Controllable TiO_2 phase transformation between rutile and anatase: the case of F^- and Cl^-

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Although many literatures have reported that F^- and Cl^- ions could influence the phase formation of TiO_2, the specific role of F^- and Cl^- in the phase transformation between rutile and anatase has still not been clarified. In this study, for the first time we demonstrate that Cl^- could adjust the phase transformation between rutile and anatase mainly by controlling the hydrolysis rate of Ti^{4+}. The F^- could control the transformation from rutile to anatase phase at room temperature, which should be ascribed to its strong coordination effect with Ti^{4+}. This finding provides a simple route for controlling TiO_2 phase transformation between rutile and anatase.

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1. Introduction

As is well known that TiO_2 has three most commonly encountered crystalline polymorphs (rutile, anatase, and brookite). [1] Among them, rutile and anatase with excellent photocatalytic activity have been widely studied. [2-4] Both anatase and rutile have tetragonal crystal structure, which can be formed via the rearrangement of TiO_6 octahedra by edge-shared bonding and vertex-shared bonding, respectively. [5] For comparison, rutile TiO_2 with high density and refractive index is more thermally stable. [6] Generally, the complete transformation from anatase to rutile needs the high temperature above 1000 °C and long reaction time, resulting in energy waste and aggregation of particles. Therefore, the realization of TiO_2 phase transformation from anatase to rutile under mild temperature is still fascinating to materials scientists.

During the past decades, F^- and Cl^- as two kinds of common anion have been widely used for adjusting the crystal phase and exposed face of TiO_2. For example, many reports have documented that the addition of F^- favors the formation of anatase TiO_2 and its exposed face adjustment via hydrothermal reactions or high temperature calcinations processes. [7-9] Very recently, we have reported F^- could control the synthesis of anatase phase at room temperature. [10] However, until now, less investigations have been performed on the specific role of F^- in the controllable fabrication of anatase TiO_2. On the other hand, many scientists found rutile TiO_2 could be fabricated by ultrasonic or hydrolysis method with a large amount of Cl^-. [11-14] For example, Zhang's group [14] has obtained rutile TiO_2 nanorods by hydrolyzing $TiCl_4$ in mixed solutions of water and ethanol at 50 °C. They demonstrated the high acidity and high concentration of Cl^- would decrease the content of OH^- in the $[Ti(OH)_nCl_m(OC_2H_5)_{6\text{-}n\text{-}m}]^{2-}$ structure, good for the vertex-shared bonding of TiO_6 octahedra to form rutile TiO_2. In fact, the hydrolysis rate would be largely accelerated at higher temperatures, however, the resultant phase transformation processes have not been paid enough attention.

In this study, for the first time we demonstrate that Cl^- could control the phase transformation of TiO_2 from rutile (stage I) to mixture of anatase and rutile (stage II) and to rutile (stage III) by gradually increasing the reaction temperature. Differently, the introduction of F^- to a Cl^- dominated reaction system could realize the phase transformation of TiO_2 from rutile to anatase at room temperature. On the basis of the experimental results, we proposed that Cl^- and F^- could control the phase transformation of TiO_2 by adjusting the hydrolysis rate of Ti^{4+} and the strong coordination effect of F^-, respectively.

2. Experimental

2.1. Synthesis of TiO_2 at room temperature

Typically, 1.1 mL of $TiCl_4$ and desired amount (0.00, 0.02, 0.10, and 0.20 mL) of hydrofluoric acid (HF) were dissolved into 100 mL of distlled water at 0 °C under strirring. Subsequently, the above solution was left to stand at room temperature for about 7 days. Then the resulting precipitate was centrifuged and washed with distilled water thoroughly, and finally dried in an oven at 50 ^{o}C for 24 h. The products obtained with adding 0.00, 0.02, 0.10, and 0.20 mL of HF were denoted as Ti-0HF-RM, Ti-0.02HF-RM, Ti-0.1HF-RM, and Ti-0.2HF-RM, respectively.

