BiOI Nanosheets Grown by Chemical Vapor Deposition and Its Conversion to Highly Efficient BiVO₄ Photoanode

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Bismuth vanadate (BiVO₄) has been identified as one of the excellent visible-light-responsive photoanode for use in the photoelectrochemical water splitting. Recently intense research efforts have been devoted to the development of highly efficient BiVO₄ photoanode. Herein, we reported a low-cost and scalable method for preparing nanostructured BiVO₄ film. A much enhanced photocurrent (1.5 mA cm⁻²) was obtained for such film, which was 6.5 times higher than that of planar film at 1.23 V [vs. RHE (Reversible Hydrogen Electrode)]. The method provides an eco-friendly, reproducible and facile way to scale up on different substrates with attractive potential.

Keywords chemical vapor deposition, bismuth vanadate, photoelectrochemical water splitting, highly efficient

Introduction

Hydrogen, produced through solar water splitting, is a promising chemical fuel without an anthropogenic carbon-footprint.[1-8] Extracting hydrogen from water by photoelectrochemical (PEC) devices using solar light is of profound significance, which enables recyclable use of hydrogen fuel in a green and sustainable way.[6-12] To expedite the PEC water splitting toward practical applications, the development of efficient and stable photoanodes is indispensable. Bismuth vanadate (BiVO₄) has risen to prominence of late as one of the most promising anodic semiconductor materials. It has a direct bandgap of 2.4 eV and an appropriate valence band position for O₂ evolution.[13] Theoretically, the maximum attainable photocurrent for a material with a 2.4 eV bandgap is 7.6 mA cm⁻² under AM 1.5G solar irradiation.[14] However, the practical photogenerated current of this photocatalyst is much lower than the theoretical calculation because of its inherent drawbacks, such as sluggish charge mobility and fast charge recombination, which result in a low solar-to-hydrogen conversion efficiency.[15] Therefore, development and design of BiVO₄ microcrystal films should be highlighted by optimization of the pristine BiVO₄ films.

To achieve highly efficient BiVO₄ photoanodes, a considerable amount of work was focused on the preparation of nanostructured BiVO₄ films by low-cost and scalable methods, including spray pyrolysis, chemical vapour deposition (CVD), electrodeposition, dip coating, and seed layer mediated growth.[15-27] However, the films produced by CVD, dip coating and seed layer growth show poor photoelectrochemical performance. And process of preparing BiVO₄ photoanodes by electrodeposition and annealing is complicated and not eco-friendly. Herein, we report a two-step fabrication of highly efficient nanostructured thin film photoelectrode combining chemical vapour deposition with subsequent mild chemical and heat treatments method together.

Experimental

Materials

Bismuth iodide (BiI₃, 98%) was purchased from Aladdin. Vanadyl acetylacetonate [VO(acac)₂, 99%] was purchased from J&K. Dimethyl sulfoxide (DMSO), sodium hydroxide (NaOH, AR), bismuth nitrate pentahydrate, glacial acetic acid and acetylacetone were obtained from Sinopharm Chemical Reagent Co., Ltd.

Preparation of BiOI thin film

BiOI thin film composed of standing nanosheets was prepared via a simple CVD process carried out in a conventional horizontal tube furnace. Typically, a ceramic boat containing 400 mg of BiI₃ powder as the source was placed at the horizontal tube furnace. Cleaned FTO glass with 1 cm × 1 cm exposure was placed approximately 11 cm away from the source in the downstream direction. The tube was then tightly sealed and carefully degassed at room temperature for about 10 min. High-purity N₂ was introduced into the tube at a flow rate of 0.1 L min⁻¹ prior to the heating process to remove any oxygen in the furnace. The temperature of the source was increased to 500 °C in 30
min and kept for 120 min with N₂ flow of 70 L·min⁻¹ and O₂ flow of 30 L·min⁻¹. The orange-red BiOI thin film deposited on FTO glass with area of 1 cm² was obtained after naturally cooling.

Preparation of the nanoporous BiVO₄ photoanode

0.1 mL of a dimethyl sulphide (DMSO) solution containing 0.4 mol·L⁻¹ vanadyl acetylacetonate [VO(acac)₂] was placed on the BiOI electrode (1 cm × 1 cm) and was heated in a muffle furnace at 450 °C for 2 h. Excess V₂O₅ present in the BiVO₄ electrodes was removed by soaking them in 1 mol·L⁻¹ NaOH solution for 30 min with gentle stirring. The resulting pure BiVO₄ electrodes were rinsed with deionized water and dried at room temperature.

