氧化鈦奈米材料之合成、結構與性質

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摘要

環保與能源是新世紀人類的兩項重要課題。氧化鈦為一無毒、經濟且儲量豐富的半導體材料，擁有多樣結構以及優越的光電化學性質，可將太陽能轉換成化學能應用於光伏打電池電極和光催化劑等。近來，二氧化鈦亦被用於鋰離子電池及超高電容電極材料上。這些應用使得氧化鈦被視為一個卓越的候選材料，可同時解決上述的兩道難題。已知光電化學反應是發生在材料的表面以及異相介面。所以，具有高比表面積、高活性位址的材料將可有效地提升反應效能。而鋰電池電極之效率則取決於鋰離子對材料的可逆嵌入。因此，研究可訂製高比表面積氧化鈦的奈米化方法，對於提高材料效能而言，是十分必須的。

本研究中，我們採用柔化學法，以市售二氧化鈦粉末與氫氧化鈉水溶液合成水合鈦酸氫鈉奈米結構。以調控各種氧化鈦奈米結構的起始物、化學組成、溫度以及鹼液濃度為手段來最佳化合成條件。在不同的實驗條件下，可得各式鈦酸鹽奈米結構，像是奈米

頁、半奈米管、奈米管、奈米帶以及次微米棒等。奈米頁為類纖鐵礦結構，得自小晶粒前驅物與低溫(<150˚C)、低濃度氫氧化鈉溶液環境(<5M)；半奈米管亦為類纖鐵礦結構，得自小前驅物、低溫、高濃度鹼液(>10M)反應；奈米管為類纖鐵礦結構，以大晶粒起始物於低溫、10M氫氧化鈉溶液環境下合成；奈米帶為類“$Cs_2Ti_6O_{13}$”結構，得自高溫(>160˚C)、高鹼液濃度條件；次微米棒為層狀類針鐵礦結構，得自更高溫(>220˚C)與高鹼液濃度環境。將產物以稀酸溶液進行完全的氫離子取代並加以熱處理後，可得到維持原來鈦酸鹽階段形貌的二氧化鈦(銳鈦礦、B型二氧化鈦或金紅石相)奈米結構。我們深入研究這些鈦酸鹽及二氧化鈦產物的微結構與形貌並推斷此類材料之成長機制。

我們進一步地測試了這些具有優選晶向的二氧化鈦奈米結構之光催化與鋰嵌入性質。發現自鈦酸氫鈉奈米頁與奈米帶轉變而來的銳鈦礦相二氧化鈦奈米結構具有極佳的光催化效能表現。此外，源自鈦酸氫鈉奈米帶之TiO_2(B)奈米帶則有很好的可逆鋰嵌入容量。我們也提出了再進一步提升效率的可能對策。

Synthesis, Structure and Properties of Titanium Oxide Nanomaterials

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ABSTRACT

The environmental protection and energy issue are two of the most important topics to all mankind in the 21st century. Titanium oxide is a non-toxic, economic and abundant semiconductor material with various structures and excellent photoelectric properties to be applied in conversion of solar energy to chemical energy as photocatalyst and solar cell electrode. Recently, it is also used on the electrode of Li-ion battery and supercapacitor. It is regarded as one remarkable candidate to resolve both the crucial subjects above-mentioned. As we know that the photo-induced process is carried out on the interface and surface of the materials. The materials with larger surface area and more active sites can significantly enhance the performance. Besides, the efficiency of electrode materials in Li-ion battery depends upon the reversible intercalation of the host materials. Thus, a tailor-made nanostructuration of titanium oxide with large surface area is necessary to improve the material's performances.

In this study, we synthesize various nanostructures of sodium hydroxo titanate from commercial TiO_2 precursors and sodium hydroxide solution by chimie-douce (solvothermal) method. The synthetic conditions had been optimized by adjusting reaction temperatures, basic concentrations and the microstructures and particle sizes of TiO_2 precursors. We can obtain various titanate nanostructures such as nanosheet, semi-nanotube, nanotube, nanoribbon and submicro-stick in the different conditions. The nanosheet is lepidocrocite type titanate obtained from small grain TiO_2 precursor in lower concentration $NaOH_{(aq)}$ (<5M) at lower temperature (<150˚C); the semi-nanotube is also lepidocrocite-type from small precursor in higher concentration $NaOH_{(aq)}$ (>10M) at lower temperature; the nanotube is lepidocrocite-type made by big grain initiator in 10M $NaOH_{(aq)}$ at lower temperature; the nanoribbon is "$Cs_2Ti_6O_{13}$"-type obtained in higher concentration $NaOH_{(aq)}$ at higher temperature (>160˚C); the submiro-stick is lamellar ramsdellite-type from higher concentration $NaOH_{(aq)}$ at much higher temperature (>220˚C). After the sodium in titantes was substituted completely by hydrogen ion in dilute acid and annealed, nanostructured titanium dioxides (anatase, TiO_2(B) and rutile) retained the morphologies in titante state were obtained. The microstructures and morphologies of titanates and titanium dioxides were studied in detail and the mechanism of growth and condensation of these materials was figured out.

In addition, some nanostructured TiO_2 with preferred orientation are examined in photocatalysis and Li-ion intercalation. We found the titanium oxides with anatase phase from the titanate nanosheet and nanoribbon have high photocatalytic efficacy, and TiO_2(B) nanoribbon from the titanate nanoribbon has good reversible lithium ion intercalation property. We also proposed some possible ways for further improvement.