



Cite this: *Nanoscale Adv.*, 2019, 1, 799

Synthesis of nanoporous Mo:BiVO₄ thin film photoanodes using the ultrasonic spray technique for visible-light water splitting†

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The use of bismuth vanadate (BiVO₄) scheelite structures for converting solar energy into fuels and chemicals for fast growth in lab to industrial scale for large-area modules is a key challenge for further development. Herein, we demonstrate a new ultrasonic spray technique as a scalable and versatile coating technique for coating pristine and doped nanoporous BiVO₄ thin film photoanodes directly on FTO-coated glass substrates for water splitting under visible irradiation. The successful Mo doping in BiVO₄ lattice was confirmed by various characterization techniques such as XRD, Raman, EDS and XPS. The Mo:BiVO₄ photoelectrode showed excellent performance with higher stability as compared to pristine BiVO₄ samples.

Received 12th September 2018
Accepted 7th November 2018

DOI: 10.1039/c8na00209f

rsc.li/nanoscale-advances

1. Introduction

Splitting water into hydrogen and oxygen through photoelectrochemical (PEC) solar energy conversion is one of the best approaches for solar fuel applications.^{1–4} The complete photoelectrochemical water splitting process includes two half reactions, namely, water reduction and oxidation. However, due to the multistep proton-coupled electron transfer process, water oxidation is more challenging in terms of thermodynamics and kinetics. This process can determine the water splitting efficiency. To date, numerous metal oxides, such as TiO₂,⁵ α -Fe₂O₃,⁶ WO₃ (ref. 7) and BiVO₄,^{8–10} have been used as photoanodes for enhancing the oxygen evolution reaction (OER) from water oxidation. From the above-mentioned photoelectrode materials, BiVO₄ is one of the most promising scheelite-type photoanode materials with an appropriate valence band position for OER. So far, BiVO₄ thin films have been deposited by chemical as well as physical techniques such as spin-coating,¹¹ dip-coating,¹² electrostatic spray/ultrasonic spray pyrolysis,^{13–15} reactive magnetron co-sputtering¹⁶ and facile successive ionic layer adsorption and reaction (SILAR).¹⁷ On the other hand, the physical technique of ultrasonic spraying is the most popular and promising technique because of its simplicity, large area production capability and absence of a non-vacuum process.

So far, the ultrasonic spray technique has been used for the synthesis of various nanomaterials including perovskite solar

cells (PSCs). To find commercial applications for solar fuels, it is highly important to develop large-area deposition techniques to fabricate uniform photoelectrodes. Furthermore, it is well-known that nanoarchitectures provide unique properties to improve the performance. Therefore, the synthesis of a uniform nanoporous layer of BiVO₄ is a key parameter in water splitting. Moreover, improving the short diffusion length of BiVO₄ by appropriate dopants, heterojunction formation or metal ion treatment is also important.^{18,19} Therefore, an effective deposition technique with positive dopants can help develop onsite applications of solar fuel. Cost saving by using less materials, low maintenance cost, highly uniform deposition for large-area application and simple assembly of equipment are the four main features of the ultrasonic spray technique. Herein, we report the synthesis of nanoporous BiVO₄ thin films by using the ultrasonic spray technique. However, it is well-known that the photoelectrochemical performance of pristine BiVO₄ is limited due to its short carrier diffusion length, which restricts the thickness of the photoelectrodes.²⁰ Therefore, the synthesized nanoporous BiVO₄ photoelectrodes have been used for water splitting under visible-light irradiation.

2. Experimental details

2.1 Chemicals and materials

FTO-coated glass substrates were purchased from TEC15, Pilkington with sheet resistance of $\sim 8 \Omega \text{ cm}^{-1}$. Precursors such as Bi(NO₃)₃·5H₂O, NH₄VO₃, (NH₄)MoO₄ and HNO₃ were purchased from Sigma Aldrich. Double distilled water was used for the preparation of precursor solutions. All these chemicals were used without further purification.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8na00209f



calibrated to 100 mW cm^{-2} by using a thermopile detector and a National Renewable Energy Laboratory – certified reference cell. J - V curves were measured by sweeping the potential in the positive direction at a scan rate of 10 mV s^{-1} in dark and under illumination. Electrochemical impedance spectroscopy (EIS) was conducted using Iviumstat (Ivium Technologies B.V., Eindhoven, the Netherlands) at an open-circuit potential at frequencies ranging from 10^{-1} to 10^5 Hz with AC amplitude of 10 mV .

