

審査の結果の要旨

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Silver phosphate microcrystalline film-based photoanodes for photoelectrochemical water oxidation

PhD thesis defended by Qi CAO

The photoactivity of silver phosphate, a n-type semiconductor with a bandgap of ≈ 2.4 eV and a valance band edge position at ≈ 2.8 V versus reversible hydrogen electrode (O_2/H_2O redox couple at 1.23 V) has been investigated in organic pollutant decomposition and water photoelectrolysis (Tennakone *et al.*, J. Chem. Soc. Chem. Comm., 496, 1988; Ye *et al.*, Nature Materials, 9, 559, 2010). Water photooxidation using nanostructures of silver phosphate has shown superior efficiency in water splitting over photocatalyst materials used as references such as $BiVO_4$ and WO_3 . However, the literature points to major issues with silver phosphate when used for water oxidation. Indeed due to the high ionic mobility of the silver ions, the material is unstable and silver precipitation is observed. Also, high photoactivity material made of silver phosphate is prepared in the form of nanopowder which makes it difficult to fabricate the layers used as the photoanodes in water oxidation. Moreover, it is possible that the nanocrystals of silver phosphate further increase the instability of this material.

Qi CAO introduces vacuum annealing to mitigate the effect of silver precipitation and also demonstrates the fabrication of a porous layer made of silver phosphate without the need for nanopowder. The manuscript consists of four Chapters.

Chapter One introduces solar water splitting and gives a review of the literature on silver phosphate used as a photoanode. Silver phosphate is found to offer high photoactivity, but at the same time suffers from poor stability and also poor light absorption. The instability of silver phosphate photoanode is thought to be the result of the combined effects of the large ionic mobility of silver ions in silver phosphate resulting in silver precipitation and of the photoanode fabrication technique using nanocrystals which are not stable. The silver precipitation is thought to be the major cause for the poor stability of this material. To confirm these literature findings, Qi proposes to control the amount of precipitated silver nanocrystals to investigate stability, light absorption and water splitting performance of the silver phosphate photoanodes. To this end, Qi developed a process to vary the amount of silver precipitation by changing the amount of hydrogen peroxide during the chemical reaction used to synthesize silver phosphate. Light absorption was found to increase with the amount of precipitated silver particles, however the observed enhanced light absorption is chiefly independent of wavelength, so that the increase in absorption by this plasmonic effect of the precipitated silver particles on the photoanode could not be demonstrated clearly. Although enhanced light scattering induced by localized surface plasmons on the

silver nanoparticles may be used to enhance light absorption, the overall effect of silver precipitation in this material is detrimental to the water splitting performance in terms of efficiency and stability, pointing to the need for different strategies to eliminate silver nanoparticles. In Chapter Two, the properties of large microcrystals of silver phosphate are improved by introducing post annealing under a vacuum. The silver phosphate photoanode synthesized at room temperature is found to poorly absorb light as suggested by the greenish dark yellow color of the fabricated photoanodes. Indeed for an efficient solar absorber with a bandgap of 2.4 eV, one usually observes a yellow/orange color. With the view of improving light absorption and stability, a post treatment consisting of annealing under vacuum was applied to the synthesized silver phosphate photoanodes. By varying the annealing temperature, a clear improvement in light absorption for a temperature of 400°C was confirmed; a brilliant yellow color was obtained and the light absorption was quantified by diffuse reflectance spectroscopy. The optimum temperature for the vacuum annealing process is governed by the onset of the recrystallization which is clearly observed for a temperature larger than 400°C. It is thought that at the optimum temperature of 400°C, silver nanoparticles are removed from the surface of the material by thermally induced silver atom migration and subsequent filling of the native silver vacancies. The material annealed at the optimum temperature exhibits stable operation for solar water splitting with a twofold improvement in the photocurrent. In Chapter Three, Qi proposes to directly fabricate a layer of porous microcrystalline silver phosphate to obtain a stable photoanode with a high surface to volume ratio. In contrast to the reported fabrication techniques, Qi's technique does not use silver phosphate nanopowder whose stability has not been demonstrated. Qi's material uses porous microcrystals to achieve both stability and a large area for chemical reaction. A solution process at room temperature is used to synthesize porous silver phosphate with large crystals by immersing a silver foil in a solution containing sodium phosphate monobasic monohydrate (phosphate source), hydrogen peroxide (oxidation agent), and a surfactant (polyvinylpyrrolidone). A large amount of hydrogen is produced during the reaction and pores are produced. The choice of the surfactant helps to control the formation of the porous structure. The porosity of the fabricated silver phosphate can be tuned by adjusting the reaction time. The best layer gives a photocurrent of 4.32 mA/cm² at 1.0 V versus Ag/AgCl, achieving a threefold increase in the photocurrent over the layer with a low porosity. A stability test of one hour reveals that the photocurrent of the porous microcrystalline silver phosphate layer is stable. This result suggests that the porous micro-crystals of silver phosphate are more stable than the nanocrystals and that the surface developed by the porous structure is the chief factor for the enhancement of the water splitting performance. The effect of subsequent annealing on the porous micro-crystals is not reported. The last Chapter gives the conclusions of the thesis.

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