

審査の結果の要旨

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

PhD thesis defended by MIRFASIH Seyed Mohammad Hassan

The control of defects in metal-oxide materials is primordial to synthesize technologically useful materials with well-controlled properties. Oxygen vacancies in metal-oxide materials are being investigated as a means to improve electrical transport in metal-oxide semiconductors. One of the promising applications lies in the fabrication of photoanodes and photocathodes for use in photoelectrochemical cells (PECs) to realize solar water splitting and convert solar energy into storable chemical energy. Indeed, the performance of metal-oxide materials used as photoanodes and photocathodes could be improved with the control of oxygen vacancies. For the study of oxygen vacancies and their effects on the performance of PECs, tungsten oxide (WO_3 monoclinic phase, n-type semiconductor used as a photoanode material) is a candidate to be selected as a model material because it is known to possess unfavorable charge transport properties and at the same time is chemically stable in electrolyte solutions (acidic environment), and has potential to reach high solar-to-hydrogen conversion (4.5%) in PECs. So far different techniques have been used to synthesize oxygen deficient tungsten oxide. The conventional strategy is to form oxygen vacancies by post-annealing of WO_3 in a reductive atmosphere (e.g., hydrogen atmosphere). However, the developed techniques are difficult to control and may not be able to achieve uniform density of oxygen vacancies.

In this thesis, a two-step synthesis technique is used to form oxygen vacancies in a controlled manner and investigate the effects of oxygen vacancies on the performance of WO_3 photoanodes in photoelectrochemical water splitting.

MIRFASIH used a two-step process to synthesize oxygen deficient tungsten oxide. First, an acid-mediated hydrothermal treatment is performed at a varied temperature

(parameter). Second a calcination treatment is performed in air at a fixed temperature. The temperature of the first step is used to control the intermediate phase, namely, low temperature gives $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and high temperature gives $\text{WO}_3 \cdot \text{H}_2\text{O}$. After the calcination step, different properties and photoelectrochemical performance of the material were found depending on the number of intercalated water molecules in the tungsten oxide hydrates. The first step also determines the morphology of the final materials, namely plate-like microstructures having a plate thickness of about 100 nm. This morphology is used to increase the surface available for photoelectrochemical reaction and also to favor transport of the minority carriers (hole diffusion length ~ 150 nm). The formation of different hydrate phases is confirmed by microstructure analyses (X-ray diffraction and Raman spectroscopy). Also, the formation of the monoclinic WO_3 phase after calcination is confirmed. The presence of defects is studied by investigating the local chemical environment (XPS), which reveals the presence of oxygen vacancies (oxidation state W^{5+}). The effect of the oxygen vacancies on the material properties is quantified in terms of the carrier type (n-type confirmed from measurement) and density (relative comparison between samples) and a difference of two orders of magnitude is observed in the carrier density caused by oxygen vacancies. The temperature range for the first step having best performance in PEC is from RT to 75°C . The efficiency of the material is characterized using the incident photon to current efficiency: a 26% efficiency was obtained at 350 nm for a potential of 1.23 V *vs.* RHE. It is found that the sample with a high density of oxygen vacancies achieved a four-fold increase in the efficiency when compared to the sample with low density of oxygen vacancies. These experimental results give clear conclusion on the improvement of the PEC performance caused by the presence of oxygen vacancies. However the mechanism for the formation of these vacancies remains to be elucidated.

The manuscript consists of five Chapters. Chapter One introduces the subject of defects in metal oxide materials and emphasizes applications of defects in the fabrication of devices particularly efficient photoelectrodes. Tungsten trioxide was chosen as a model material for the control of defects because WO_3 possesses a large number of nonstoichiometric species. However, the control of defects in this material is still a challenge. MIRFASIH suggests that the formation of WO_3 through a wet chemistry process may help to control defects because different intermediate phases in the form of tungsten trioxide hydrates ($\text{WO}_3 \cdot n\text{H}_2\text{O}$) can be formed by wet chemistry. The defects are formed during the calcination of the intermediate phases $\text{WO}_3 \cdot n\text{H}_2\text{O}$, so that different $\text{WO}_3 \cdot n\text{H}_2\text{O}$ may produce different defects due to the difference in the

starting materials. In Chapter Two, MIRFASIH shows that the temperature of the wet chemistry process can be used to control the formation of the hydrate phase, the dihydrate $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ being obtained at a low temperature and the monohydrate $\text{WO}_3 \cdot \text{H}_2\text{O}$ at a high temperature. Subsequent calcination of the two different hydrate phases result in different performance of the final material when used as a photoanode in solar water splitting. The improved performance of the WO_3 photoanode obtained from $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ is correlated with a large amount oxygen vacancies, as revealed by the presence of the W^{5+} oxidation state and a large carrier density. In Chapter Three, the conventional techniques for defect generation are used to further understand defects mediated through the calcination of tungsten trioxide hydrates. Using annealing under oxygen deficient environment (vacuum), a large variation in defects is being produced (formation of black tungsten oxide is achieved), but the performance in water splitting is degraded. Although the second annealing in vacuum is effective in increasing the carrier density of the material, the defects generated are detrimental to the conversion of photon to carrier, as a result the performance of the material is not improved. In Chapter Four, electrical transport is discussed by determining the conduction activation energy of the material by using temperature dependent current-voltage measurements. It is found that the best performing material obtained through the calcination of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ has a lower conduction activation energy than the material prepared from $\text{WO}_3 \cdot \text{H}_2\text{O}$. It is concluded that electrical transport is favored in the sample obtained through the calcination of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$. The conclusions of the manuscript are given in Chapter Five.

よって本論文は博士（工学）の学位請求論文として合格と認められる。