3. Results and discussion

The surface morphology of the as-deposited samples was studied by scanning electron microscopy (SEM) (Fig. S1†). The SEM micrograph of as-deposited pristine BiVO_4 sample exhibited irregular deposition and agglomeration of nanoparticles (Fig. S1a†), whereas as-deposited Mo:BiVO_4 showed uniform coating with porous nanostructures (Fig. S1b†). To crystallize and remove the remaining solvent, we annealed these samples at 450°C for 2 h. Fig. 2 shows the top view and cross sectional SEM images of pristine and Mo:BiVO_4 thin films at different magnifications. The pristine BiVO_4 sample showed agglomerated nanoparticle morphology. In contrast, the Mo:BiVO_4 sample showed more nanoporous networks compared to pristine sample. These networks along with porous nanostructures were obtained due to volatilization of H_2O and HNO_3 and decomposition of by-products. To check the thickness of fabricated Mo:BiVO_4 photoelectrode, scanning electron microscopy (SEM) images were acquired for both samples. The SEM micrographs revealed that the surface of FTO substrate was uniformly coated with BiVO_4 films with $1.1\text{--}1.2 \mu\text{m}$ thickness. This nanoporous architecture facilitated better penetration of aqueous Na_2SO_4 electrolyte solution into either BiVO_4 or Mo:BiVO_4 films.

Fig. 3 shows the XRD patterns of un-doped BiVO_4 and Mo:BiVO_4 thin film samples. The XRD patterns revealed the formation of single phase BiVO_4 crystals with scheelite

structures and monoclinic phase.²¹ The lattice constants were calculated to be $a = 5.0195 \text{ \AA}$, $b = 11.701 \text{ \AA}$, and $c = 5.092 \text{ \AA}$, which matched well with literature data (JCPDS no. 014-0688). On the other hand, Mo:BiVO_4 did not show any significant peak for Mo doping, which might be due to weak diffraction intensities of Mo compared to those of pristine BiVO_4 or due to very less amount of Mo (2%) employed in this synthesis. However, the characteristic peak of Mo:BiVO_4 sample at $2\theta = 28.822^\circ$ corresponding to the (hkl) plane (-121) slightly shifted and appeared at $2\theta = 28.889^\circ$ due to compressive lattice strain.²² Furthermore, the peak for (-130) at $2\theta = 28.586^\circ$ disappeared. Raman spectra showed the same features for pristine BiVO_4 and Mo:BiVO_4 thin films (Fig. 4). The prominent peak at 827.53 cm^{-1} was assigned to stretching mode ν_s (V–O) vibration.

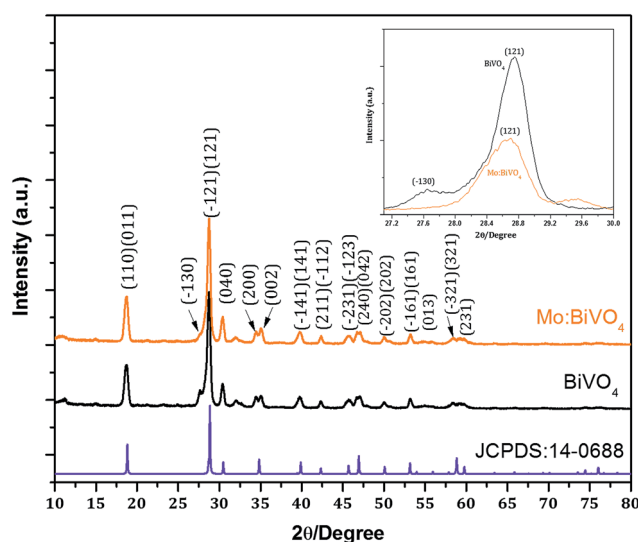


Fig. 3 XRD patterns of bare BiVO_4 and Mo:BiVO_4 thin films synthesized by the ultrasonic spray technique. For comparison, standard diffraction pattern of JCPDS no. 14-0688 is given. The inset shows characteristic peak shift to higher angle 2θ position.