The control sample was prepared through metal-organic decomposition method on the FTO substrates. Typically, Bi(NO₃)₃•5H₂O in glacial acetic acid (0.2 mol·L⁻¹) and vanadyl acetylacetonate (0.03 mol·L⁻¹) in acetylacetone were mixed with a 1 : 1 mole ratio of Bi/V. The solution was obtained after ultrasonication at room temperature. 20 µL of the solution was dropped on FTO (SnO₂:F on glass) with 1 cm × 1 cm exposure and dried at 80 ℃ for 30 min, followed by annealing at 470 ℃ for 30 min.

Characterization

Crystallographic information of the thin film was obtained with X-ray diffraction (XRD, Bruker D8 Advanced diffractometer, Cu Kα radiation, 40 kV). The morphology and structure of the film were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, F20, 200 kV). The optical absorption spectra of the samples were recorded in a Cary 500 UV/vis spectrophotometer.

Results and Discussion

The SEM image of BiOI shown in Figure 1a, depicts that the film was composed of smooth square-shaped flake arrays. These flakes are typically in the thickness of ca. 50 nm, with a height of ca. 500 nm (Figure S1, ESI). Most of the flakes are uniformly vertically aligned or slightly tilted, leading to better pathway for carriers’ migration. After mild heat and chemical treatments, BiVO₄ thin film is obtained with nanoporous morphology (Figures 1b and c) and the nanoparticles are mainly ca. 250 nm. The side-view SEM image shows the thickness of the BiVO₄ film is around 800 nm (Figure 1d).

As shown in Figure 2a, the yellow hue of the obtained film is a strong indication of the entirely conversion to pure BiVO₄ from red BiOI. For the as-prepared film by CVD, the peaks at 29.2° and 54.6° are indexed to that of tetragonal BiOI (JCPDS No. 10-0445 with a = b = 3.944 Å, c = 9.149 Å) and the other peaks are ascribed to that of FTO glass (JCPDS No. 46-1088). The purity and crystal structure of the porous BiVO₄ photoanode (monoclinic scheelite structure) were confirmed with X-ray diffraction (Figure 2b), as all the diffraction peaks can be indexed to the monoclinic phase BiVO₄ (JCPDS No.14-0688). In addition, peaks of SnO₂ film substrate match well with the FTO glass. The EDS patterns shown in Figure S2 clearly confirm that the existence of iodine element in the obtained CVD film, while no iodine element can be detected and the ratio of Bi/V is almost 1 : 1 after annealing and chemical treatment. The bandgap of the obtained BiVO₄ film can be estimated from the UV-vis absorption spectrum (Figure S3, ESI) according to the Tauc plot [(αhν)² versus hν] (Figure S4, ESI). [13] The calculated bandgap of BiVO₄ is approximately 2.5 eV, which is consistent with the literature values. [13] To obtain more detailed information about the crystalline structure of the BiVO₄ nanoparticles.
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cles, transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were conducted. Figure 2c shows that the size of BiVO₄ nanoparticles is around 250 nm, which is consistent with the SEM results. In the HRTEM image (Figure 2d), the BiVO₄ nanoparticles are highly crystalline and the lattice fringes of 0.2127 nm and 0.1995 nm can be assigned to the (051) and (~231) lattice planes of BiVO₄ crystal structure with an angle of 51.25°. The corresponding selected area electron diffraction (SAED) pattern in the inset of Figure 2d confirms the high crystallinity of BiVO₄ nanoparticles.

The PEC performance was tested in 0.5 mol•L⁻¹ potassium phosphate (KPi) solution (pH 7.0) by illuminating the BiVO₄ from the back side with AM 1.5G simulated light. Planar BiVO₄ photoanode was prepared by metal-organic decomposition method of BiVO₄ nanoparticles on FTO substrate (Figure S5, ESI†). As shown in Figure 3a, the porous BiVO₄ prepared by CVD and annealing (CVD-BiVO₄) obtains a photocurrent of 1.5 mA•cm⁻² at 1.23 V (vs. RHE), which is 6.5 times higher than that of the planar film (0.2 mA•cm⁻²). The photocurrent value of 1.5 mA•cm⁻² is comparable to the highest photocurrents reported in the literatures for undoped BiVO₄ photoanodes (Table 1).[15-27]

