Enhanced solar photocurrent of LaTaON₂ photoanodes via electrochemical treatment

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Abstract. Having a theoretical 18.5% solar-to-hydrogen efficiency, LaTaON₂ has emerged as a promising photoanode material. However, its performance is crucially limited by low photocurrent in the past reports. To improve its solar photocurrent, a negative electrochemical treatment was applied for the LaTaON₂ photoanode. The sample powder was successfully synthesized by a flux assisted-nitridation with precursor derived from solid state sintering. And the LaTaON₂ photoanodes were fabricated by electrophoretic deposition with a post-necking procedure. The solar photocurrent of as-fabricated LaTaON₂ photoanode has increased to 1.2 mA cm⁻² at 1.6 V_RHE after the negative electrochemical treatment in the dark. The photoanodes with and without the electrochemical treatment were investigated by scanning electron microscopy (SEM), Mott–Schottky test, transient photocurrent and open-circuit photovoltage. The results showed that the enhancement maybe ascribed to the soared carrier density and elimination of surface recombination centre. Therefore it is proposed that the electrochemical treatment eliminates the surface recombination centre of the oxynitrides leading to increased solar photocurrent. It was also found that the SrTaO₂N photoanode had increased photocurrent after the electrochemical treatment. This study provides a facile and general way to improve the solar water-splitting current of photoanodes.

1. Introduction

With the depletion of fossil fuels, a clean way to obtain energy is the only access to our sustainable development. On figuring out this way, photoelectrochemical water splitting seems to be the best choice [1]. It feeds on sunlight and water, produces hydrogen and oxygen. However, the availability of high efficient photoelectrodes is now hampering the realization of this technique [2]. Tremendous amount of effort has been paid to implement the full photoelectrochemical performances ofBiVO₄, Fe₂O₃, WO₃ and TiO₂ [3]. (Oxy)nitrides, which possess ideal band structures and promising high solar-to-hydrogen (STH) efficiencies, may become the alternative photoanode material to address this dilemma [3]. At present, the solar photocurrents of the majority of (oxy)nitrides are far from their theoretical values.

The slow kinetic process of water oxidation and the existence of surface recombination centre could be the main limiting factors for the improvement of photoanodes. To accelerate the kinetic process of water oxidation, surface modification of oxygen evolution catalyst is adopted to improve
the solar water-splitting current of (oxy)nitride photoanode [4-6]. On the other hand, surface recombination centre on the photoanodes has been revealed by the transient absorption spectroscopy [7]. Therefore, the elimination of surface recombination centre would offer another way to ameliorate the photoelectrochemical performance of the photoelectrodes [8].

Overlayer has been deposited on hematite photoanodes to passivate surface states via atomic layer deposition [8]. Due to the high synthetic temperature accompany with aggressive ammonia flow, regular (oxy)nitride films are hard to obtain [3]. (Oxy)nitride photoanodes are usually particle-ensemble films, which may be hard for the deposition of overlayers. Recently, the photocurrents of BiVO₄, Fe₂O₃, WO₃ and TiO₂ are enhanced by surface treatment electrochemically [9-12], which may be an alternative viable strategy to applied on the particle-ensemble (oxy)nitride films. Taking LaTaON₂ as the study subject [13], the electrochemical treatment is adopted to improve its solar photocurrent for the first time. The sample powders were successfully synthesized by a flux assisted-nitridation with precursor derived from solid state sintering. And the LaTaON₂ photoanodes were fabricated by electrophoretic deposition with a post-necking procedure. Recently, the photocurrent of as-fabricated LaTaON₂ photoanode has increased to 1.2 mA cm⁻² at 1.6 V_RHE after the negative electrochemical treatment in the dark. And (photo-)electrochemical measurements are carried out to quest for the cause of the enhancement [14]. The results show that the enhancement may be due to the increased carrier density and suppressed surface recombination center. This study has proved that the electrochemical treatment is a facile and general way to improve the solar water-splitting current of (oxy)nitride.

2. Experimental section

2.1. Synthesis of the sample
The LaTaON₂ powder sample was synthesized by a two-step method, which combined solid state reaction and the following flux-assisted nitriding. Briefly, 2 mmol La₂O₃ and 2 mmol Ta₂O₅ were thoroughly grounded with an agate mortar and pestle. Then, the mixture was transferred into a corundum boat, and calcined at 1623 K for 10 h. The as-obtained oxide precursor was thoroughly mixed with an equal weight of KCl, after which it was sintered at 1223 K for 10 h under the flowing ammonia (500 mL/min). The sample was washed with deionized water for several times to remove the excess flux, and was dried at 333 K overnight.

