


謝誌

二年的研究生涯告一段落，辛苦後總算得到代價了，多虧了許多人的幫忙協助，我才能順利完成論文，首先，我得謝謝我的指導教授 張叔閔老師，在她悉心的引導之下，讓我真正了解做研究應該有的精神與態度。除了實驗工作之外，不管是在為人處世與生活上也都相當關心，跟我們相處就像學姐與學弟妹之間的關係，感覺親切又有熱心。也謝謝董瑞安老師提供相當完善的實驗設備讓我能順利進行實驗，並且感謝白曠綾老師、黃暄益老師、閻明宇博士對本論文悉心指正並提供許多建議，使本論文更趨於充實完善。



另外，實驗室同學品欣跟我可以說是一起辛苦幫忙建立實驗室到現在，共患難的朋友，學妹品涵、維斯、學弟精榮，更增添了實驗室內熱鬧的氣氛並不時地帶來歡樂。謝謝董老師實驗室的學長俊錡、添進、平善、學姊世慧、世芬、家敏、同學依琳、涵云、唐興在實驗上的幫助及其他生活上種種的協助，跟你們相處就像在同一個實驗室那樣的親切。

最後謝謝靜樺，一直陪伴在我身邊替我打氣加油並與我分享喜悅，也能夠體諒我，讓我有時間來專心完成論文。

傑耀

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中文摘要

三辛基氧化磷包覆之二氧化鈦奈米晶粒已成功地使用非水解性溶膠凝膠法製備出來。為了解熱處理對於三辛基氧化磷包覆之二氧化鈦奈米晶粒微結構、電子結構以及表面特性的影響，高解析度穿透式電子顯微鏡、X 射線繞射儀、傅立葉紅外光光譜儀、X 光光電子能譜儀、熱重分析儀以及紫外光可見光光譜儀都被用來鑑定鍛燒過的樣品 (250~950 °C)。因為鍛燒的過程將表面氧化三辛基磷分子熱分解並形成磷酸分子之關係，使得加熱 750 °C 以下之樣品表面由疏水性轉變成為親水性。然而疏水性質又在鍛燒 950 °C 後產生在奈米晶粒表面上。參雜進入晶體結構內之鋁離子與磷離子增加了銳鈦礦晶體的熱穩定性，即使是加熱到了 950 °C 之高溫也沒有晶相的轉變。除此之外，當鍛燒溫度小於 750 °C 時，晶粒的大小維持在 10.2-10.8 奈米，並且在鍛燒 950 °C 顯著地增加到 16.1 奈米。能隙之大小隨著晶粒大小的變化從 3.4 電子伏特減少到 3.2 電子伏特。鍛燒到 550 °C 之樣品因為擁有低介達電位以至於較鍛燒 950 °C 之樣品表面有較多的布忍斯特酸基。然而鍛燒 950 °C 的樣品較初製備及鍛燒 250 °C 與 550 °C 的樣品有更高的表面活性。而路易斯酸被認為是鍛燒 950 °C 之樣品有高活性的主要原因。

Abstract

Trioctylphosphine oxide (TOPO) capped Zr^{4+}/TiO_2 anatase nanocrystals were successfully prepared by a non-hydrolytic sol-gel route. To understand the effect of thermal treatment on the microstructures, electronic structures, and surface properties of the TOPO-capped Zr^{4+}/TiO_2 nanocrystals, the samples calcined at elevated temperatures (250-950 °C) under air atmosphere were examined by means of HRTEM, XRD, TG-DSC, XPS, FTIR and UV-vis spectroscopy. Calcination below 750 °C converted the surface of the nano-crystals from hydrophobic to hydrophilic as a result of decomposition of the surface TOPO and formation of phosphate moiety. However, hydrophobic property was further obtained at 950 °C due to dehydroxylation. The introduced P^{5+} and Zr^{4+} enhanced the stability of the anatase form till 950 °C without any phase transformation. Moreover, the crystallite sizes of the samples were maintained at 10.2-10.8 nm at 250-750 °C and were remarkably increased to 16.1 nm as the calcination temperature rose to 950 °C. The band gaps of the samples declined from 3.4 to 3.2 eV upon the increasing crystallite sizes. Calcination at 550 °C resulted in lower zeta-potential and higher surface Bronsted acidity than those at 950 °C. However, the sample calcined at 950 °C showed the highest surface activity than the as-prepared nanocrystals and the samples calcined at 250 or 550 °C. Lewis acidity is considered to be responsible for the high photoactivity at 950 °C.

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