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Photoelectrochemical water splitting at titanium dioxide nanotubes coated with tungsten trioxide
Electrosprayed heterojunction WO₃/BiVO₄ films with nanotextured pillar structure for enhanced photoelectrochemical water splitting

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We demonstrate that the addition of a tungsten oxide (WO₃) layer beneath a bismuth vanadate (BiVO₄) photocatalyst layer with a nanotextured pillar morphology significantly increases the photocurrent density in photoelectrochemical water splitting. The WO₃–BiVO₄ bilayer films produced a photocurrent of up to 3.3 mA/cm² under illumination at 100 mW/cm² (AM1.5 spectrum). The bilayer film was characterized by scanning electron microscopy, X-ray diffraction, and photoelectrochemical methods, which confirmed the superiority of the bilayer film in terms of its morphology and charge separation and transport ability. Both WO₃ and BiVO₄ were deposited by electrostatic spraying under open-air conditions, which resulted in nanotextured pillars of BiVO₄ atop a smooth WO₃ film. The optimal coating conditions are also reported. © 2015 AIP Publishing LLC.

Despite the merits of photoelectrochemical (PEC) water splitting,¹–⁵ identification and realization of semiconductors that yield the best photocurrent density during the PEC water-splitting process remains quite challenging.⁶–¹⁴ Metal oxides have been identified as good candidates based on their good PEC properties and material stability.¹⁵ Monoclinic bismuth vanadate (BiVO₄) (Eg = 2.4 eV) is a particularly promising material for PEC anodes.¹⁶ BiVO₄ can, in theory, produce a maximum photocurrent of ~7.5 mA/cm² at 1.23 V_RHE and 1 sun illumination.¹⁷ However, the photoactivity (i.e., solar-to-hydrogen efficiency) of BiVO₄ has been reported to be disappointingly low (<1%) with a photocurrent density of <1 mA/cm² at 1.23 V_RHE because of rapid electron/hole recombination. PEC performance of BiVO₄ can be improved by varying the precursor (Bi:V) atomic ratio¹⁸,¹⁹ or metal doping.²⁰ Several attempts have been made to improve the photoreponse of BiVO₄ by doping with Mo or W or by coupling BiVO₄ with another semiconductor.²¹,²² Coupling of BiVO₄ with tungsten oxide (WO₃) to form a WO₃/BiVO₄ heterojunction has been demonstrated to be a viable means to improve performance of BiVO₄-based photoelectrodes.²³

WO₃ has also been widely investigated for water splitting and related applications.²⁴–²⁷ It has been examined for photocatalytic and PEC applications because of its absorbance of the visible portion of the solar spectrum, good charge-carrier transport properties, and stability.²⁸ The photoactivity of WO₃ in the visible region of the solar spectrum is attributed to its indirect band-gap of 2.7–3.0 eV. The band positions of WO₃ and BiVO₄ are such that the conduction band electrons can be injected from BiVO₄ to WO₃ when coupled, which enhances charge transport in a bilayer system combining the two materials.

In the present study, we fabricated WO₃/BiVO₄ heterojunction films via electrospray deposition for use in photoelectrochemical water splitting. The optimal PEC performance was investigated by testing five different WO₃/BiVO₄ combinations. The electrostatic spray deposition (ESD) technique is well known for its ability to deposit uniform films through the production of extremely fine, self-dispersive, highly wettable, and adhesive droplets. The crystallinity, morphology, film thickness, and deposition rate can all be controlled by adjusting the voltage, flow rate, precursor concentration, and substrate temperature.²⁹–³¹ During ESD, charged droplets are accelerated towards a substrate, which offers improved targeting resulting in a high deposition efficiency and low material consumption. Furthermore, in the case of BiVO₄, the ESD process can be tuned to produce highly porous nano-textured pillar-like structures with high surface area, which improves the PEC water splitting activity.³²

