学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　　　　博士（総合化学）　　　　氏名　　許　華

学 位 論 文 題 名

Study of Advanced TiO_2-based Materials towards Superior Photocatalytic Properties
（高活性酸化チタン光触媒の研究開発）

Semiconductor photocatalysis has attracted considerable attention as a promising solution to the environmental pollution and energy crisis. Among the various photocatalysts, TiO_2 has been proven to be the benchmark photocatalyst because of its superior photoreactivity, nontoxicity, long-term stability, low cost, and environmental friendly features. Nevertheless, there are still some limitations in the aspects of light absorption, charge recombination, and surface reactivity for TiO_2 photocatalysis, which need to be further improved for the practical application.

In this thesis, the topic is design and development of advanced TiO_2 based materials for the superior photocatalytic properties via enhancing the light absorption, charge separation, and surface reactivity. Firstly, via adopting Mie's scattering effect into the light absorption region of TiO_2, the light utilization efficiency is largely enhanced, accompanied with higher activity in H_2 evolution. Next, to enhance the charge separation efficiency, Cu_2O/TiO_2 nanojunction material is fabricated; this material exhibits much higher photocatalytic activity than pure TiO_2 because of its modified nanojunction structure. Furthermore, considering many physical and chemical processes take place on the surface of TiO_2 in the photocatalytic reaction, TiO_2 single crystals exposed with high-active facets are prepared; via optimization of the surface reactivity, the photocatalytic performance is largely enhanced.

Chapter 1 provides an overview of the photocatalysis, photocatalytic water splitting, CO_2 photoreduction. This chapter also summarizes the TiO_2 based photocatalysis, and strategies of achieving high photocatalytic activities for TiO_2.

In Chapter 2, to enhance the light utilization efficiency, a novel strategy of coupling Mie's scattering effect into the light-absorption region of TiO_2 was developed. TiO_2 spheres with different diameters (330-750 nm) were controllably fabricated. It was found that both the scattering effect and the photocatalytic activity vary with the size of the TiO_2 spheres.

Among them, TiO_2 spheres with diameter of 380 nm exhibited the highest photocatalytic activity, which is attributed to its highly efficient scattering happened in the light-absorption region of TiO_2 ($\lambda < 387$ nm).

In Chapter 3, to enhance the charge separation efficiency, porous-structured Cu_2O/TiO_2 nanojunction materials were successfully fabricated. The well-designed nanojunction structure between Cu_2O and TiO_2 is beneficial for the charge separation. In parallel, the porous structure of the material can facilitate the CO_2 adsorption and offer more reaction active sites. Thus, both the charge separation efficiency and the CO_2 adsorption simultaneously enhanced, leading to the excellent photocatalytic performance in the CO_2 photoreduction.

In Chapter 4, anatase TiO_2 nanosheets with 95% active {100} facets exposed and a relatively large surface area of 57.1 m^2/g were successfully prepared. This percentage (95%) is the highest among previously reported {100} facet exposed anatase TiO_2. Both the higher percentage of exposed {100} facets and larger surface area can offer more surface active sites in the photocatalytic reaction. On the other hand, the superior electronic band structure which is resulted from the higher percentage of {100} facet is also beneficial for the higher activity in both H_2 evolution and CO_2 photoreduction.

In Chapter 5, for the first time, {111} facet exposed anatase TiO_2 single crystals were prepared via both F^- and ammonia as the capping reagents. In comparison with the intensively investigated {001}, {100}, and {101} facets for anatase TiO_2, {111} facet owns a much higher surface energy of 1.61 J/m^2 and more under-coordinated Ti and O atoms, in addition with a superior electronic structure. Both the superior surface atomic structure and electronic band structure make the great contribute to the marked photocatalytic activity.

Chapter 6 summarizes the importance and originality of this research, and provides future prospects of this work. This thesis revealed that the photocatalytic properties of TiO_2 are largely affected by the light absorption, charge separation, and surface reactivity. Mie's scattering effect happened in the light absorption region of TiO_2 can greatly enhance the light utilization efficiency in the H_2 evolution. Porous-structured nanojunction material is beneficial for both the charge separation efficiency and CO_2 adsorption in the CO_2 photoreduction test. Furthermore, fabrication of TiO_2 single crystals with high-active crystal facet exposed can largely promote the surface reactivity and offer more reaction sites in the photocatalytic reaction, is proved to be an effective approach to achieve advanced and excellent performance over photocatalysts.