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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（理学）　　氏名　孟　憲光

学 位 論 文 題 名

Effect of Reaction Environment on Photo-driven Catalytic Properties
（反応環境場の制御による光触媒特性への影響に関する研究）

Photocatalysis is a green technology and has attracted extensive attentions due to its potential applications for solar-to-chemical energy conversion. However, great efforts are still needed to further increase the efficiency of current photocatalytic system for practical application. Previous work mainly focused on how to design efficient photocatalysts to enhance the photocatalytic performances. In this work, the research target is to investigate how reaction environment modulates the photocatalytic performance of current reaction system. The reaction environments herein include both the chemical and physical reaction environments which can exert positive effects on increasing the photocatalytic activity. Especially, the influence of a simple chemical reaction environment, alkaline reaction environment, on various photocatalytic reactions, including photocatalytic degradation, H_2 evolution, and CO_2 conversion was studied. Moreover, the influence of a photophysical phenomenon, surface plasmon resonance (SPR) on highly efficient CO_2 conversion with H_2 and CH_4 was investigated.

Chapter 1 gave a general introduction of the material design of heterogeneous photocatalyst, the typical photocatalytic reactions related to this work, and the significance of reaction environment modulation in enhancing the photocatalytic performance.

Chapter 2 investigated the influence of NaOH (solid base) loading on the photocatalytic performance of WO_3 for gaseous organics degradation under visible light. The influence of NaOH loading on photocatalytic reactions included two aspects. The first was that NaOH changed the surface crystal structure through mild reaction with WO_3 (an acidic oxide) surface and lifted the surface energy band position of photocatalyst. This promoted the oxygen reduction ability of conduction band electrons during the photocatalytic degradation. Secondly, it is well known that H_2O_2, an important intermediate in photocatalytic degradation, is very unstable in alkaline environment. Therefore, the loading of NaOH on the surface of WO_3 promoted the decomposition of H_2O_2. Since the accumulation of H_2O_2 suppressed the consumption of photoexcited electrons on WO_3, NaOH loading overcame this drawback and enhanced the photocatalytic degradation.

In addition to the photocatalytic degradation, an alkaline reaction environment is also favorable for photocatalytic H_2 production and CO_2 reduction, as shown in chapter 3 and 4. Since the two reactions generally require the semiconductor with high conduction band positions, TiO_2 was used as the main component of photocatalysts in these studies.

The alkaline reaction environment enhanced deprotonation process in electrooxidation of alcohol over Au electrodes has been reported in the previous electrocatalysis studies. In Chapter 3, this function was employed for photocatalytic H_2 evolution over plasmonic Au/TiO_2 composites. Under the excitation of Au SPR band in the visible light range, H_2 production was remarkably boosted over $Au/TiO_2/Pt$ photocatalyst in alkaline reaction environment. The photoelectrochemical studies showed that alkaline environment promoted the photooxidation of alcohol over plasmonic Au nanoparticles (NPs), which accelerated the consumption of holes in Au NPs.

Due to the acidic nature of CO_2 molecules, loading of alkali on photocatalyst will promote the chemisorption and possible activation of CO_2. This found application in the photocatalytic CO_2 reduction over TiO_2 in chapter 4. Surface modification of TiO_2 with NaOH was found to be an effective way for the CO_2 adsorption, activation, and led to highly effective conversion of CO_2 into CH_4 without any noble metal cocatalyst loaded.

In order to further enhance the current CO_2 conversion efficiency, H_2 and CH_4 were used as hydrogen sources for CO_2 conversion in chapter 5. The influences of SPR-induced photothermal or local electric field on these reactions were investigated. The results showed that CO_2 conversion with these hydrogen sources achieved much superior efficiency to water. Compared with photothermal CO_2 conversion with H_2 over Ru nanocatalyst, CH_4 is a more promising hydrogen source due to an uphill reaction. In the reaction of CO_2 reforming with CH_4, Au NPs were used as plasmonic promoter and co-loaded with Rh nanometal catalyst on SiO_2. Rh NPs only shows UV plasmonic behavior and its SPR effect cannot be induced by visible light irradiation. Therefore, conventional Rh catalyst does not show photoenhanced activity for CO_2 reforming with CH_4. When co-loaded with Au NPs, an enhanced SPR effect was induced by interparticle coupling effect between Au and Rh NPs under the visible light irradiation in the SPR band of Au NPs. Accordingly, photoenhanced activity was observed over Au and Rh co-loaded catalysts. During the decay of SPR, some meaningful process, such as the hot electron production, surface polarization, electronic disturbance, or local heating effect will make positive effect on CO_2 reforming with CH_4. Especially, the results show that the SPR effect plays important role on CO_2 activation during the reforming reaction.

In summary, this thesis revealed the significance of surface reaction environment on photocatalytic reactions. The function of surface reaction environment was realized through changing the photocatalyst itself or the photocatalytic reaction pathway. The results of this thesis demonstrated that modulation of surface reaction environment is a promising strategy for enhancing the performance of current photocatalytic reaction systems.