Thin layers of WO₃ on indium-doped tin oxide (ITO)–coated glass substrates were fabricated by ESD. The spray solution was prepared by mixing tungsten(VI) ethoxide (C₆H₁₃O₅W) in absolute ethanol (Alfa Aesar) with polyethylene glycol (C₈H₁₆O₇). WO₃ films were fabricated by electrospraying for 20 min followed by air annealing at 550 °C for 30 min. To deposit the BiVO₄ layer, stoichiometric amounts of bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, ≥98%, Sigma-Aldrich) and vanadium(III) acetylacetonate (C₅H₇O₂V, 97%, 0.78 g, Sigma-Aldrich) precursors were mixed in 10 ml of acetic acid (CH₃COOH, 99.7%, Samchun Chemicals). The solution was stirred at room temperature and electrostatically sprayed on top of the WO₃ layer. The spraying time was varied to be 10, 20, 40, 60, or 80 min. The obtained films were annealed at 550 °C for 10 min.

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Thus, in Na$_2$SO$_4$, water is oxidized at the working electrode, sulfite is a sacrificial reagent that acts as a hole scavenger. As the electrolyte, we used 0.5M Na$_2$SO$_4$ (Fluka Analytical, Sigma-Aldrich, pro-analysis in highly pure water, pH 1.0M Na$_2$SO$_3$ (Sigma-Aldrich, 7) or ¼ 9). In Na$_2$SO$_3$, it is the SO$_3$ that is oxidized. The electrolyte solution was purged with nitrogen to remove dissolved oxygen before testing. A xenon arc lamp (Newport, Oriel Instruments, USA) was used to illuminate the photoelectrode at a light intensity of 100 mW/cm$^2$. The illumination source for the photocatalytic study was a 400 W xenon arc lamp fitted with a water filter to reduce the output in the IR region. Samples were stabilized in the electrolyte after each scan by monitoring the open circuit voltage for at least 10 min. The dark current and photocurrent of the working electrode versus the external bias voltage were recorded using a scanning potentiostat (VersaSTAT-3, Princeton Applied Research, USA), at a scan rate of 10 mV/s.

Figure 1 shows X-ray diffraction (XRD) patterns of representative ESD-generated WO$_3$, BiVO$_4$, and WO$_3$/BiVO$_4$ bilayer films. Diffraction peaks corresponding to the ITO substrate (JCPDS–391058) were observed at 20 = 30°, 35°, and 50°. In the XRD patterns of pure WO$_3$, peaks corresponding to the (002), (110), (111), (202), (122), and (310) planes were observed at 20 = 22.48°, 23.86°, 28.16°, 33.76°, 41.3°, 46.44°, and 55.04°, respectively. The monoclinic structure of the WO$_3$ films was confirmed by comparing the experimental data with literature data (JCPDS card No. 872404). The monoclinic phase of WO$_3$ is highly stable at room temperature and yields greater PEC activity than the orthorhombic phase.33

The XRD pattern of pure BiVO$_4$ shows diffraction peaks corresponding to the (110), (121), (200), (211), (150), (132), (240), (161), and (123) planes at 20 values of 18.6°, 28.6°, 34.5°, 39.5°, 42.1°, 45.4°, 46.8°, 52.9°, and 58.2°, respectively. Comparison of this data with JCPDS card No. 14–0688 confirmed the monoclinic scheelite structure of BiVO$_4$. The PEC activity of monoclinic BiVO$_4$ has been observed to be better than that of the zircon or tetragonal scheelite BiVO$_4$ crystal structures.34 Figure 1 also displays the XRD pattern of the WO$_3$/BiVO$_4$ bilayer film, which shows diffraction peaks corresponding to WO$_3$ and BiVO$_4$; the peaks corresponding to BiVO$_4$ are stronger than those of WO$_3$ because less WO$_3$ was deposited.

