論 文 の 内 容 の 要 旨

論文題目　Plasmonic Materials on Periodic Titania Mesostructures for Photoelectrochemical and Photovoltaic Applications
（酸化チタン周期構造上へのプラズモン材料構築とその光電気化学および光電変換への応用）

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Since the first discovery, plasmon-induced charge separation (PICS) has received growing attention because of its unique properties and wide application in photocatalysis, photovoltaics, and photochromism. PICS is an uphill electron transfer process from a metal nanostructure to the conduction band of a contacted semiconductor under light irradiation. In the study of PICS, disordered and sparsely distributed metal nanoparticles (NPs) have been used as the plasmonic nanostructure in most cases. Therefore, it is important to turn our attention to more sophisticated plasmonic nanostructures. The aim of this work is to develop novel plasmonic nanostructures with the aid of periodic TiO_2 mesostructured templates and exploit them for PICS-based photocatalysis and photovoltaics.

Chapter 1 provides a brief introduction of this research. The fundamental knowledge, such as surface plasmon resonance (SPR) and plasmon-induced charge separation (PICS), is firstly introduced. I mainly focus on the mechanism and applications of PICS, as well as the plasmonic material prepared and used. Then, aim and outline of this work are presented.

In Chapter 2, I develop plasmonic photoelectrodes with an ordered and continuous Au semishell or halfshell structure. They are fabricated by sputtering or evaporating Au onto self-assembled SiO_2@TiO_2 core-shell colloidal crystals. Sputtering leads to formation of structures more like core-shell particles, while evaporation gives almost perfect Au halfshells. Both of the electrodes exhibit PICS-based short-circuit photocurrents under light irradiation at 500-800 nm in an aqueous electrolyte containing hydroquinone as an electron donor, but the evaporated ones show higher photocurrents than the sputtered ones. The Au halfshell thickness is optimized to 55 nm in terms of the PICS efficiency. Next, the effects of SiO_2 core size is examined. The absorption and photoresponses of the Au halfshell arrays depend on the SiO_2 diameter. The photoelectrode with the middle-sized SiO_2 cores of 374 nm diameter shows the highest PICS-based photocurrent responses. Finite-difference time-domain (FDTD) calculation is carried out to simulate the electric field distribution to explore the reason why the middle-sized SiO_2 cores are favourable for PICS.

In Chapter 3, I report the solid-state photovoltaic cells based on Au, Ag and Cu halfshell arrays. The cells are designed by taking advantage of the interconnected Au halfshell array, which serves both as a light absorber and a current collector (counter electrode). In the dark, the cell shows good rectification behavior. Under visible light irradiation, open-circuit photovoltage (V_{oc}) and short-circuit photocurrent (I_{sc}) are generated. The effects of the thickness of TiO_2 shell and hole transport layer (MoO_3 and spiro-OMeTAD) are discussed. At last, the photovoltaic properties of the cells with Au, Ag and Cu halfshell arrays are compared. The cell with the Ag halfshell array shows the highest V_{oc}, I_{sc}, fill factor (FF) and power conversion efficiency (PCE) values, in comparison with the cells using the Au and Cu halfshell arrays. The PCE of 0.112% is the highest value among the solid-state PICS devices. The material-dependent PICS efficiency is explained by the difference between the photon energy and Schottky barrier height, and the effect of the interband transition.

In Chapter 4, I report a plasmonic photoelectrode with Au nanoholes and Au nanoplates. Optical responses to the changes of refractiv index are investigated. The Au nanostructrues exhibit high refractive index sensitivity of ca. 390 nm RIU^{-1}. Photocurrent responses in the presence of ethanol of the electrodes with TiO_2 holes of different thicknesses are also measured. The electrode with thicker TiO_2 shows larger photocurrents over the visible to near infrared (NIR) range. FDTD simulation is performed for the calculation of optical spectra and electric field distributions.

In Chapter 5, conclusions about this work are made. The future work maybe focused on is also pointed out, including application Au halfshell array to H_2 generation, fabrication of Ag and Au composite solid-state cell for the further improvement of photovoltaic performance and stability, and development of other plasmonic structures.