2.2. Fabrication of the photoanodes
The LaTaON₂ photoanodes were fabricated by an electrophoretic deposition method (EPD) followed by a post-necking procedure. In a typical procedure, 20 mg sample powder and 5 mg iodine were added to 25 mL acetone. The ultrasonic dispersion was applied on the mixture for 30 min, after which a suspension was formed. Two fluorine-doped tin oxide substrates (FTO) with their conductive sides face to face were immersed in the suspension and kept at 10 V for 1 min. The as-obtained electrode film was dried at room temperature and then 30μL 10 mM TiCl₄ methanol solution was dripped to the particle-ensemble film with a 5 min heat-treatment at 473 K. After the drip and heat treatment route were repeated for several times, the electrode film was kept at 713 K for 30 min under the flowing ammonia (300 mL/min).

2.3. Characterization of the sample and electrodes
The X-ray diffraction (XRD) pattern of the as-synthesized powder sample was obtained with an Ultima III X-ray diffractor (Rigaku), and the absorption spectrum of the sample by a UV2550 UV-vis spectrophotometer (Shimadzu). The morphology of the powder and photoanodes was observed by a scanning electron microscope (SEM) (Nova NanoSEM).

2.4. Electrochemical treatment and (photo-)electrochemical measurement of the electrodes
Both electrochemical measurement was carried out with a CHI633c electrochemical workstation. The three-electrode configuration was used with the LaTaON$_2$ photoanode, Pt foil and the saturated calomel electrode (SCE) serving as the work electrode, the counter electrode and the reference electrode. 1M NaOH (pH=13.6) was used as the electrolyte. The applied bias reported here are against the reversible hydrogen electrode (RHE) according to the conversion relationship:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \times pH + 0.242$$

where pH represents the pH value of the electrolyte. For the photovoltaic measurement, an Oriel Sol3A Class AAA Solar Simulator, which was calibrated to 100 mWcm$^{-2}$ (AM1.5G) by a Newport 91150 reference cell, was used as the light source. To ensure the incident areas of different photoanodes, a black mask with a 6 mm hole was pasted on the back of the electrode (glass). Therefore, all the photocurrents were normalized to 1 cm$^2$.

3. Results and discussion

3.1. Characterization of the sample powder

The XRD pattern (figure 1(a)) of the as-obtained powder matches the standard pattern (PDF#47-1366) well. In other words, the LaTaON$_2$ sample powder, derived from the two-step method, has been successfully obtained [13]. The XRD pattern with sharp peaks indicates the as-obtained sample powder is of high crystallinity without strong orientation. As shown in figure 1(b), the as-obtained orange powder has an optical absorption edge at ca.650nm. The inset of Tauc plot based on the absorption spectrum indicates that the as-obtained powder possesses an indirect band gap of ca. 1.9 eV, which is in consistent with the literature [15, 16].

Figure 1. XRD pattern (a) and the absorption spectrum (b) of the as-obtained sample powder, the inset shows the Tauc plot of the sample based on the spectrum.

Figure 2 shows the surface morphology of the as-obtained LaTaON$_2$ powder. The sample powder is a mixture of large particles with several micrometres and small particles with several hundred nanometres. As shown in figure 2(a), it appears that the large particle is formed by the aggregation of small particles. All particles are of smooth surface, which may be originated from the flux-assisted nitriding procedure [17]. It is supposed that voids are formed for most of the (oxy)nitrides during the high-temperature nitriding procedure. As for LaTaON$_2$, three O$^{2-}$ ions are substituted by two N$^{3-}$ ions during the forming process. In a direct nitriding route, the oxide precursor (LaTaO$_4$) would transform to large LaTaON$_2$ particles with voids and stress [13]. In the flux-assisted route, the substance moves more easily in the molten KCl and the stress maybe released. As for the oxide precursor, there is a phase transition of LaTaO$_4$ at around 513 K [18], which indicates stress could be formed in the particle
during the natural cooling-down process of the solid state reaction and the heating-up process of the nitriding procedure. Thus, the molten KCl may help the transformation to LaTaON₂ and releasing the stress, which might force the large oxide precursor particles to change into porous large particles or to break into small ones.

