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一種高活性二氧化鈦混晶光觸媒的製備及其混晶特性鑑定的研究

Preparation of a Highly Active Bicrystalline Tio2 Photocatalyst and the Characterization of the Synergetic Effect of Its Dural Crystalline Phases

林秋薰

Abstract

The primary goal of this three-year proposal is to investigate whether there is a synergetic effect between two metal oxide semiconductors with different band structure (which is the positions of conduction and valence band and band gap energy) within a bicrystalline photocatalyst. A photoelectrochemical method using methyl viologen will be established to measure the flat band potential of all the metal oxide semiconductors. A diffuse-reflectance UV-Vis spectrometer will be used to measure the band gap energy. By combining both measurements, we will be able to determine exactly the band structures of metal oxide semiconductors. In the first year of the project, a hydrothermal method will be utilized to synthesize titania particles with well-defined crystalline phase (including anatase, rutile and brookite) and particle size. We will investigate how the variation in titania particle size modifies their band structures. Furthermore, TiO2 (B) nanotube/titania nanoparticle bicrystalline mixtures will be prepared using dry physical mixing and wet mixing to investigate synergetic effect between the two components. In the second year, a precipitation method using aqueous ammonia and metal salts will be used to prepare SiO2, Fe2O3, SnO2 and ZrO2 powder, which will be mixed with TiO2(B) nanotubes to prepare bicrystalline mixture. Nanoparticles contained in a sol solution will be impregnated on the TiO2(B) nanotubes for preparing a better dispersed bicrystalline mixture. The mixtures from both preparation methods will be used to investigate the synergetic effect between TiO2 (B) and four different metal oxides. In the third year, we will attempt to prepare sulfated TiO2(B) nanotubes. They will be prepared by impregnating TiO2 (B) nanotubes with sulfate solution. The effect of volume/mass ratio of SO4 2- solution/TiO2(B), SO4 2- concentration, sulfate source (such as H2SO4 or (NH4)2SO4) and the calcination temperature on the physical and acidic properties as well as the band structure of the sulfated TiO2(B) nanotubes will all be investigated. Metal oxide nanoparticles will also be dispersed onto sulfated TiO2 (B) nanotubes to prepare a sulfated TiO2 (B) nanotube/metal oxide bicrystalline mixture for synergetic effect investigation. All the above photocatalysts will be characterized by various spectroscopic methods such as XRD, SEM, TEM, BET, TPD/NH3, DRIFTS/pyridine, diffuse-reflectance UV-Vis spectroscopy, XPS and photoelectrochemical measurements for their physical (particle size, surface area, morphology, fine structure, band structure and phase composition) and chemical properties (acidity, sulfate structure, oxidation state and content of sulfur). The activities of the above single or bicrystalline photocatalysts will be measured by photocatalytic degradation of salicylic acid in aqueous solution to see whether there is a synergetic effect. The kinetic data of the photocatalytic degradation will be analyzed using Langmuir-Hinshelwood model to obtain the degradation rate constant, and the adsorption of salicylic acid on these titania photocatalyst will also be performed to obtain the adsorption equilibrium constant. Combining both set of data, we can obtain the scientific reasons underneath the synergetic effect. Furthermore, Pt metal will be deposited on TiO2(B) nanotube/anatse particle and TiO2(B)/metal oxide by photodeposition method, respectively. Subsequently, XPS and TEM will be used to analyze the location of the deposited Pt, from which we can verify the validity of the synergetic effect predicted by the measured band structure.

Key words：Synergetic effect; TiO2 (B); Flat band potential; Bicrystalline; Composite

中文摘要

本 3 年研究計劃最主要的目的是求証兩个能帶結構不同的氧化物半導體，是否在光催化過程中存在著混晶效應。吾人將建立一種利用 methyl viologen 分子為氧化還原介質的光/電化學的方法，來量測導帶和價帶的能量位置。結合此資料與從紫外光-可見光光譜儀所測得的帶隙能，我們便能夠知道氧化物半導體的能帶結構。在第一年計劃中，吾人將利用水熱法合成不同晶粒大小的銳鈦礦、金紅石和板鈦礦，並量測其能帶結構如何隨晶粒大小而變化。我們會利用乾式和溼式混合法，來製備 TiO2(B)奈米管 /二氧化鈦粒子的雙晶相混合物，並用來測試混晶效應。在第二年計劃中，吾人將利用金屬鹽類和沈澱法來製備 SiO2, Fe2O3, SnO2 and ZrO2 等 4 種粉末，並以乾式和溼式混合法製備 TiO2(B)奈米管/4 種氧化物的雙晶相混合物。為了增加氧化物在 TiO2(B)奈米管上的分散度，我們也會製備含有這 4 種氧化物奈米粒子的溶膠，並含浸此溶膠於 TiO2(B) 奈米管上。此二種 TiO2(B)奈米管/氧化物雙晶相混合物，均會用來測試混晶效應。在第三年計劃中，我們會嘗試使用含浸硫酸根溶液的方法，製備含有硫酸根的 TiO2(B)奈米管。各種製備條件如浸硫酸根溶液體積/TiO2(B)奈米管質量比、硫酸根濃度和來源、鍛燒溫度對所製備出來的含硫酸根的 TiO2(B)奈米管的物性和化性均會做詳細的探討。當然吾人也會製備含硫酸根的 TiO2(B)奈米管/氧化物雙晶相混合物，並測試其混晶效應。以上所製備的光觸媒均會以適當的光譜儀像 XRD、SEM、TEM, 、BET、TPD/NH3、 DRIFTS/ pyridine、diffuse-reflectance UV-Vis、XPS 和光/電化學的方法，詳細鑑定其物性(包括晶粒大小、表面積、晶相組成/結晶性、形態、細微結構和能帶結構)及化性 (酸性、表面硫酸根結構及硫的氧化態和含量)。另外，上述單晶或雙晶的光觸媒的活性，均以在水溶液中分解水楊酸來測量並以較完整的 Langmuir-Hinshelwood 模型來分析其動力學數據，再結合水楊酸在上述光觸媒的吸附實驗，就可分別求得水楊酸在上述各種觸媒的分解速率常數和吸附平衡常數。從兩者的大小，我們得以知道造成混晶效應的真正成因。最後我們擬利用光置放的方法把 Pt 金屬，置放在 TiO2(B)奈米管/銳鈦礦粒子和 TiO2(B)奈米管/氧化物兩種雙晶相混合物上，並利用 XPS 和 TEM 來偵測 Pt 附著的晶相，如此我們可以得知利用所量測的雙晶混合物的能帶結構所預言的混晶效應是否正確。

關鍵字：混晶效應; TiO2 (B)奈米管; ?晶混合物; 能帶結構; 硫酸根