Research Article

Facile Growth of Porous Hematite Films for Photoelectrochemical Water Splitting

Shaohua Shen, Jiangang Jiang, Penghui Guo, and Liejin Guo

International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shaanxi 710049, China

Correspondence should be addressed to Shaohua Shen; shshen.xjtu@mail.xjtu.edu.cn

Received 2 December 2012; Accepted 10 February 2013

Academic Editor: Krisztina Gajda-Schranz

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We introduced a simple fabrication method of porous hematite films with tunable thickness in an aqueous solution containing FeCl_3 as the single precursor. We demonstrated that the optimized thickness was necessary for high performance photoelectrochemical water splitting, by balancing photon absorption and charge carrier transport. The highest photocurrent of *ca.* 0.15 mA cm^{-2} at 1.0 V versus Ag/AgCl was achieved on the 300 nm thick porous hematite film as photoanode, with IPCE at 370 nm and 0.65 V versus Ag/AgCl to be 9.0%. This simple method allows the facile fabrication of hematite films with porous nanostructure for enabling high photon harvesting efficiency and maximized interfacial charge transfer. These porous hematite films fabricated by this simple solution-based method could be easily modified by metal doping for further enhanced photoelectrochemical activity for water splitting.

1. Introduction

Since Fujishima and Honda reported water splitting in a photoelectrochemical (PEC) cell using TiO_2 as photoanode and Pt as cathode in 1972 [1], solar hydrogen production via PEC water splitting has been of great interest as the most promising way to convert solar light and water to chemical energy. In the past decades, numerous efforts have advanced considerable progress on high performance water splitting, and synchronously various semiconductor materials have been developed as photoelectrodes to show PEC activity [2–9]. However, the solar hydrogen conversion efficiency is still very low, due to the lack of suitable materials. The ideal photoelectrode material must be strongly absorptive in solar spectrum, have excellent electronic properties for efficient separation of photoexcited charges, have and high reactivity for surface chemical reactions (generally water oxidation reaction for photoanodes). Unfortunately, such an ideal material has not been found yet.

By comparing other metal oxides such as TiO_2 , WO_3 , and ZnO, hematite ($\alpha\text{-Fe}_2\text{O}_3$) has been extensively studied

as a strong photoanode candidate for solar water oxidation, because its narrow band gap permits light absorption in wide range solar spectrum, and additionally it is low cost, nontoxic, chemically stable [10]. However, its PEC performance has been severely limited by some unfavorable characteristics, such as small optical absorption coefficient, poor carrier mobility, and ultrafast recombination of photogenerated carriers. In spite of this, recent efforts on metal doped and nanostructured hematite photoanodes have resulted in encouraging advances in high performance PEC water splitting by increasing visible light response as well as promoting charge transport. For example, various n-type dopants such as Ti^{4+} [11], Zr^{4+} [12], Sn^{4+} [13], Pt^{4+} [14], and Ta^{5+} [15] have been introduced into hematite lattice to improve electrical conductivity for efficient charge transfer and separation, which, without exception, gave rise to enhanced PEC performances for water splitting on these metal doped hematite. Kay et al. [16] produced a very successful system of Si doped cauliflower-type Fe_2O_3 prepared by atmospheric pressure chemical vapor deposition (APCVD). A high photocurrent, 2.2 mA cm^{-2} at 1.23 V versus

the reversible hydrogen electrode (RHE) in 1 M NaOH at standard solar condition, was obtained on this photoanode. They also successfully increased the performance of hematite photoelectrodes for solar water splitting by preparing an extremely thin layer (12.5 nm) of this visible light absorber on a nanostructured scaffold (SiO_x) using a spray pyrolysis method [17]. The SiO_x monolayer could change the hematite nucleation and growth mechanism, increasing its crystallinity and reducing the concentration of carrier trapping states of the ultrathin hematite films. Very recently, Lin et al. [18] fabricated an innovative p-n hematite junction using atomic layer deposition (ALD) method. When grown on n-type hematite, the p-type layer was found to create a built-in field that could be used to assist PEC water splitting reactions.

