Chelation-assisted Hydrothermal Synthesis of TiO2 with Hierarchical Structures Using Water-soluble Titanium Complexes

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授　与　学　位	博士（工学）
学位授与年月日	平成２４年９月２５日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）化学工学専攻
学位論文題目	水溶性チタン錯体を用いたキレート水熱法による階層構造を有する TiO_2 の合成
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論文内容要旨

Chelation-assisted Hydrothermal Synthesis of TiO_2 with Hierarchical Structures using Water-soluble Titanium Complexes

(水溶性チタン錯体を用いたキレート水熱法による階層構造を有する TiO_2 の合成)

The work presented here is composed of the synthesis of novel water-soluble titanium complex and hydrothermal synthesis using those complexes for the production of titania structures with hierarchical features. One of the main interests is to use environmentally benign process for the synthesis of hierarchical structures in which ligand play roles as chelating agent as well as structure-directing agent.

Chapter 1 Introduction

Water-soluble titanium compounds are convenient, nontoxic and environmentally friendly precursors for the solution-based synthesis of titanium oxide and titanium-based materials. Water-soluble complexes of titanium have been proved to be very promising reagents for environmentally benign synthesis of titanium dioxide materials in a bottom-up controlled manner. It has been intensively explored that titanium complex is an excellent precursor for the controlled synthesis of four polymorphs of titania by tailoring the solution pH, concentration of the complex or hydrothermal condition. Nevertheless, under such condition, the morphology control of the obtained titania is rather limited. For better control over size and shape, the use of structure-directing agent is crucial. In the synthesis method using titanium complex, ligand itself can play a role as structure-directing agent. The interaction between ligands may promote the assembly of primary particles into hierarchical structures. The chelation of ligand to primary nanocrystals surface may restrain the crystal growth in some specific direction, resulting in the growth of specific shaped crystals. Therefore, the main objective of this work is the synthesis of novel titanium complex and to extend this synthetic approach beyond simple nanocrystals to hierarchical structures by means of chelation-assisted synthesis, opening up the opportunities to explore novel chemical and physical properties of these materials.

Chapter 2 Experimental section

Chapter 2 has described the general synthetic approach, characterization method, as well as the photocatalytic hydrogen production system.

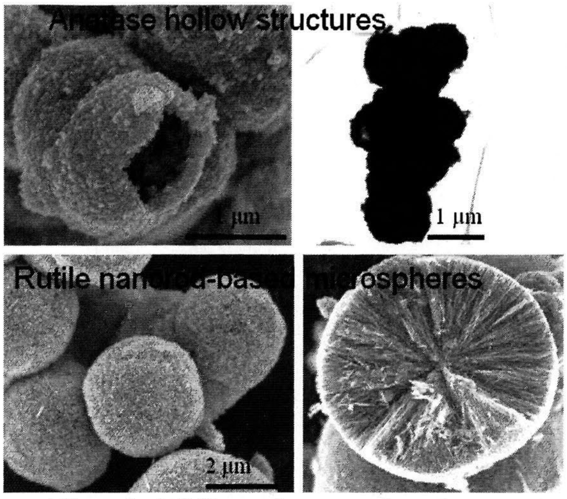

Fig. 1. TiO_2 microspheres

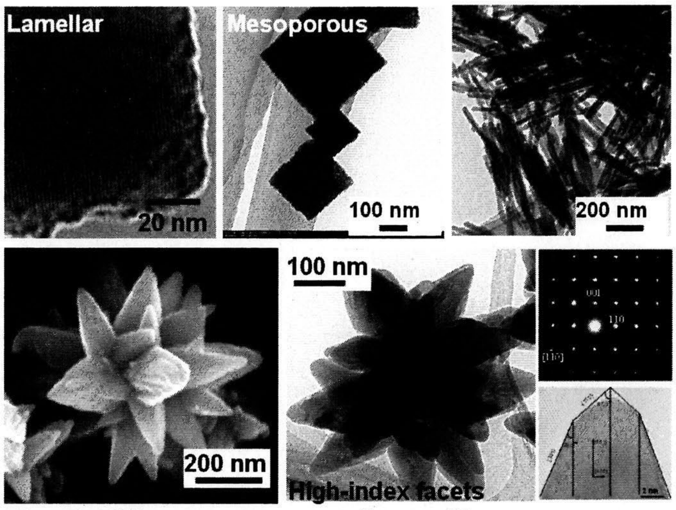

Fig. 2. TiO_2 mesoporous, flowerlike structures

Chapter 3 Chelation-assisted Self-Construction of TiO_2 Hollow Structures

Chapter 3 deals with the synthesis of titania hollow structures. It is a long-standing problem in the synthesis of TiO_2 hollow structure relating to the use of toxic fluoride compounds which cause the corrosion, toxicity accompanied with low yields, fluoride adsorbed surface, etc. This chapter introduces a novel chelation-assisted dissolution approach to construct titania hollow structures with controllable structural features (Fig. 1). Titania hollow structures were obtained by hydrothermal treatment of titanium complex with oxalic acid or malonic acid. The hollowing process relies on the chemical conversion, in which solid cores were transformed to water-soluble species by reacting them with a complexing agent such as oxalic acid, malonic acid. The approach allows to control crystalline structure, size, shell thickness, and organized manner by tailoring pH, ligand or amount of ligand.