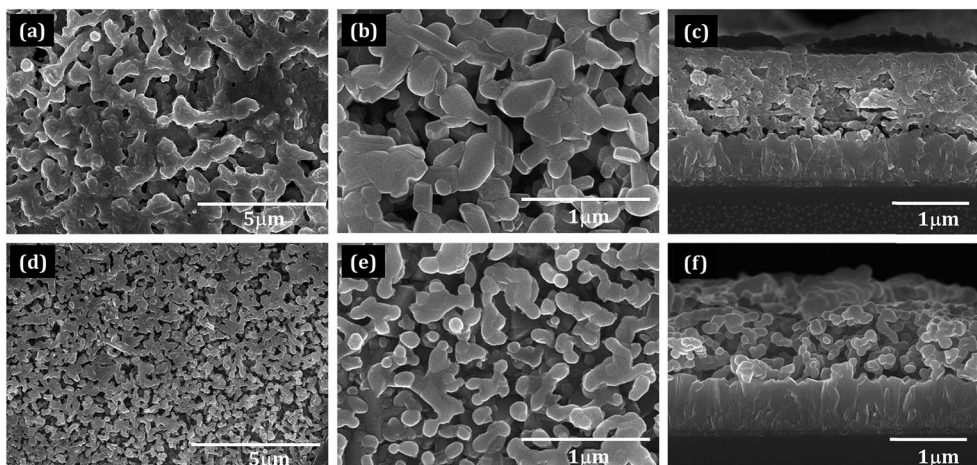


Fig. 2 Scanning electron microscopy images of pristine BiVO_4 (a and b) and Mo:BiVO_4 (d and e) thin films deposited by the ultrasonic technique. (c) Cross-section of BiVO_4 thin film electrodes. (f) Cross-section of Mo:BiVO_4 thin film electrodes (both samples were annealed at 450°C for 2 h).



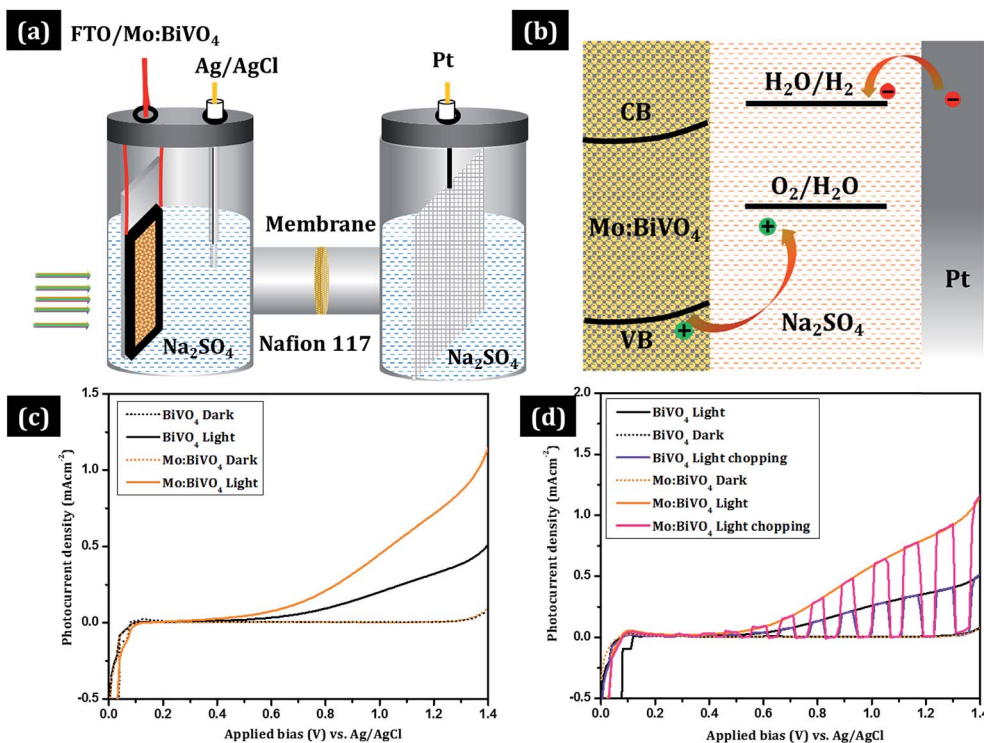


Fig. 7 (a) Experimental set-up of an H-shaped photoelectrochemical cell with two separate compartments for photocatalytic oxidation of water to O_2 ; (b) mechanism of photoelectrochemical water splitting; (c) photocurrent density–potential curves recorded under dark (dotted line) and light (solid line) (scan rate = 10 mV s^{-1}); (d) chopping performance.