Hematite films can be successfully fabricated by different methods, including APCVD [16], pulse laser deposition [19], ALD [20], and reactive DC magnetron sputtering [21], with facile control of chemical composition, deposition parameters, and excellent reproducibility. However, these techniques and related manufacturing equipments are of high cost, which severely limits their application for the fabrication of large surface area hematite films. In contrast, solution-based growth methods are always economic and manageable and thus have attracted great interest to be used for hematite film growth. For example, Lionel and coworkers developed a low temperature aqueous chemical growth method for the fabrication of hematite nanorod arrays for PEC water splitting [22, 23]. Despite of its low PEC activity even after doping metal, the nanorod structure is still supposed to favor charge transport [24, 25]. Wang et al. [26] reported a simple deposition-annealing process for the fabrication of transparent, mesoporous hematite films on FTO ($\text{F}:\text{SnO}_2$) substrate, using nontoxic FeCl_3 as the Fe precursor, as well as their implementation as photoanodes for efficient water oxidation. Grätzel group [27, 28] demonstrated the formation of mesoporous hematite films using a nanoparticle suspension by the doctor-blade method. This solution-based colloidal route offers an inexpensive path to electrodes with highly attractive morphologies for enabling high photon harvesting efficiency and maximized interfacial charge transfer, which resulted in the highest photocurrent reported for a solution-processed hematite photoanode.

In this study, a simple solution-based method was developed for growing porous hematite films on FTO substrates using FeCl_3 as the only precursor. It was found that the film thickness could be easily controlled by the concentration of FeCl_3 aqueous solution, which was supposed to be the critical factor determining the PEC activities of these porous hematite films for solar water splitting.

2. Experimental Section

Porous $\alpha\text{-Fe}_2\text{O}_3$ films with tunable thickness were facily grown on FTO (Pilkington, TEC7) substrates in an aqueous solution containing ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) as the only precursor. Typically, two back-to-back FTO glasses were placed, leaning against the wall, in a cap-sealed glass bottle containing ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)

aqueous solution with different concentrations. After heated in a regular oven at 100°C for 24 h, the resultant yellow or light yellow films were washed with distilled water and dried, then annealed at 750°C for 5 min with ramping rate of $25^\circ\text{C}/\text{min}$. These $\alpha\text{-Fe}_2\text{O}_3$ films, grown in 0.02, 0.05, 0.10, and 0.15 M FeCl_3 aqueous solution, were denoted as Fe_x ($x = 0.02, 0.05, 0.10$, and 0.15), respectively.

Scanning electron microscopy (SEM) images were obtained with a Hitachi environmental field emission scanning electron microscope (model S-4300SE/N) operating in secondary electron detection mode. Raman scattering study was performed on a Jobin Yvon LabRAM HR spectrometer using 514.5 nm irradiation from an argon ion laser at 20 mW. Spectral transmittance and absorptance measurements were taken on the samples with a commercial thin film metrology system (Scientific Computing International, FilmTek Par 3000 SE). The X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos spectrometer (AXIS Ultra DLD) with monochromatic Al $K\alpha$ radiation ($h\nu = 1486.69\text{ eV}$) and with a concentric hemispherical analyzer.

PEC measurements were conducted by a potentiostat (Pine Instruments Bipotentiostat) in 0.5 M NaCl (pH 6.7) using a three-electrode configuration, with the porous $\alpha\text{-Fe}_2\text{O}_3$ film as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. A 1 cm^2 masked-off, sealed area of the $\alpha\text{-Fe}_2\text{O}_3$ sample was irradiated with a 300 W Xe lamp solar simulator through an AM 1.5G filter (Oriel) with light intensity set as $100\text{ mW}\cdot\text{cm}^{-2}$. Incident photon-to-current conversion efficiency (IPCE) measurements were performed using a 300 W Xe lamp integrated with a computer-controlled monochromator (Beijing Optic Instrument Factory), a photo chopper (PARC), and a lock-in amplifier (Signal Recovery) used for photocurrent detection. IPCE measurements were performed in 0.5 M NaCl solution with potential controlled at 0.65 V as versus Ag/AgCl reference electrode (i.e., 1.23 V versus reversible hydrogen electrode (RHE), calculated from $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.1976 + 0.057\cdot\text{pH}$). N_2 gas was continuously bubbled in solution before and during all these electrochemical experiments to remove any dissolved O_2 and therefore suppress the reduction of O_2 at the counter electrode.

3. Results and Discussion

In this study, we introduced a new facile fabrication method of porous $\alpha\text{-Fe}_2\text{O}_3$ films with controlled thickness in an aqueous solution only containing FeCl_3 as the single precursor and demonstrated the PEC property depending on the thickness which was influenced by the concentration of FeCl_3 aqueous solution.