2.2. The synthesis of TiO_2 at different temperature

Typically, 1.1 mL of $TiCl_4$ and desired amount of HF (0.00, 0.02 and 0.20 mL) were dissolved into 100 mL of distlled water at 0 ^{o}C under strirring, the obtained solution was denoted as solution A, solution B and solution C, respectively. Then 20 mL of solution A or B or C was transferred into a 25 mL Teflon-lined stainless-steel autoclave and subsequently heated in a furnace at different temperature (50 ^{o}C, 100 ^{o}C, 150 ^{o}C or 200 ^{o}C) for 24 h, respectively. Then, the resulting precipitate was centrifuged and washed with distilled water thoroughly, and finally dried in an oven at 50 ^{o}C for 24 h. The samples obtained at different temperatures with a addition of 0.00 or 0.02 or 0.20 mL of HF wered denoted as Ti-50, Ti-100, Ti-150, Ti-200, Ti-0.02HF-50, Ti-0.02HF-100, Ti-0.02HF-150, Ti-0.02HF-200, Ti-0.2HF-50, Ti-0.2HF-100, Ti-0.2HF-150, and Ti-0.2HF-200, respectively.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded by using a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. The influence of Cl^- in TiO_2 phase transformation

It has been proved in our previous work that rutile TiO_2 could be obtained during the hydrolysis of titanium tetrachloride ($TiCl_4$) in distilled water at room temperature. [15] This should be closely related to the high acidity and high concentration of Cl^- that could decrease the content of OH^- in the $[Ti(OH)_{6-n}Cl_n]^{2-}$ structure, resulting in the formation of rutile TiO_2 by vertex-shared bonding of TiO_6 octahedra. [14] Besides, the temperature is another important factor influencing the hydrolysis reaction, which should control the phase transformation of TiO_2. As shown in Fig. 1, although pure rutile phase could be obtained at room temperature, the increasement of temperature promotes the transformation from rutile to anatase. For example, the weak diffraction peak of anatase appeared at 50 ^{o}C (see $2\theta = 25.4^{o}$). Besides, when the temperature was increased to 100 ^{o}C, anatase became dominated. The crystallinity of anatase TiO_2 could be enhanced gradually with higher temperature. Interestingly, when the temperature achieved to 200 ^{o}C, we found most of the anatase phase transformed into rutile phase again. Moreover, the average sizes of the TiO_2 nanoparticles derived at different temperature were calculated by using Scherrer equation. The average sizes of rutile nanoparticles obtained at room temperature, 150 ^{o}C, and 200 ^{o}C were 8.5, 10.5, and 42.0 nm, respectively. While the average sizes of the anatase nanoparticles obtained at 150 ^{o}C and 200 ^{o}C were 7.1 and 19.5 nm, respectively. Obviously, higher temperature facilitated the crystal growth of both rutile and anatase phase. According to Rietveld analysis, the mole fraction of anatase first increased and then decreased with the temperature increasing (the mole fractions of anatase were 4.63 %, 81.38 %, and 1.66 % at 50 ^{o}C, 150 ^{o}C, and 200 ^{o}C, respectively).

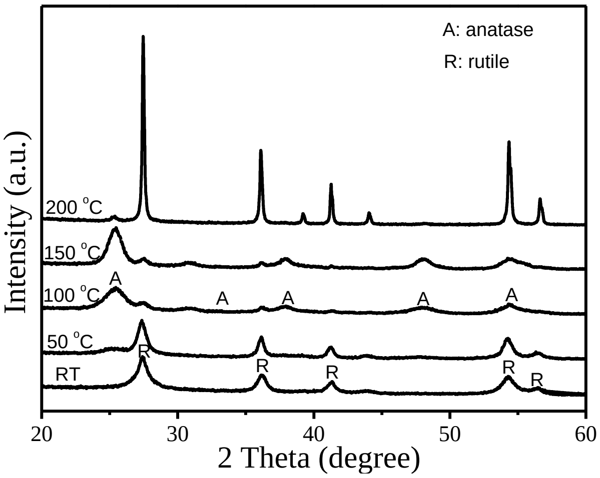

Fig. 1. XRD patterns of TiO_2 without HF obtained at different temperatures

To investigate the reappearance of rutile phase at higher temperature, we further study the XRD patterns of samples obtained at 200 ^{o}C during different reaction time. As shown in Fig. 2, when the reaction time was shorter than 3 h, anatase phase dominated. If the reaction time prolonged to 6 h, rutile phase appeared, and its ratio in the mixed phase gradually increased with the reaction time prolonging. Pure rutile phase could be formed when the reaction time proceed to 36 h at 200 ^{o}C, confirming the higher reaction temperature facilitate the transformation from anatase to rutile. To the best of our knowledge, such phase transformation process need much lower energy than that in the high temperature calcination process.

