology and phase content in the crystalline TiO₂ nanoparticles synthesized from aqueous TiCl₄ solution by precipitation. *Mater. Chem. Phys.* 2005, 93, 237–242. [CrossRef]
- 20. Tung, N.T.; Huyen, D.N. Effect of HCl on the Formation of TiO₂ Nanocrystallites. J. Nanomater. 2016, 2016, 1–7. [CrossRef]
- 21. Tung, N.T.; Dung, M.X.; Huyen, D.N. Simultaneous Synthesis of Anatase Colloidal and Multiple-branched Rutile TiO₂ Nanostructures. *Bull. Korean Chem. Soc.* **2017**, *38*, 401–405. [CrossRef]
- 22. Zou, J.; Gao, J.C.; Xie, F.Y. An amorphous TiO₂ sol sensitized with H₂O₂ with the enhancement of photocatalytic activity. *J. Alloys Compd.* **2010**, *497*, 420–427. [CrossRef]
- 23. 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*, 1104–1107.

- 24. Zhang, W.F.; He, Y.L.; Zhang, M.S.; Yin, Z.; Chen, Q. Raman scattering study on anatase TiO₂ nanocrystals. *J. Phys. D Appl. Phys.* **2000**, *33*, 912–916. [CrossRef]
- 25. Iliev, M.N.; Hadjiev, V.G.; Litvinchuk, A.P. Raman and infrared spectra of brookite (TiO₂): Experiment and theory. *Vib. Spectrosc.* **2013**, *64*, 148–152. [CrossRef]
- 26. Krishnan, R.S. Raman spectrum of ammonium chloride and its variation with temperature. *Proc. Indian Acad. Sci.* **1947**, *26*, 432–449. [CrossRef]
- 27. Choi, H.C.; Jung, Y.M.; Kim, S.B. Size effects in the Raman spectra of TiO₂ nanoparticles. *Vib. Spectrosc.* **2005**, 37, 33–38. [CrossRef]
- 28. Dai, S.; Wu, Y.; Sakai, T.; Du, Z.; Sakai, H.; Abe, M. Preparation of highly crystalline TiO₂ nanostructures by acid-assisted hydrothermal treatment of hexagonal-structured nanocrystalline titania/cetyltrimethyammonium bromide nanoskeleton. *Nanoscale Res. Lett.* **2010**, *5*, 1829–1835. [CrossRef]
- 29. Hanaor, D.A.H.; Sorrell, C.C. Review of the anatase to rutile phase transformation. *J. Mater. Sci.* 2011, 46, 855–874. [CrossRef]
- 30. Barnard, A.S.; Zapol, P.; Curtiss, L.A. Modeling the morphology and phase stability of TiO₂ nanocrystals in water. *J. Chem. Theory Comput.* **2005**, *1*, 107–116. [CrossRef]
- 31. Barnard, A.S.; Zapol, P. Effects of particle morphology and surface hydrogenation on the phase stability of TiO₂. *Phys. Rev. B* **2004**, *70*, 23. [CrossRef]
- 32. Roberts, G.W.; Satterfield, C.N. Effectiveness Factor for Porous Catalysts. Langmuir-Hinshelwood Kinetic Expressions. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 288–293. [CrossRef]

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