博士論文（要約）

Oxygen-deficient tungsten-oxide-based photoanodes for solar water splitting

（太陽光による水分解のための酸素欠乏酸化タングステン光アノード）

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Abstract

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Developing cost-effective and efficient routes towards harvesting and implementing clean renewable sources of energy has been the center of research focus in the recent decades due to growing global warming phenomenon. Renewable energy sources such as wind power, biomass, biofuels, geothermal and solar energy have the potential to generate many times the amount of our current energy of fossil fuels. Among them, solar energy has attracted great attention. In fact, the sun is a viable and clean energy resource that can provide the annual energy need for the mankind during one hour of irradiation. Storing harvested solar energy in the form of chemical bonds such as H_2 seems to be a viable route for storing solar energy.

Photoelectrochemical water splitting (PEC) provides a facile route towards solar-driven hydrogen production by utilizing the interface between the immersed semiconductor and water under illumination. This is due to the formation of a band-bending at the interface between the photoelectrode (the working electrode in a photoelectrochemical cell) and the electrolyte that can assist the electron-hole separation, so that they can be consumed in oxygen and hydrogen evolution reactions. Indeed, this happens after sufficient charge transfer between the different liquid redox potential and Fermi level in the adjacent semiconductor to form an equilibrium between them.

Downward band bending (upward band bending) is formed in photoanodes (photocathodes) promoting oxygen evolution (hydrogen evolution) reaction.

WO_3 has been considered as a promising candidate to be employed for the fabrication of photoanodes. It possesses a bandgap energy of 2.5-2.8 eV and can absorb 12% of solar spectrum mainly from UV range and partially from the visible portion of solar spectrum up to around 470 nm wavelength. Besides its moderately favorable absorption properties, tungsten trioxide possesses impressively longer hole diffusion length and higher carrier mobility.

On the other hand, unlike most of the metal oxides, tungsten trioxide is thermodynamically stable in acidic electrolytes (pH < 4). Still, the reported efficiencies obtained using the WO_3–based photoanode are significantly lower than the maximum theoretical solar-to-hydrogen (STH %) calculated under the assumption of perfect solar light collection. Several strategies have been used to enhance the photocurrent obtained by these photoanodes including nanostructure engineering, crystal structure tailoring, doping with transition metals and non-metal elements. Besides all the mentioned strategies, the introduction of an adequate number of oxygen vacancies has more recently been investigated as a promising method to increase the carrier density in metal oxide photoanodes. Thus their conductive properties would be enhanced.

In this study, plate-like tungsten oxide photoanodes were fabricated using a facile acid-mediated hydrothermal treatment and the effect of the effect of alteration of fabrication parameters in oxygen vacancies concentration and photoelectrochemical performance has been studied. The synthesis process was comprised of two stages; first acid-mediated

hydrothermal treatment of tungsten sheet pieces and consequently annealing the treated sample in air. The temperature of acid-mediated hydrothermal treatment was varied as 25, 50, 75, 100, 125, 150 and 175˚C. It was found out that the variation of acid treatment temperature could influence the concentration of oxygen vacancies in the prepared tungsten oxide photoanodes. These defects act as electron donors therefore, they can contribute to the enhancement of photocurrent. Using x-ray diffraction (XRD) and Raman spectroscopy analyses it was revealed that there is a correlation between the number of intercalated water molecules in $WO_3 \cdot nH_2O$ ($n = 1$ or 2) with the formation of oxygen vacancies in the calcination step. This was also confirmed using X-ray photoelectron spectroscopy (XPS) and Mott-Schottky analyses. At the optimum acid-mediated hydrothermal treatment temperature (75˚C), a photocurrent of 1.06 $mA.cm^{-2}$ at 1.23 V *vs.* RHE was obtained. This value is about six times higher than the photocurrent generated by the sample prepared by acid-mediated hydrothermal treatment at the highest temperature of 175˚C. Moreover, an Incident-Photon-to-Current-Efficiency (IPCE) of 36.2% was obtained for the sample prepared under the optimized conditions. As for comparison, the IPCE of this optimized sample was three times higher than the IPCE acquired by the sample prepared by acid-mediated hydrothermal treatment at 175˚C. This indicates that the mild acid-mediated hydrothermal treatment enhances the photocurrent and photoelectrochemical water oxidation performance due to an increase in the concentration of oxygen vacancies.