Chapter 4 Growth of TiO_2 Nanorods into 3D Hierarchical Microspheres

The growth and assembly of hierarchical nanorod-based microspheres are discussed in Chapter 4. In particular, one-dimensional TiO_2 nanostructures have attracted much attention due to their unique optical and electrical properties promoting a fast charged transport through a continuous conducting pathway. In this work, hierarchical TiO_2 microspheres assembled from 1D nanostructures are synthesized by hydrothermal treatment of titanium oxalate complex in an acidic solution (Fig. 1). Based on the experimental result above-mentioned, the morphological evolution has been described as follows: formation of nanorod structures, assembly of the primary nanocrystals into bundles, followed by oriented attachment growth and dissolution-recrystallization to produce the porous hierarchical structures. Oxalic acid as a ligand played a crucial role in gathering primary nanocrystals into an ordered microsphere, based on the chelation of its functional groups on the titania surface.

Chapter 5 A Novel Microporous Titanium Picolinate Lamellar Nanostructures: Synthesis, Structural Characterization, and its Conversion to Mesoporous TiO_2

Chapter 5 reports the synthesis and characterization of novel microporous titanium picolinate with lamellar structure. The hydrothermal reaction of titanium-picolinate complex with picolinic acid under mild condition led to the formation of a layered nanohybrid (Fig. 2). The layered materials show high specific surface area of 289 m^2 g^{-1} with 170 m^2 g^{-1} as internal micropores and a micropore volume of 0.074 cm^3 g^{-1}. Hydrothermal treatment of the complex solution under different condition enables to produce the hybrids with various structural features such as nanoplatelet, nanocube, nanorod and microspheres. The organic ligand, picolinic acid, not only acts as an intercalation molecule for the formation of a layered organic–inorganic hybrid structure, but also provide pi-pi interaction for directing the growth of hybrid and titania structures with various morphology. The removal of intercalated organic compound by calcination yielded porous titania structures with retaining geometry and uniform pore sizes.

Chapter 6 Hierarchical Rutile Nanostructures with Exposed High-Index Facets

Novel hierarchical rutile nanostructures with exposed high-index facets are presented in Chapter 6 (Fig. 2). A facile synthesis of rutile bound by high-index facets is described involving the use of titanium-glycolate and titanium-lactate or titanium-citrate as precursors and picolinic acid as structure-directing and capping agent. Picolinic acid with its unique structure provides effective tools for self-assembly of hierarchical flowerlike structures. The mutual π-stacking and selective adsorption of picolinic acid on specific {111} facets cause the competitive growth of {110} facet and {111} facet, resulting in the formation of such unique nanocrystal branches with exposed high-index planes.

Chapter 7 General conclusions

From above research, it can be concluded that ligand, based on its chelating properties, provides capping effect for the growth of crystals with specific shape. More importantly, the mutual interactions of ligand such as hydrogen bonding or pi-pi interaction are crucial for the formation of the hierarchical structures. Particularly, the self-assembly is mainly driven by these interactions, which provide an effective and elegant tool for building unusual shapes and complex patterns. The chelation-based synthesis may open up new opportunities for facile creation of novel hierarchical nanostructures with desired functional properties.

論文審査結果の要旨

本論文は「Chelation-assisted Hydrothermal Synthesis of TiO_2 with Hierarchical Structures Using Water-soluble Titanium Complexes (水溶性チタン錯体を用いたキレート水熱法による階層構造を有する TiO_2 の合成)」と題し、7章から構成されている。

第1章「Introduction (序論)」では、水溶性チタン錯体を用いた酸化チタン合成に関する過去の研究についてレビューし、本論文の位置づけと価値について述べている。

第2章「Experimental Section (実験方法)」では、キレート水熱法の実際を詳述し、得られた酸化チタンの物性評価の方法を述べている。

第3章「Chelation-assisted Self-Construction of TiO2 Hollow Structures (キレート支援による中空酸化チタン粒子の合成)」では、シュウ酸もしくはマロン酸を可溶化キレート剤として導入し、酸化チタン粒子内部を溶解させることで、サイズの制御された酸化チタン中空粒子を製造できることを述べている。

第4章「Growth of TiO_2 Nanorods into 3D Hierarchical Microspheres (酸化チタンナノロッドの集積化による階層構造制御されたマイクロ球状粒子の合成)」では、1次元的な酸化チタンナノロッドを集積化する方法を述べ、特にシュウ酸をキレート剤に用いると、酸化チタンナノ結晶表面とシュウ酸との強い相互作用により、ナノロッドが球状に集積化するメカニズムを提案し、その妥当性について議論している。

第5章「A Novel Microporus Titanium Picolinate with Lamellar Structure and its Conversion to Mesoporous TiO_2 (マイクロポーラスを有するラメラ構造のピコリン酸チタン及びそれを用いたメソポーラス酸化チタンの合成)」では、ピコリン酸チタンの水熱処理により得られるラメラ構造が積層した有機無機ハイブリッドを仮焼することでメソポーラス酸化チタンを製造できると述べている。

第6章「Hierarchical Rutile Nanostructures with Exposed High-Index Facets (高面指数面が露出した階層構造制御されたルチルナノ構造)」では、ピコリン酸をキャッピング試薬として用いることで、高面指数の面が露出したルチル型酸化チタンを簡単に合成できることを示している。

第7章「General Conclusions (総括)」では、本論文の全体を総括し、本論文で得られた結論、今後の展望について述べている。

よって、本論文は博士(工学)の学位論文として合格と認める。