The thickness of porous $\alpha\text{-Fe}_2\text{O}_3$ films as a function of the concentration of FeCl_3 aqueous solution was investigated by SEM images in Figures 1 and 2. As shown in Figures 1(a) and 2(a), the $\text{Fe}_{0.02}$ film showed FTO substrate partially uncovered, due to the low concentration of FeCl_3 aqueous solution. With the concentration of FeCl_3 aqueous solution increasing from 0.02 M to 0.15 M, the FTO substrates were covered by $\alpha\text{-Fe}_2\text{O}_3$ films (Figures 1(b)–1(d)) and simultaneously thickness

FIGURE 1: Top view SEM images of porous α - Fe_2O_3 films grown in FeCl_3 aqueous solution. (a) Fe0.02, (b) Fe0.05, (c) Fe0.10, and (d) Fe0.15.

FIGURE 2: Cross-sectional SEM images of porous α - Fe_2O_3 films grown in FeCl_3 aqueous solution. (a) Fe0.02, (b) Fe0.05, (c) Fe0.10, and (d) Fe0.15.

FIGURE 3: The Raman spectra of porous α - Fe_2O_3 films grown in FeCl_3 aqueous solution.

increased from 300 nm up to 550 nm (Figures 2(b)–2(d)). Except for the Fe0.02 film with FTO substrate exposed, all the other films were of porous structure. Such porosity structured films are of highly attractive morphologies for enabling a high photon harvesting efficiency with hematite and providing large contact area between semiconductor photoanode and electrolyte to promote interfacial charge transfer [27]. Furthermore, the thickness of the porous α - Fe_2O_3 films could be easily controlled by varying FeCl_3 precursor solution concentration during the solution-based process.

The crystal structure of these prepared α - Fe_2O_3 films was confirmed by the Raman spectra. As shown in Figure 3, the films of Fe0.05, Fe0.10, and Fe0.15 exhibited characteristic peaks ascribed to hematite crystalline phase [29], while the Fe0.02 film mainly showed the Raman bands which arose from the FTO (fluorine-doped SnO_2) substrate [30], due to the small thickness of α - Fe_2O_3 or the partial coverage of FTO by α - Fe_2O_3 (see SEM image in Figures 1(a) and 2(a)). The additional peak located at approximately 657 cm^{-1} should be assigned to magnetite (Fe_3O_4), and its existence has been previously reported in some other high-valence metal-doped or high-temperature annealed hematite photoelectrodes [14, 29]. This should be related to the doping of high-valence metal or diffusion of Sn^{4+} from FTO substrate into the lattice of hematite, which induced the appearance of Fe^{2+} (Fe_3O_4) to keep the electric neutrality.

XPS spectroscopy was performed on these porous α - Fe_2O_3 films to analyze the chemical states of Fe and Sn in hematite crystal lattice. The Fe 2p spectra shown in Figure 4(a) revealed that iron exists predominately as Fe^{3+} , with binding energies for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ levels located at *ca.* 710.9 and 724.3 eV, respectively. With the decreasing film thickness, the emerging peak located at *ca.* 716.6 eV should be related to Sn 3p, due to the diffusion of Sn from

FTO substrate to hematite lattice. This was also confirmed by Sn 3d spectra, as shown in Figure 4(b). The increasing intensity of Sn 3p peak (Figure 4(a)) and Sn 3d peak (Figure 4(b)) indicates that the decreasing film thickness from Fe0.15 to Fe0.02 makes it increasingly easy for Sn to diffuse from FTO substrate to hematite near-surface region. As a result, the surface molar ratio of Sn : Fe obviously increased, for the thinnest film of Fe0.02 especially, as shown in Figure 4(c). By carefully checking the position at *ca.* 713.8 eV in Fe 2p spectra, the increasing intensity could be associated with the superposition of XPS peak (satellite) of divalent iron in the form of Fe_3O_4 [31, 32]. The existence of Fe_3O_4 , to maintain charge neutrality by compensating for Sn^{4+} diffusion, could be reasonable as also evidenced by the Raman spectra.

The color of the prepared α - Fe_2O_3 films varied from red brown to light yellow, depending on the decreasing concentration of FeCl_3 precursor solution. As reflected in optical spectra shown in Figure 5(a), the transmittance decreased in the whole visible spectrum for these films, due to the thickness gradually increasing from Fe0.02 to Fe0.15. It is indicated the thickness of α - Fe_2O_3 films affects their photon absorptivity. However, the band gaps of these α - Fe_2O_3 films were quite similar and at 2.1–2.2 eV (Figure 5(b)), as estimated from (1) (Kubelka-Munk equation) [33] as follows:

$$\alpha h\nu = C(h\nu - E_g)^m \quad (1)$$

where α is the absorption coefficient of the material, $h\nu$ is the photon energy in eV, E_g is the band gap in eV, and C is a proportionality constant. m is also a constant, being 1/2 for a direct and 2 for an indirect band gap semiconductor. In this case, m is equal to 2 for α - Fe_2O_3 as an indirect band gap semiconductor [17, 21]. The onset of electronic transition at *ca.* 3.7 eV for Fe0.02 and Fe0.05 should be derived from FTO substrate, due to their small thickness of α - Fe_2O_3 . That is to say, the various thicknesses mainly affected the absorptivity rather than the band gap of these prepared α - Fe_2O_3 films. The influence of thickness on the PEC activity will be discussed in the following section.