The morphological properties of the prepared films were studied by high resolution-scanning electron microscopy (HR-SEM). Figure 2 shows cross-sectional and top-view (inset) images of the W20-B0, W20-B10, W20-B20, W20-B40, W20-B60, and W20-B80 films; the numbers indicate the spraying time in minutes. The pure WO$_3$ film had a uniform thickness of about 100 nm. The surface morphology of the film was uniform, compact, and smooth because of the homogeneous distribution of the WO$_3$ nanoparticles via electrospaying.

A BiVO$_4$ layer was electrosprayed onto the WO$_3$ layer to generate bilayer films. The spraying time was varied between 10 and 80 min. Nanotextured BiVO$_4$ pillars formed on the WO$_3$ layer at BiVO$_4$ spraying times greater than 30 min. The pillars appeared not to be well-connected and increased in height with increasing spraying time of the precursor solution. The approximate heights of the pillars in the
W20-B40, W20-B60, and W20-B80 films were 2, 3, and 5 μm, respectively. The films produced with less than 30 min of electrospraying (i.e., W20-B10 and W20-B20) showed no evidence of the nanotextured pillars. Discernable growth of these pillars was observed when the spraying time exceeded 40 min. These pillars form as a result of simultaneous diffusive, thermophoretic, and electrophoretic transport of the electrospray-produced particles. As the film roughens, the electrostatic forces parallel to the substrate attract particles to the tips of pillars and repel particles in the valleys between pillars.

Current–potential measurements were performed on WO3/BiVO4 films with a ~100 nm thick WO3 underlayer (W20) and varying BiVO4 layer thicknesses (B00–B80). All measurements were carried out under the same experimental conditions. Figure 3 displays linear sweep voltammograms for the WO3/BiVO4 films with varying BiVO4 layer thicknesses. A pronounced enhancement in the photocurrent with increasing BiVO4 layer thickness is evident. For example, W20-B40 produced a photocurrent of 2.1 mA/cm². The higher photocurrent density of W20-B40 films relative to that of the pure BiVO4 film is attributed to improved electron/hole transport, which suppresses the recombination of charge carriers. A further increase in the BiVO4 layer thickness causes a dramatic decrease in the photocurrent. This poor performance reflects a trade-off between increased absorbance by a thicker film and increased transport limitations in a thicker film. The photocurrent densities of the W20-B60 and W20-B80 dropped to near 1 mA/cm².

The conduction-band and valence-band positions of WO3 are more positive than the band positions of BiVO4. Exposure of the WO3/BiVO4 photoanode to light results in the excitation of valence electrons to the conduction bands of both WO3 and BiVO4. The potential difference between these two materials promotes rapid electron transport from the conduction band of BiVO4 to that of WO3 and hole transport from the valence band of WO3 to that of BiVO4, enhancing charge carrier separation and therefore photocurrent density. In addition, the high photocurrent of the BiVO4 film in the present study is attributed to the formation of nanotextured pillars on the ITO substrate; these nanostructures provide a higher surface area, compared to a flat film, improving the transport of holes to the electrode-electrolyte interface. The nanotextured pillar-like structure of BiVO4 contributes to the photoreponse by creating more sites for water oxidation and shorter transport lengths for holes in the BiVO4, relative to a dense film. Kim and Choi produced highly photoactive nanoporous BiVO4 films by a multi-step process involving electrodeposition of BiOI nanoplatelets, followed by coating with a solution of vanadyl acetylacetonate and thermal annealing.35 On the other hand, here, we produced nanotextured pillars via thermophoretically and electrophoretically modified diffusion-limited aggregation during electrostatic spraying in open air.32 The maximum photocurrent density of 2.1 mA/cm² achieved in this study for the 20/40 WO3/BiVO4 film under 1 sun (100 mW/cm²) corresponds to 28% of the theoretical maximum of 7.5 mA/cm² that is achievable under standard conditions for BiVO4 with a 2.4 eV band-gap. Moreover, the photoactivity of WO3/BiVO4 is 1.6 times higher than that of pure BiVO4.