**Figure 2.** The SEM images of the as-obtained sample powder.

3.2. Electrochemical treatment on the LaTaON₂ photoanodes

Typically, the photocurrent of (oxy)nitride without modification of oxygen evolution catalyst decreases severely in minutes during the stability test, even after the first run of the linear voltammetry [6]. But the key factors for the rapid decay have not yet been found. In figure 3(a), the as-fabricated LaTaON₂ photoanode shows a saturated ca. 1 mA cm⁻² at 1.6 V_RHE with an onset potential of ca. 0.9 V_RHE. In the second run of the linear voltammetry, the photocurrent at 1.6 V_RHE sharply decreases to 0.5 mA cm⁻², while the onset potential becomes ca. 1.1 V_RHE. With the electrochemical treatment, the photocurrent at 1.6 V_RHE increases to 1.25 mA cm⁻² with a similar onset potential of ca. 0.9 V_RHE. This enhancement, however, did not maintain at the second run with a photocurrent of ca. 0.65 mA cm⁻² at 1.6 V_RHE. The result shows that it may provide us with a facile and practical way to improve the solar water-splitting current of photoanodes. Thus, it is necessary to figure out the electrochemical treatment and its effect on the LaTaON₂ photoanodes.

**Figure 3.** Photocurrent characteristics of the LaTaON₂ photoanodes without (a) and with (b) electrochemical treatment. The dash lines show the current of the LaTaON₂ photoanodes in the dark. The scan rates were 30 mVs⁻¹.

Before the electrochemical treatment, cyclic voltammograms of the as-fabricated LaTaON₂ photoanode in the dark show decreasing current densities during the first few cycles, and the dark current minimized and stabilized after the fifth cycle, as shown in figure 4(a). The initial cyclic
voltammogram shows 0.1 mA cm\(^{-2}\) at 1.6 V\(_{\text{RHE}}\), indicated some reduced species exist on the surface of the photoanode. In the second one, the dark current decreases to 0.03 mA cm\(^{-2}\) at 1.6 V\(_{\text{RHE}}\), indicated the reduced species may be irreversible or had been removed. In the fifth one, the dark current minimized and stabilized at 0.01 mA cm\(^{-2}\). After the cyclic voltammetry in the dark, the photocurrent reaches 0.9 mA cm\(^{-2}\) at 1.6 V\(_{\text{RHE}}\). Compared with the second scan of the photocurrent test in figure 3(a), the photocurrent of the same photoanode after electrochemical treatment increases to 1.15 mA cm\(^{-2}\) at 1.6 V\(_{\text{RHE}}\), which is close to the electrochemical treated one in figure 3(b). The cyclic voltammograms of the electrochemical treatment are shown in figure 4(c). During the cyclic scans between -1.48 V\(_{\text{RHE}}\) and -0.5 V\(_{\text{RHE}}\), large amount of hydrogen formed on the surface of the photoanode. It should be noted that bare FTOs could not be immersed in the electrolyte while being conducting the electrochemical treatment, or the tin oxide would dissolve in the electrolyte resulting in insulated substrates. The similar current responds of the five scans shows that the electrochemical treatment mainly acts on the surface of the particle-ensemble film. Someone may argue that some reduced species could be produced during the electrochemical treatment, thus the increased photocurrent would come from these easily oxidized species. After the treatment, a cyclic voltammetry in the dark was performed. As shown in figure 4(d), the reduced species did exist, and exhausted after the first scan, resulting in decreasing dark current. Therefore, the increased photocurrent should not be due to the easily oxidized species formed during the electrochemical treatment.

Figure 4. Cyclic voltammograms of the LaTaON\(_2\) photoanode before (a) and after (d) the electrochemical treatment in the dark at the scan rate of 100 mVs\(^{-1}\). (b) the photocurrent characteristics of the LaTaON\(_2\) photoanodes before and after the electrochemical treatment at the scan rate of 30 mVs\(^{-1}\). (c) Cyclic voltammograms of the electrochemical treatment on the LaTaON\(_2\) photoanode at the scan rate of 200 mVs\(^{-1}\). Figure 5 shows the morphologies and cross sections of the LaTaON\(_2\) photoanodes before and after the electrochemical treatment. As shown in figure 5(a) and figure 5(c), the particle-ensemble films are composed of large porous particles and small particles with TiO\(_x\) gluing them. The particle-ensemble
films are of ca.1 μm thick, as shown in figure 5(b) and figure 5(d). The SEM images indicate no obvious difference between the LaTaON$_2$ photoanodes before and after the electrochemical treatment. It is supposed that a few atomic layers of the sample particle would have excess oxygen impurity that deviated from stoichiometric ratio. And it has been confirmed that the removal of the superficial oxygen on the SrTaO$_2$N particles will arise the electro-conductivity and lead to improved photocurrent. However, it requires high-temperature anneal in 5% hydrogen in argon. The electrochemical treated LaTaON$_2$ photoanodes may go through similar process leading to the decrease of the oxygen content on the surface. However, the electrochemical treated LaTaON$_2$ photoanode was sensitive to the air. After the treatment the LaTaON$_2$ photoanode was placed in air for several minutes, the photocurrent was slightly higher than the as-fabricated one. Therefore, the several electrochemical measurements were performed on the LaTaON$_2$ photoanodes before and after the electrochemical treatment.