It has been reported that high temperature annealing, which induced Sn diffusion from FTO substrate to hematite lattice and thus the appearance of Fe^{2+} , was very effective for enhanced PEC activity. It was proposed that diffused Sn^{4+} (like some dopants such as Ti^{4+} [11], Zr^{4+} [12], Pt^{4+} [14], etc.) could act as electron donating substitutional impurities for increased electronic conductivity [28] meanwhile, the existence of both Fe^{3+} and Fe^{2+} contributed to the improvement of electron transport by a polaron hopping mechanism [31, 34]. Thus, a high temperature annealing process was used in this study to activate the porous α - Fe_2O_3 films for efficient PEC water splitting. Considering the same activation process for all these α - Fe_2O_3 films, some other reasons should be responsible for their different PEC activities, for example, film thickness. Indeed, film thickness is a key factor affecting the PEC activity of photoelectrodes by simultaneously influencing photon absorption and charge carrier transport. In order to achieve optical thickness for enough charge carriers created by photons, physically thick structures are always required. However, the thick films

FIGURE 4: XPS analysis results of prepared porous α -Fe₂O₃ films. (a) Fe 2p spectra, (b) Sn 3d spectra, and (c) surface molar ratio of Sn : Fe.

would result in long diffusion distance for charge carriers to be transferred to surface before recombination.

The PEC performance for these porous α -Fe₂O₃ films, with different thickness, is shown by sweeping current-potential scans in 0.5 M NaCl electrolyte (pH 6.7) with chopped illumination of solar simulator (AM 1.5 G, 100 mW cm⁻²) in Figure 6. The Fe0.02 film exhibited a quite low photocurrent, due to its very small thickness which greatly limited the photon absorption. With thickness increasing to 300 nm for the Fe0.05 film, the PEC performance was remarkably enhanced with photocurrent

at 1.0 V versus Ag/AgCl increased by about 15 times. This is because the much thicker film could absorb enough photons to create electrons and holes for PEC water splitting. However, when the film thickness further increased for Fe0.10 and Fe0.15, the photocurrents gradually decreased. This should be related to the long diffusion distance for charge carriers hampered their facile transfer to surface before recombination. Figure 7 revealed the change tendency of IPCE at 370 nm for these porous α -Fe₂O₃ films, which increased from 1.8% for Fe0.02 to 9.0% for Fe0.05, and then gradually decreased to 3.3% for Fe0.15. Consequently,

FIGURE 5: (a) Spectral transmittance and (b) Tauc plots of porous α - Fe_2O_3 films grown in FeCl_3 aqueous solution.

FIGURE 6: Chopped current-voltage curves of porous α - Fe_2O_3 films grown in FeCl_3 aqueous solution. Inset: photocurrent of porous α - Fe_2O_3 films at applied potential of 1 V versus Ag/AgCl.

FIGURE 7: IPCE of porous α - Fe_2O_3 films with potential controlled at 0.65 versus Ag/AgCl.

optimized film thickness to balance photon absorption and charge carrier transport is of great importance for high performance PEC water splitting.

4. Conclusions

In this study, porous hematite films with tunable thickness were facilely fabricated in an aqueous solution containing

FeCl_3 as the single precursor. With the concentration of FeCl_3 aqueous solution increasing, the thickness gradually increased, whereas the photoelectrochemical performance increased first and then decreased. The optimized thickness was found to be necessary for high performance photoelectrochemical water splitting, by balancing photon absorption and charge carrier transport. It is believed that these porous hematite films fabricated via a facile solution-based method

could show enhanced photoelectrochemical activity for water splitting after further modification (e.g., metal doping).

Conflict of Interests

The authors declare no conflict of interest.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (no. 51102194, and no. 51121092), the Doctoral Program of the Ministry of Education (no. 20110201120040), the Natural Science Foundation of Shaanxi province (no. 2011JQ7017), and the National Basic Research Program of China (no. 2009CB220000). One of the authors (S. Shen) was supported by the Fundamental Research Funds for the Central Universities.

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