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Charge separation promoted by phase junctions in photocatalysts

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ABSTRACT

Since the 1980s, photocatalysis research has expanded at an unexpected rate. Fabrication of phase junctions has proved to be an effective method to enhance photocatalytic performance. As a model photocatalyst, titanium dioxide (TiO_2) has been extensively studied. This feature article mainly reviews the study on TiO_2 surface phase junctions, including the characterization of the surface phases of TiO_2, the use of anatase: rutile TiO_2 phase junctions in photocatalytic hydrogen production, and the current understanding of how TiO_2 phase junctions work in photocatalysis. The surface structure of TiO_2 can be well characterized by ultraviolet (UV) Raman spectroscopy, unlike X-ray diffraction and visible Raman spectroscopy. Based on these results, the mechanism of phase transformation processes of TiO_2 was clearly identified. The infrared (IR) spectra of probe molecules CO and CO_2 on TiO_2 further characterized the surface structure of TiO_2, strongly supporting the UV Raman results. Furthermore, the typical visible emission of anatase and near-infrared emission of the rutile phase of TiO_2 make photoluminescence (PL) a suitable technique to characterize the surface phase structure of TiO_2. PL can also provide information about the carrier dynamics of TiO_2 in photocatalysis. Because of the surface phase junction formed between anatase and rutile, the mixed-phase structure of TiO_2 exhibits a superior H_2 production activity to those of pure anatase or rutile phase. The activity of Degussa P25 TiO_2 can be further increased by three to five times by tuning the phase structure through thermal treatment. Moreover, the phase transformation of TiO_2 from anatase to rutile can be controlled by surface modification with Na_2SO_4, resulting in catalysts with activity six times higher than that of P25. High-resolution transmission electron microscopy provided a clear phase-junction image of TiO_2, which showed atomic contact at the interface of the phase junction. The mechanism of phase junctions improving photocatalytic performance was investigated by time-resolved spectroscopic techniques. The charge transfer process across the anatase: rutile phase junction was confirmed by the results of time-resolved IR measurements, and electron transfer from anatase to rutile phases is proposed to occur in mixed-phase TiO_2. These studies on the phase junctions of TiO_2 improve our understanding of photocatalysis and may inspire new ideas for the design of promising photocatalytic systems.

1. Introduction

As a promising strategy to address environmental and energy issues, photocatalysis is attracting increasing attention [1–3]. Though extensive research on photocatalysis has been conducted, the crucial factors determining the efficiency of

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photocatalysis are still not well understood. Usually, photocatalytic reactions involve three major steps: (1) generation of electron-hole pairs on a semiconductor by absorption of photons with energy equal to or greater than its bandgap; (2) separation of electron-hole pairs and migration of these charge carriers to the surface of the semiconductor; (3) surface reduction and oxidation reactions involving electrons and holes, respectively, at the semiconductor surface. These three steps correspond to the three crucial factors of light absorption, charge separation and reaction kinetics. Among these, charge separation is the most complicated and important step.

Among semiconductor photocatalysts, TiO_2 is the earliest and most extensively investigated photocatalyst because it is cheap, stable, nontoxic, and environmentally friendly. Since the work by Fujishima and Honda published in 1972 [4], research on TiO_2 has dramatically increased and been extended to applications in environmental purification, self-cleaning, water splitting, CO_2 reduction, organic synthesis, and solar cells. An interesting phenomenon of TiO_2 is that the highest activity is usually not obtained for its two major crystalline forms, anatase and rutile, but from samples with a mixture of anatase and rutile phases. P25, a commercial TiO_2 material with mixed anatase and rutile phases, is the best example of this phenomenon. This produces questions about the intrinsic qualities that affect photocatalytic activity, and the step that the anatase: rutile mixed phase promotes, which need to be answered. Recently, the anatase:rutile mixed phase structures of TiO_2 have been systematically investigated [5–9]. The formation of anatase: rutile surface phase junctions has been confirmed, and is regarded as the main factor inducing the high photocatalytic activity of TiO_2 with mixed phase structure because of its excellent charge separation ability.

In this feature article, some sophisticated techniques and how they are used to characterize the surface phase structure of TiO_2 are first introduced. Then, research on the discovery of anatase: rutile TiO_2 phase junctions and how this concept has directed subsequent investigations is reviewed. Finally, the investigation of phase junctions by time-resolved mid-infrared (IR) spectroscopy to examine the mechanism behind its charge separation ability is discussed. This feature article also covers some other important factors related to the performance of TiO_2 photocatalysts.

2. Characterization of TiO_2 with different phase structures

As mentioned above, the phase structure of TiO_2 strongly affects its photocatalytic activity. Numerous techniques have been used to characterize the structure of TiO_2, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman and Fourier transform infrared (FT-IR) spectroscopies. Herein, three typical spectroscopic techniques used to investigate the phase structure of TiO_2 are introduced. The unique features of these techniques can further our understanding of the structure and even the carrier dynamics of TiO_2.

In heterogeneous catalysis, reactions take place on the surface of the catalysts. Therefore, the catalytic performance largely depends on the surface properties of the catalyst. Ultraviolet (UV) Raman spectroscopy has recently been proved a powerful tool in materials science [10], mainly because it can efficiently avoid the interference from fluorescence in visible Raman spectra and simultaneously enhance the Raman signal because of its short wavelength and the resonance Raman effect [11]. Here, UV Raman spectroscopy is used to monitor the phase transformation process of TiO_2 [6]. Because TiO_2 strongly absorbs UV light, UV Raman spectroscopy is more sensitive to the surface structure of TiO_2 than XRD and visible Raman spectroscopy. The results obtained from these techniques for the phase transformation process of TiO_2 disagree, which indicates that the surface region of anatase phase detected by UV Raman spectra is more stable at higher temperatures than that in bulk TiO_2 detected by XRD and visible Raman spectra. TEM images show that the phase transformation process of TiO_2 is accompanied by growth of anatase particles. If the surface of anatase particles is covered by dispersed lanthanum oxide (La_2O_3), the phase transformation can be efficiently restrained [6]. Based on these results, a clear phase transformation mechanism for TiO_2 is shown in Fig. 1. With increasing temperature, the phase transformation process of TiO_2 initiates from the surface of integrated anatase particles. The bulk of the new

Can Li *(Dalian Institute of Chemical Physics, Chinese Academy of Science)* ***received the Catalysis Achievement Award (the Dayu Zhang Award) in 2014****, which was presented by The Catalysis Society of China. Professor Can Li received his Ph.D. degree in Physical Chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1993. He did postdoctoral research on catalysis and UV Raman spectroscopy at Northwestern University and was visiting professor at Lehigh University, the University of Liverpool, and The Queensland University, and he was awarded the JSPS Professor at Waseda University, Tokyo University of Technology, and Hokkaido University. He was an invited professor at Université Pierre et Marie Curie, Paris VI. He was the President of the International Association of Catalysis Societies (2008–2012). Currently, he is the director of the State Key Laboratory of Catalysis, and the director of the Dalian National Laboratory for Clean Energy (DNL). His research interests include (1) UV Raman spectroscopy and ultrafast spectroscopy; (2) environmental catalysis and green catalysis; (3) heterogeneous asymmetric catalysis; and (4) solar energy utilization based on photocatalysis, photoelectrocatalysis and photovoltaic cells. He has published more than 500 peer-reviewed papers with over 10 000 citations.*