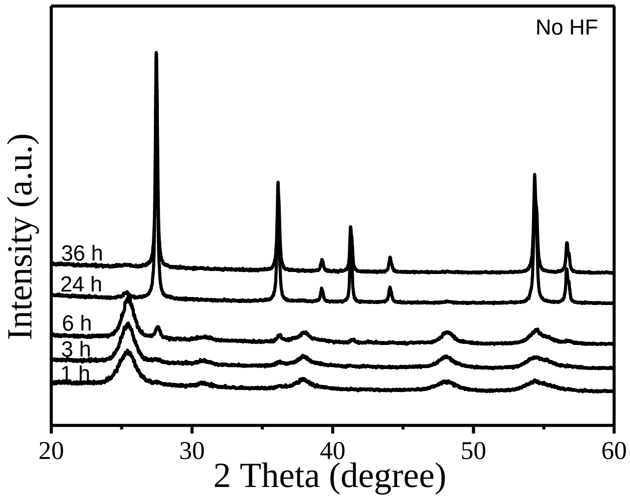

Fig. 2. XRD patterns of TiO_2 without HF obtained at 200 °C under different reaction stages

It is thought that when the temperature was elevated, the hydrolysis reaction rate of $TiCl_4$ would be accelerated, thus the content of OH^- in $[Ti(OH)_{6-n}Cl_n]^{2-}$ complexes would increase and some edge-shared TiO_6 octahedra formed by the dehydration reaction of $[Ti(OH)_{6-n}Cl_n]^{2-}$. Therefore, the phase ratio of anatase versus rutile gradually increased when the temperature was promoted. When the temperature was further elevated to 200 °C, the dehydration reaction rate was further accelerated, so anatase phase formed at the first stage. However, the surface energy of formed anatase particles was much high, the rutile phase as thermodynamically stable phase appeared. We conclude that the Cl^- could adjust the phase transformation between rutile and anatase mainly by controlling the hydrolysis rate of Ti^{4+} assisted with the thermally stability of different phase.

3.2. The influence of F^- in TiO_2 phase transformation

Fig. 3 shows that at room temperature, pure rutile TiO_2 could be obtained in the absence of HF solution in the reaction system. When 0.02 mL HF was added into the solution, the rutile phase of TiO_2 did not show obvious change except for a slow decrease of the diffraction peak intenstiy, indicating the addition of HF could inhibit the crystal growth of rutile phase. Interestingly, when the amount of HF solution was more than 0.10 mL, the rutile phase transformed to anatase phase completely, which reveals the presence of HF facilitated the growth of anatase phase TiO_2. Meanwhile, the slight increase in diffraction peak intensity with increasing amount of HF solution confirms the promotion effect of HF on anatase crystalline grain growth. This reaction can be completed at room temperature, requiring lower energy than the previous methods performed in hydrothermal reaction or calcination process. It is thought that the F^- has smaller ionic radius and stronger electronegativity than that of Cl^- and OH^-, so F^- as strong ligand can form complex with Ti^{4+} easily. Considering the strong electronegativity of F^- leading to the strong attract between Ti^{4+} and F^-, which can strongly decrease the elecron density around Ti^{4+} and make the electron on OH^- shift to Ti^{4+} in $[Ti(OH)_{6-n-m}Cl_nF_m]^{2-}$. Therefore, the introduction of F^- should shorten the distance between Ti^{4+} and OH^-, favoring for the edge-shared combination mode between TiO_6 octahedras and thus promote the formation of anatase TiO_2.

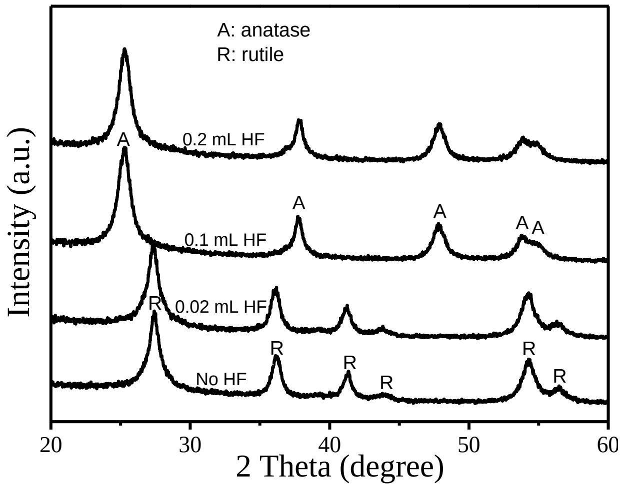

Fig. 3. XRD patterns of TiO_2 obtained with different amount of HF under room temperature

