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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 YU Zhehan

学 位 論 文 題 名

Facile Fabrication of Various Titanium Oxide Particles for the Visible Light Photocatalytic Application

(可視光光触媒用途のための様々な酸化チタン粒子の容易な製造)

Nanotechnology is one of the most attracting research objectives in the world. Due to the small size, nanomaterials usually show unique properties, making it useful in many fields of research. Titanium dioxide, TiO_2 , which is one kind of metal oxide materials, has become the most widely used material. In chapter 1, an overview of this dissertation is given. At first, a review of metal oxide nanomaterial is given, which focuses on TiO_2 with its different structure. In addition, other metal oxide materials are mentioned in this chapter. Then, an introduction of photocatalysis is summarized, containing the structure of dyes (Rhodamine B, methylene blue) and the general photodegradation mechanism of dyes.

In chapter 2, two different fabrication methods are reported for the fabrication of TiO_2 . Black TiO_2 nanoparticles (b- TiO_2) with superior solar-thermal water evaporation performance are prepared using a one-step solution plasma process (SPP) in ambient conditions. It is found that radicals that are generated during SPP play a critical role in b- TiO_2 formation by comparing several water-alcohol electrolyte environments for the SPP synthesis. Our results show that the radical-induced formation of a black TiO_{2-x} layer on the Ti electrode is necessary for b- TiO_2 formation, which was ignored in previous studies. A two-step mechanism for b- TiO_2 formation in SPP synthesis is proposed: (I) pre-oxidation of a Ti electrode surface; and (II) quenching and aggregation of sputtered molten TiO_x clusters to form b- TiO_2 particles. In addition, EC-SPSC method is also used for the fabrication of TiO_2 . Although it is proved that EC-SPSC is able to form TiO_2 , the morphology of the product is very unstable, resisting the further research.

In chapter 3, a new kind of TiO_2 is fabricated by a one-step method for the visible light utilization. This new TiO_2 has ellipsoidal shape, so it is called e- TiO_2 . e- TiO_2 is single crystal structure, with oxygen vacancies and low-valance Ti components. In the fabrication method, hydrogen peroxide was used for the oxidation of titanium plate, and ammonia fluoride was used for the microparticle morphology controlling and pore introducing. Characterizations and calculations have proved that our as-synthesized TiO_2 microparticles were in anatase phase with meso pores, single crystal structure and Ti (III) component. UV-vis-NIR spectra have also indicated that the bandgap of the e- TiO_2 was 2.4 eV, much lower than typical anatase materials (3.2 eV). Rhodamine B and methylene blue were introduced as dyes for the photodegradation test of the e- TiO_2 compared to commercial P25- TiO_2 . Our e- TiO_2

had better adsorption of both dyes and very high efficiency for the photodegradation of Rhodamine B under visible light illumination, whose kinetic constant is four times as much as P25-TiO₂. Thus, the one-step synthesized e-TiO₂ has high efficiency for visible light dye photodegradation.

In chapter 4, a facile modification method is introduced to increase the visible light activity of TiO₂ samples. Titanium isopropoxide (TTIP) is used as the raw Ti source, then hydrolyzing in acidic and alkaline solutions, respectively, to fabricate different TiO₂ samples as pretreatment TiO₂ together with P25-TiO₂. Only hydrogen peroxide and ammonia fluoride are used for this facile modification method, and three TiO₂ samples are modified for the visible light degradation. The present method could promote the transformation of crystalline TiO₂ from rutile to anatase, increase the specific surface area, and the bandgap of samples shift to lower energy (2.2 – 3.0 eV) after the modification. For the visible light photodegradation tests, all the three modified samples show a higher visible light photodegradation efficiency. The highest kinetic constant of Rhodamine B and methylene blue degradation is 7 and 2 times that of P25, respectively. In addition, TiO₂ fabricated by TTIP in alkaline solution and its as-modified sample show the highest adsorption of methylene blue dye, whose adsorption rate reaches 9 times that of P25. Thus, the present facile modification can effectively improve the photocatalytic ability of TiO₂ under visible light.

In chapter 5, an overall conclusion of this dissertation is summarized.

All in all, this dissertation thesis presents a series of systematic research on the enhancement of TiO₂ metal oxide materials, for the enhancement of visible light utilization. This work shows three different pathways to improve the visible light activity of TiO₂ materials. Fabricating new TiO₂ can directly obtain the desired product. However, the yield of both b-TiO₂ and e-TiO₂ are low, which prevents them from further research. Modification is another way for the visible light activity improvement. At this point, the modification of TiO₂ by H₂O₂ + NH₄F can effectively increase the visible light photodegradation efficiency. This method has higher yield than fabricating new TiO₂. In addition, this method can be combined with other modification methods. Therefore, this pathway will be the focus of future research in this experiment.