![SEM images of the LaTaON$_2$ photoanodes before (a,b) and after (c,d) the electrochemical treatment.](image)

**Figure 5.** SEM images of the LaTaON$_2$ photoanodes before (a,b) and after (c,d) the electrochemical treatment.

In the Mott-Schottky test, the as-fabricated LaTaON$_2$ photoanode shows a flat band position of ca. 0 V$_{RHE}$, and the flat band position does not change obviously after two scans of photocurrent tests, as shown in figure 6(a). In addition, there is a turning point on the Mott-Schottky plot, which may be due to the intermediate state in the bandgap [19]. After the electrochemical treatment, the photoanode shows a flat band position of ca. 0.4 V$_{RHE}$, and the flat band position comes closer to 0 V$_{RHE}$ after each scan of photocurrent test, which is the flat band position of the as-fabricated one, as shown in figure 6(b). And the turning point on the Mott-Schottky plot seems to emerge after the second scan of the photocurrent test. The lower slope of the Mott-Schottky plot of the electrochemical treated one indicates higher density of charge carrier [8]. The missing turning point may indicate the elimination of the intermediate state in the bandgap, probably due to the removal of the surface recombination centre. After the second scan of the photocurrent test, the surface recombination centres seem to form, indicating that it may relate to the reaction intermediate of water oxidation. Further analysis should be obtained from the in-situ surface sensitive techniques.
Figure 6. The left column (a, c, e) shows the electrochemical test results of the as-fabricated LaTaON$_2$ photoanodes, while the right column (b, d, f) shows the corresponding electrochemical treated ones. All the electrochemical tests were conducted before the photocurrent tests of the photoanodes, and each photoanode had been tested twice. (a, b) the Mott-Schottky test results of the photoanodes, (c, d) the open circuit voltage of the LaTaON$_2$ photoanodes in the dark and under illumination and (e, f) the transient (photo-)current of the LaTaON$_2$ photoanodes under different bias for 30s.

The as-fabricated LaTaON$_2$ photoanode shows photovoltage of 0.15 V with similar responds to the illumination after the photocurrent test, as shown in figure 6(c). The electrochemical treated LaTaON$_2$ photoanode shows smaller photovoltage of ca. 0.1 V in figure 6(d). The responds to the illumination is different from the as-fabricated one, and the open circuit voltage in the dark becomes higher after the following photocurrent tests. As shown in figure 6(e) and figure 6(f), both photoanodes show large transient photocurrent once the light was on, and the transient photocurrent of the electrochemical treated photoanode is larger than the as-fabricated one. Once the light is off, the transient currents of
both photoanodes disappear at bias larger than 0.2 V RHE. As discuss previous, the electrochemical treated LaTaON2 photoanode is sensitive to air, keeping it from further experiments, such as XPS. The electrochemical treatment was also conducted on SrTaO2N photoanodes. It is shown in figure 7 that the photocurrent of SrTaO2N photoanode increases from 0.3 mAcm⁻² for the as-fabricated one to 0.6 mAcm⁻² for the electrochemical treated one at 1.6 V RHE. More (oxy)nitride photoanodes are now being electrochemical treated in our laboratory to test the validity and trying to probe the changes before and after the treatment.

4. Conclusion
The negative electrochemical treatment on the LaTaON2 photoanodes boosts the photocurrent from ca. 1 mAcm⁻² to 1.25 mAcm⁻² at 1.6 V RHE in 1M NaOH under stimulated sunlight (100 mWcm⁻²). The treatment can eliminate the surface recombination center, resulting in the soaring of charge carrier. No further experiment could be conducted due to the sensitive of the treated surface of the LaTaON2 photoanodes in the electrolyte or air. The negative electrochemical treatment on the SrTaO2N photoanodes also shows increase of the photocurrent, which indicates that it would be a facile and general strategy to improve the solar water-splitting current of photoanodes. More in-situ characterization techniques should be conducted to monitor the changes during the electrochemical treatment, which might cast light on the construction of high-efficient photoelectrodes.

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