

Chapter 5. General Conclusions

Today, environmental protection and search for reversible energy sources have been two global critical tasks. Titanium oxides and titanates are regarded as powerful candidate of solar energy application materials due to its non toxic, low cost, and good photo-electric-chemical properties. However, the photocatalytic efficiency still is developable. For improving the photocatalysis performance, we modify material structure to enhance the capability and effective photon absorbability. The nanostructuring of TiO_2 is a direct route to achieve the ambitions.

Chimie douce (hydrothermal) method provides a controllable artifice by gradually polycondensation of titanium hydroxo initiator to alkali titante and finally TiO_2 . To employ this method, alkali titante nanostructures were obtained from aqueous basic solution at much lower temperature (100°C - 200°C) than traditional solid state method (800°C - 1000°C). These nanomaterials were verified having large specific surface area ($200\text{-}400\text{ m}^2\text{g}^{-1}$) and good photo-electro-chemical properties after appropriate modification (ion exchange, anneal, doping...etc.). Although the structure has not been decided yet, the titanate nanotubes were reported applicable on lithium intercalation, photocatalyst, solar cell and hydrogen storage.

The relationships between synthesis conditions and various morphologies of sodium hydroxo titanate products have been studied to improve the comprehension of adjustable titanate nanostructures. We changed reaction conditions such as grain size and structure of precursors, autoclaved temperatures, basic concentrations and quantities of additive sodium or carbonate.

We discovered that bigger grain sized precursor can form larger titanate layer when these precursors have the same phase. The anatase initiator preferred transforming to lepidocrocite type titanate product, and rutile one forms lamellar ramsdellite type one. That implies the intermediate structure and size is designed by the nature of precursor. The temperature and

basic concentration also sensitively affect intermediate morphology. We can observe more dense products in higher temperature. That may be due to higher pressure and smaller intermediate building block. Besides, the more basic condition makes titanate layer more curvature and dispersed until monolayer rolling up as tubes. When basic concentration is over saturated, the product is amorphous. The additive sodium or carbonate source is conducive to adjust titanate product morphology, which can effectively enhance the growth along (011) plane (length and width).

The nanoribbon structure is “ $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ ” lepidocrocite type (C-center) titanate with stacking of sub-lattice NaO and TiO (layer by layer) along [010]. The cell distance misfit between NaO and TiO sub-lattice cause the observation of a series fringe (repeating unit) distance 10\AA between stepped layerd tritanate (9\AA) and tetratitanate (12\AA) in HRTEM. The nanotube and nanosheet have similar structure with nanoribbon, but exhibit as primitive symmetry with less amount of sodium and more hydroxyl which leads to more curved structure. The submicro-sticks obtained at 220°C from small crystalline and rutile phase precursor is rutile derive new layer structure as lamellar ramsdellite.

The final product structures depend on the nature of initiator and the intermediate from it. In low temperature condition ($<180^\circ\text{C}$), the anatase and brookite phase precursor can form zigzag chain building block and then reconstruct to lepidocrocite type layer structure. The rutile one may deconstruct to linear chain liked unit and form also lepidocrocite in lower temperature condition. However, we can observe lamellar ramsdellite phase in rutile case at medium temperature as 180°C . The linear chain unit may directly construct to double chain building block of ramsdellite when temperature $>180^\circ\text{C}$. The anatase initiator is not easy to transform to lamellar ramsdellite type titanate, beside of small crystalline initiator high temperature at 220°C , because of their shorter zigzag chain intermediate can further deconstruct to small building block for reconstruction of linear chain or double chain unit of ramsdellite structure.

These titanate nanostructures can transform to tiania and remain their special shapes after proton exchanging and annealing. This property provides a novel simple route of nanostructured TiO_2 (from bulk TiO_2 to nano TiO_2).

We also studied the temperature effect of size control in potassium titanate nanowire synthesis. We used TiOCl_2 as precursor reacting with KOH to obtain various sized nanowire in different autoclaved temperature condition. The size of nanowire is bigger as the reaction temperature raise.

In the study of photocatalytic activity, we discovered that the nanoribbon, nanosheet and nanofiber (small nanoribbon) which sodium in titanates was substituted completely by hydrogen ion in dilute acid and then annealed are photoactive. They all have similar even better efficiency than P25, but lower adsorbability of reactant due to the existence of absorbed carbonate. The nanoribbon and nanofiber have better photoactivity due to the better crystallized, even though their specific areas are smaller than the one of nanosheet. Therefore, the most important key to improve the efficiency is less defects and more surface with high density of active site, the second is bigger specific surface.

In the study of lithium intercalation, we found the $\text{TiO}_2(\text{B})$ phase samples have better property. The structural carbonate causes an irreversible capacity in the beginning. As the rule mention above, the structure designs the property of material; the smaller crystal size has better efficiency (larger capacity and faster diffusion rate) when considering a same phase.

Before this thesis, there is no systematic study of correlations between reaction conditions (initiator nature, solution concentration, temperature and carbonate additive) and various product morphologies. We have studied the structure of each titanate nanostructures obtained and proposed possible growth mechanisms. Furthermore, we also examined and confirmed the titania nanostructures from nano-titanate with preferred orientation has better photo-electro-chemical property, which provide a easy and possible route to improve the efficiency of photo-induced process.

In perspectives, we will employ the comprehension of morphologic control of titanate nanostructures to adjust and design new materials for further applications, such as water splitting, photobattery...etc. To synthesis hybrid with other materials for properties modification is also a developable subject. On the other side, we will try to in-situ observe the formation of intermediate building block for advanced attesting our conclusions. Besides, we will keep searching possible applications of the titanate nanostructures, such as water splitting, photo battery...etc. Moreover, to complete the assignment of Raman band and EXAFS study will be helpful to further structural discuss.