To testify the excellent photoelectrochemical performance of CVD-BiVO₄ electrode, the photoelectrochemical properties were examined in the presence of 1 mol•L⁻¹ sodium sulphite (Na₂SO₄), which served as the hole scavenger. The oxidation of sulphite is thermodynamically and kinetically more favorable than water oxidation, thus sulfite oxidation test enables investigation of the photoelectrochemical properties of BiVO₄ independently of its inherent poor water oxidation kinetics.[13,16] Indeed, with the addition of sulphite, an early onset potential and a remarkably high photocurrent [5.1 mA•cm⁻² at 1.23 V (vs. RHE)] are generated by the CVD-BiVO₄ photoanode, while the planar BiVO₄ showed an average photocurrent [1.2 mA•cm⁻² at 1.23 V (vs. RHE)] for sulphite oxidation. The fact further proves the excellent fill factor and photoelectrochemical capability of CVD-BiVO₄, implying the possibility of achieving a similar photocurrent when coupling with an appropriate cocatalyst.[17]

A comparison of the UV-vis absorbance spectra of the planar and porous electrodes reveals that the light absorption is enhanced by approximately 50% at the range of 400–470 nm for the porous BiVO₄ compared to planar film, which can be attributed to light scattering within the nanoporous structure and dense distribution of nano particles (Figure S3, ESI). In order to quantitatively investigate the photoactivity, incident photon to current efficiency (IPCE) measurements were performed at 1.23 V (vs. RHE) (Figure 3b). The IPCE spectra of the planar and porous BiVO₄ electrodes both exhibit photoresponse up to ca. 530 nm, as expected from the absorption edge of BiVO₄. The maximum IPCE is achieved at 420 nm with 32% for the porous CVD-BiVO₄ electrode. It should be emphasized that the IPCE of the porous BiVO₄ film is drastically improved compared to the planar film.

To clearly exploit the origin of the higher PEC performance, further study of electrochemical measurements is necessary. Interfacial properties between the electrode and the electrolyte were analyzed using electrochemical impedance spectroscopy (EIS) measurements.[29] As depicted in Figure 3c, the series resistance (Rₛ) values of both electrodes are almost the same, while the charge-transfer resistance (Rₜ) on the photoanode of porous CVD-BiVO₄ electrode is obviously smaller than that of the planar BiVO₄. The smaller arch observed in the EIS spectroscopy of porous CVD-BiVO₄ electrode

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**Table 1** Synthesis and typical PEC performance of several undoped bare BiVO₄-based photoanodes

<table>
<thead>
<tr>
<th>Authors</th>
<th>Method</th>
<th>Scan rate/ (mV•s⁻¹)</th>
<th>Electrolyte (pH)</th>
<th>J(H₂O) at 1.23 V RHE/(mA•cm⁻²)</th>
<th>J(Na₂SO₄) at 1.23 V RHE/(mA•cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kang et al.[15]</td>
<td>Hydrothermal deposition</td>
<td>—</td>
<td>0.5 mol•L⁻¹ Na₂SO₄ electrolyte (6.8)</td>
<td>0.85</td>
<td>—</td>
</tr>
<tr>
<td>Choi et al.[16]</td>
<td>Electrodeposition</td>
<td>10</td>
<td>0.5 mol•L⁻¹ phosphate buffer (7.0)</td>
<td>1.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Choi et al.[17]</td>
<td>Electrodeposition</td>
<td>10</td>
<td>0.5 mol•L⁻¹ phosphate buffer (7.0)</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Stefkik et al.[18]</td>
<td>Atomic layer deposition</td>
<td>10</td>
<td>0.5 mol•L⁻¹ phosphate buffer (6.8)</td>
<td>—</td>
<td>1.1</td>
</tr>
<tr>
<td>Wijayantha et al.[19]</td>
<td>Aerosol-assisted CVD</td>
<td>10</td>
<td>1 mol•L⁻¹ Na₂SO₄ electrolyte</td>
<td>0.2</td>
<td>—</td>
</tr>
<tr>
<td>Luo et al.[20]</td>
<td>Chemical bath deposition</td>
<td>—</td>
<td>1 mol•L⁻¹ Na₂SO₄ electrolyte (7.0)</td>
<td>0.9</td>
<td>—</td>
</tr>
<tr>
<td>Sayama et al.[21]</td>
<td>Metal-organic decomposition</td>
<td>50</td>
<td>0.5 mol•L⁻¹ Na₂SO₄ electrolyte (6.6)</td>
<td>1.2</td>
<td>—</td>
</tr>
<tr>
<td>Xie et al.[22]</td>
<td>Hydrothermal deposition</td>
<td>10</td>
<td>0.5 mol•L⁻¹ Na₂SO₄</td>
<td>5 µA•cm⁻²</td>
<td>—</td>
</tr>
<tr>
<td>Liu et al.[23]</td>
<td>Chemical solution deposition</td>
<td>25</td>
<td>1 mol•L⁻¹ Na₂SO₄ (pH 7.0)</td>
<td>0.85</td>
<td>—</td>
</tr>
<tr>
<td>Krol et al.[24]</td>
<td>Spray deposition</td>
<td>—</td>
<td>0.5 mol•L⁻¹ K₂SO₄ aqueous solution</td>
<td>0.6</td>
<td>1.7 (H₂O₂)</td>
</tr>
<tr>
<td>Mullins et al.[25]</td>
<td>Reactive ballistic deposition</td>
<td>25</td>
<td>0.5 mol•L⁻¹ Na₂SO₄ electrolyte</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Jia et al.[26]</td>
<td>Polymer-assisted deposition</td>
<td>—</td>
<td>0.5 mol•L⁻¹ Na₂SO₄ solution (5.5)</td>
<td>0.18</td>
<td>—</td>
</tr>
<tr>
<td>Yoon et al.[27]</td>
<td>Electrostatic spray deposition</td>
<td>—</td>
<td>0.5 mol•L⁻¹ Na₂SO₄ electrolyte</td>
<td>0.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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Figure 3  (a) J-V curve of CVD-BiVO₄ electrode and planar BiVO₄ measured in a 0.5 mol·L⁻¹ phosphate buffer (pH 7.0) with and without 1 mol·L⁻¹ Na₂SO₃ as hole scavenger under AM 1.5G, 100 mW·cm⁻² illumination (scan rate is 10 mV·s⁻¹). (b) IPCE of CVD-BiVO₄ and planar BiVO₄ obtained at 1.23 V (vs. RHE) in 0.5 mol·L⁻¹ KH₂PO₄ (pH 7.0). (c) EIS spectra of CVD-BiVO₄ and planar BiVO₄ photoanode under the open-circuit potential in dark in Kpi (pH 7.0). (d) Mott-Schottky plots of CVD-BiVO₄ and planar BiVO₄ obtained at 5 kHz in dark in Kpi (pH 7.0).