As a second test, PEC measurements for pure BiVO4 and the bilayer film with optimal performance (W20-B40) were carried out in the presence of the sacrificial reagent Na2SO3, which acts as a hole scavenger. Sulfite oxidation is favored over water oxidation, both thermodynamically and kinetically.35 Figure 4 compares typical current-potential curves of W20-Bi40 (in Na2SO3), BiVO4 40 (in Na2SO3), W20-Bi40 (in Na2SO4), and BiVO4 40 (in Na2SO4). For sulfite oxidation (using Na2SO3), the photocurrent onset potential shifted to more negative values compared to water oxidation (using Na2SO4). The onset of oxidation occurs at about −0.35 V for sulfite oxidation, compared to −0.2 V for water oxidation. A rapid increase in the photocurrent density is observed for sulfite oxidation between −0.2 V and +0.2 V, whereas for the water oxidation photocurrent increases more gradually with increasing applied voltage. At 0.7 V, the photocurrents obtained for BiVO4 and WO3/BiVO4 in sulfite oxidation are 1.95 and 3.3 mA/cm², respectively. This increase is attributed to the favorable kinetics and thermodynamics of the sulfite oxidation process involving electrodeposition of BiOI nanoplatelets, followed by coating with a solution of vanadyl acetylacetonate and thermal annealing.35 On the other hand, here, we produced nanotextured pillars via thermophoretically and electrophoretically modified diffusion-limited aggregation during electrostatic spraying in open air.32 The maximum photocurrent density of 2.1 mA/cm² achieved in this study for the 20/40 WO3/BiVO4 film under 1 sun (100 mW/cm²) corresponds to 28% of the theoretical maximum of 7.5 mA/cm² that is achievable under standard conditions for BiVO4 with a 2.4 eV band-gap. Moreover, the photoactivity of WO3/BiVO4 is 1.6 times higher than that of pure BiVO4.
oxidation. Na$_2$SO$_3$ acts as a hole scavenger, ensuring that the oxidation at the photoanode surface is not rate limiting, and the measured PEC reflects the rate of charge carrier generation and separation in the semiconductor bilayer film. Favorable band positions of WO$_3$ and BiVO$_4$ further improve the electron/hole transport, which is reflected in the 3.3 mA/cm$^2$ photocurrent density at just 0.7 V.

Table I compares the PEC performance of the electrostatically sprayed WO$_3$/BiVO$_4$ bilayer films with literature data.$^{19,36,37}$ The PEC performance of these films is better than that of films prepared by reactive sputtering and spin coating, which indicates the advantage of electrostatic spray deposition over these techniques. The photocurrents achieved by ESD in this work and glancing angle deposition assisted with physical sputtering are quite comparable. However, the simplicity and energy- and material-efficiency of ESD make it more attractive from a practical perspective, compared to high vacuum deposition techniques. In their study, Hong et al.$^{23}$ prepared WO$_3$/BiVO$_4$ multilayered heterojunction films by polymer-assisted direct deposition. For the preparation of the composite multilayered electrodes, calcination of each layer was needed prior to adding the next layer, which made the fabrication process quite long and cumbersome.

High-performance water splitting was achieved by optimal combination of WO$_3$/BiVO$_4$ films prepared by ESD followed by annealing. This produced the most photocatalytically active phase for both WO$_3$ and BiVO$_4$. At the optimal point (W20-Bi40), maximum photocurrent densities of 2.1 mA/cm$^2$ for water oxidation and 3.3 mA/cm$^2$ for sulfite oxidation were achieved using a photoanode with a dense $\sim$100 nm thick WO$_3$ underlayer topped with a $\sim$2 $\mu$m thick film made up of porous BiVO$_4$ nanopillars. The enhanced PEC performance was mainly attributed to the generation of high-surface area nanotextured BiVO$_4$ pillars on the WO$_3$ layer. The favorable band positions of the WO$_3$ and BiVO$_4$ layers enhanced charge-carrier separation and transport. The fabrication of such high-performance photoanodes by ESD from simple precursors provides a promising practical route to improved photoelectrochemical water splitting.

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