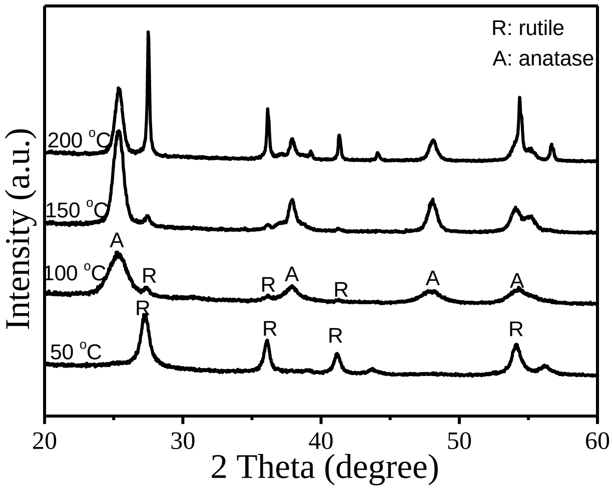

Fig. 4. XRD patterns of TiO_2 with 0.02 mL HF obtained at different temperatures

For further understanding the control function of F^- in the formation of anatase phase of TiO_2, we study the influence of temperature on its phase transformation with different content of F^- in the reaction system. Compared with the reaction system without HF (Fig. 1), we found the ratio of anatase phase was higher with the addition of 0.02 mL HF in the reaction system at the temperature above 50 °C (see Fig. 4, according to Rietveld analysis, the mole fractions of anatase were 0.00%, 89.16 %, and 29.11 % at 50 °C, 150 °C, and 200 °C, respectively). When the amount of HF increase to 0.20 mL, only anatase phase TiO_2 was obtained at any reaction temperature, but the diffraction peak intensity increased with the reaction temperature elevated (see Fig. 5). These results confirmed that the introduction of F^- could promote the formation of anatase TiO_2. Although the temperature could accelarate the hydrolysis of $[Ti(OH)_{6\text{-}n\text{-}m}Cl_nF_m]^{2-}$, the strong coordination and electronegativity of F^- could shorten the distance between Ti^{4+} and OH^-, which favored for the edge-shared combination mode betwwen the TiO_6 octahedras. On the other hand, the surface adsorbed F^- ions on formed anatase particles should decrease their surface energy, so the transformation from anatase to rutile should be retarded under current conditions.

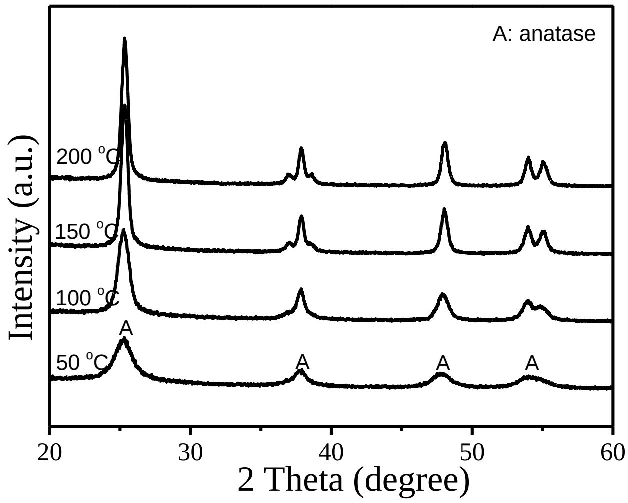

Fig. 5. XRD patterns of TiO_2 with 0.20 mL HF obtained at different temperatures

4. Conclusions

In summary, we have realized the transformation via a rutile to mixture of rutile and anatase and to rutile by Cl^- controlled hydrothermal process, the hydrolysis rate of Ti^{4+} and the thermally stability of different phase are the major factor responsible for the transformation between rutile and anatase. Differently, the F^- could control the transformation from rutile to anatase at room temperature, its strong coordination effect with Ti^{4+} was considered to be the major reason.

Acknowledgements

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