implies the smaller interfacial charge-transfer resistance, which confirms that the porous electrode possesses more efficient charge transfer than the planar film. The Mott-Schottky plots were used to estimate the carrier density (N_d) and the potential of flat band (V_fb) (Figure 3d).[13] The N_d can be calculated using the following equation:[27]

\[ N_d = \frac{2e\varepsilon_0}{\varepsilon \varepsilon_0} \left[ \frac{d}{dV} \left( \frac{1}{C^2} \right) \right]^{-1} \]

where e is the electron charge, \( \varepsilon_0 \) is the vacuum dielectric constant, \( \varepsilon \) is the relative dielectric constant (ca. 68 for BiVO₄\(^{[31,32]} \)).

All samples show positive slopes as expected for n-type BiVO₄ semiconductors. The V_fb of porous CVD-BiVO₄ determined form the extrapolation of X intercepts in Mott-Schottky plots was found to be 0.025 V positively shift compared to that of planar BiVO₄. The higher V_fb potential indicated a decrease in bend bending,\(^{[13]} \) which mainly results from the increased semiconductor/electrolyte interface, as reported previously.\(^{[33]} \) The N_d for porous CVD-BiVO₄ film (ca. 1.2 × 10¹⁸) is enhanced but of the same order of magnitude compared to that of planar film (ca. 0.76 × 10¹⁸), which may also contribute to the enhanced photoelectrochemical performance. Therefore, the enhanced PEC performance is a synergistic result of superior visible light absorption, charge transfer property and charge carrier density for the CVD nanoporous BiVO₄.

Conclusions

In summary, we have reported a simple, cost-saving and easily scalable synthetic strategy to prepare efficient nanoporous BiVO₄ photoanode via a two-step method, which involves a chemical vapour deposition of nanosheet BiOI and mild annealing and chemical treatments. The CVD process shows great potential to be industrialized due to its low cost and facility. The obtained porous BiVO₄ photoelectrode demonstrates a decent photoelectrochemical performance in comparison with previous reported great performance of bare BiVO₄ film without doping and catalyst loading. Among all the BiVO₄ electrodes prepared by various methods, our nanoporous electrode shows a 1.5 mA·cm⁻² photocurrent at 1.23 V (vs. RHE). The porous BiVO₄ photoanode can be further enhanced by doping and loading efficient oxygen evolution catalyst, which is in progress. Furthermore, the synthetic method is of vast industrial prospect, which paves a way for large-scale production.
of highly efficient bismuth vanadate or other Bi-based semiconductors.

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