

論文の内容の要旨

Abstract

論文題目 Silver phosphate microcrystalline film-based photoanodes for photoelectrochemical water oxidation

(微結晶リン酸銀膜光電極を用いた水の酸化反応)

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Since the first report of electrochemical photolysis of water using a TiO_2 electrode under ultraviolet light irradiation, photoelectrochemical (PEC) water splitting process has captivated tremendous research interest as a promising technology for sustainable production of the clean energy carrier – H_2 , from solar light and water. The advances in PEC technology substantially depend on the development of highly stable and efficient photoelectrodes, especially photoanodes, since the oxygen evolution reaction (OER, *i.e.* water oxidation) happening on the anode is usually more thermodynamically complex and dynamically sluggish than hydrogen evolution reaction (HER, *i.e.* water reduction) happening on the cathode. The photoanode allowing the occurrence of water oxidation is thus more dominant for development of overall water splitting technology. Traditional TiO_2 -based electrodes usually suffer a lot from the low visible-light absorption induced by their large bandgaps. Meanwhile, sulfides and (oxy)nitrides show poor stability over long-term operation in actual conditions. These have highlighted WO_3 , BiVO_4 , $\alpha\text{-Fe}_2\text{O}_3$, and Ag_3PO_4 as novel alternatives to the above-mentioned photoanode

materials towards efficient and stable water oxidation. In 2010, as an important benchmark report, Yi *et al.* demonstrated that Ag_3PO_4 as the photoanode material, with the presence of AgNO_3 in electrolyte as an electron scavenger, could offer much higher photocatalytic activity for water oxidation than other well-established anodic catalysts including BiVO_4 and WO_3 . This superior performance could be further improved through the strategies like facet and morphology engineering. However, till now still not much work has been reported on using Ag_3PO_4 as the photoanode material for PEC water splitting due to the difficulty in fabrication of highly adhesive Ag_3PO_4 layers on conductive substrates as membrane photoanodes. More importantly, the two major intrinsic shortcomings of Ag_3PO_4 , *i.e.* the poor structural stability and low bandgap absorption resulted from the native defects of silver vacancy (V_{Ag}), silver interstitial (Ag_i), and simultaneously decomposition-induced precipitation of Ag^0 nanoparticles (NPs) on the surface, have together limited its further usage as photoanode materials for PEC water oxidation.

In this thesis, solution-processed large-area ($4.5 \times 4.5 \text{ cm}^2$) Ag_3PO_4 microcrystalline films are first prepared *via* a room-temperature, air-exposed immersion reaction. The multiple effects of the native defects in Ag_3PO_4 , *i.e.* V_{Ag} , Ag_i , and surface precipitation of Ag^0 NPs, are first demonstrated experimentally. By changing the addition amount of the oxidation agent H_2O_2 during the synthetic reaction, Ag_3PO_4 microcrystalline films with different amounts of Ag^0 NPs on the surface are obtained. It is found that despite the favorable superior conductivity and plasmonic effect having improved the interfacial charge transfer and light absorption of the Ag_3PO_4 film photoanode, the defective film with the largest amount of Ag^0 NPs on the surface finally exhibits the lowest current density, due to the disadvantageous effects involving the decreased crystalline quality, easier decomposition of active material of Ag_3PO_4 , decreased electrochemical surface area with a high content of Ag^0 NPs covering the surface of Ag_3PO_4 , and also serving as the recombination centers. As a result, even the Ag_3PO_4 microcrystalline film which has achieved the highest photocurrent density fails to demonstrate considerable stability. These results have further highlighted the significance of mitigation of native defects of Ag_3PO_4 fundamentally towards enhanced water oxidation stability and efficiency of the microcrystalline film photoanodes.

Typically, the post-treatment of vacuum annealing at different temperatures (*i.e.* 100, 200, 300, 400 and 500 °C) has been investigated as a strategy for solving the problem of native defects and low light absorption of Ag₃PO₄. It is found that below 400 °C is the |Recovery| stage for Ag₃PO₄ microcrystals when defect amount decreases and therefore crystallinity increases. From 400 °C, the |Recrystallization| stage and also precipitation of Ag₃PO₄ bulk crystals start, and afterwards till 500 °C is the |Recrystallization + Grain growth| stage for Ag₃PO₄, when more faceted and larger bulk crystals of Ag₃PO₄ precipitate extensively. In this series of Ag₃PO₄ film photoanodes, the same variation in [$J_{\text{light}} - J_{\text{dark}}$] *vs.* E curves is found as the light absorption profiles, *i.e.* 400 °C > 500 °C > 300 °C > 200 °C > non-annealed > 100 °C-annealed Ag₃PO₄ film, indicating that light absorption, especially the bandgap absorption could be the dominant factor to the PEC performance. Particularly, much improved PEC water oxidation stability and efficiency of the 400 °C-annealed Ag₃PO₄ film photoanode are demonstrated compared with the non-annealed Ag₃PO₄ film, suggesting that the methodology of vacuum annealing could be utilized for improving the PEC performance of Ag₃PO₄ film photoanodes because of its ability to mitigate the unfavorable effects of the native defects like V_{Ag} , remove the Ag⁰ NPs on the surface, and substantially increase the bandgap light absorption of these Ag₃PO₄ microcrystalline films.

Next, from the viewpoint of advanced structural design, in consideration that the usage of microcrystalline film photoanode might cause the problem of decreased active surface area despite its relatively higher stability than nanocrystalline powder-deposited photoanode, the possibility of introducing porous structures into these microcrystalline Ag₃PO₄ film photoanodes is also investigated towards further improved photoactivity and stability. Particularly, it is demonstrated that the porous degree of the as-obtained Ag₃PO₄ films could be tuned by changing the reaction time from 1 h to 2 h, 5 h, 9 h, 20 h and 24 h, with the usage of specific reaction parameters. These porous Ag₃PO₄ films, in spite of having left the native defects not recovered and Ag⁰ NPs on the surface not removed, finally could demonstrate improved surface areas and light absorption, owing to which improved PEC performance has also been achieved. Specifically, the optimal highly porous 20-h Ag₃PO₄ microcrystalline film photoanode shows superior water oxidation efficiency with a photocurrent density of 4.32

mA/cm² which is almost three times higher than that of non-porous 1-h Ag₃PO₄ microcrystalline film (1.48 mA/cm²) at 1.0 V vs. Ag/AgCl. This value of photocurrent density is also higher than that of the 400 °C-annealed non-porous Ag₃PO₄ film photoanode.

Overall, it could be concluded that: a) The instability of the Ag₃PO₄ microcrystalline films is originated from the native defects involving V_{Ag} and Ag⁰ NPs precipitated on the surface, thus the methodology of vacuum annealing, typically at 400 °C, turns out to be more favorable for improving the stability because it can fundamentally solve, or at least mitigate the various problems induced by native defects; b) Light absorption is a crucial factor to the PEC performance, whereas the surface area which would largely determine the final process of PEC water oxidation, *i.e.* the surface redox reaction is also important, thus the porous Ag₃PO₄ microcrystalline film photoanodes can achieve even higher efficiency in spite of leaving the defect and absorption issues not solved; c) Trying to make a combination of these two techniques, *i.e.* taking both the fundamental properties of the material (*e.g.*, defects and absorption) and the advanced structural design (*e.g.*, larger surface area) into concern, may provide further possibility towards more stable and efficient Ag₃PO₄ film photoanodes for PEC water oxidation.