0.5 M Na_2SO_4 electrolyte. The measured photocurrent–density curves *versus* applied potential for both type of electrodes are shown in Fig. 7c. During measurement of current in the dark, a very negligible current of $\sim 0.05 \text{ mA cm}^{-2}$ was observed at $\sim 1.3 \text{ V}$ (*vs.* Ag/AgCl), which may be due to the non-faradic reaction. To measure the rate of hydrogen and oxygen production by water splitting, current–voltage measurements are the best option. Fig. 7c shows the J – V plots of pristine $BiVO_4$ and $Mo:BiVO_4$ samples measured under illumination. It is clear that the photo-generated current density for $Mo:BiVO_4$ is much higher than that of pristine $BiVO_4$. This enhanced photoelectrochemical water oxidation for $Mo:BiVO_4$ can be ascribed to the enhanced hole diffusion length and increased charge separation, which reduces the charge transfer resistance for water oxidation. Furthermore, it is noted that Mo doping facilitates improved electron mobility. It is also noted that the nanoporous network facilitates enhanced electronic transport due to Mo doping. Interestingly, these photoelectrodes are quite stable and show good photocurrent stability as well as switching behaviour (Fig. 7d).³⁰ Electrochemical impedance spectroscopy (EIS) measurements of pristine sample and $Mo:BiVO_4$ sample were further obtained to investigate the charge transfer resistance and separation efficiency. As shown in Fig. 8, the arc radius of $Mo:BiVO_4$ under light is smaller than that of pristine $BiVO_4$, thus indicating that $Mo:BiVO_4$ has lower resistance than pristine $BiVO_4$ and accelerated interfacial charge-transfer process. To check the long-term stability under chopped light, we recorded the transient properties of $BiVO_4$ (Fig. S5a and

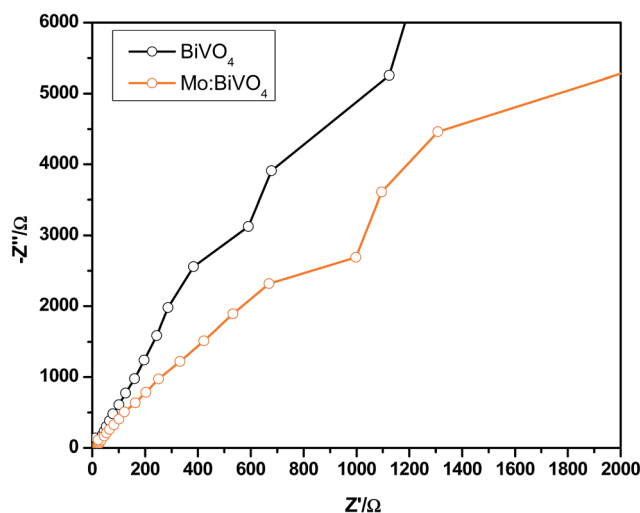


Fig. 8 Electrochemical impedance spectroscopy (EIS) of pristine and $Mo:BiVO_4$ samples under illumination.

S5b†) and $Mo:BiVO_4$ (Fig. S5c and S5d†) electrodes in Na_2SO_4 electrolyte (Fig. S5†). The pristine $BiVO_4$ sample initially shows 0.241 mA cm^{-2} current density, which further decreases up to 0.185 mA cm^{-2} after 500 s; furthermore, decrease is observed up to 0.140 mA cm^{-2} after 3600 s. However, in the case of $Mo:BiVO_4$, the initial current density of 0.618 mA cm^{-2} decreases slightly up to 0.594 mA cm^{-2} at 200 s, and there is no observable decrease up to 3600 s. From stability analysis, it is



clear that the Mo:BiVO₄ sample shows much higher stability and performance than the pristine BiVO₄ electrode.

4. Conclusions

In conclusion, we have successfully developed a new method to synthesize pristine and doped BiVO₄ nanoporous thin films using the ultrasonic spray technique for efficient water splitting under visible-light irradiation. The pristine and Mo-doped BiVO₄ nanoporous thin films were characterized by XRD, HRTEM and XPS. Our water splitting results revealed enhanced photocurrent density for Mo:BiVO₄ against that for pristine BiVO₄ due to the nanoporous structure and Mo doping. The present ultrasonic spray technique opens a new approach toward large-area deposition of nanoporous BiVO₄ photoelectrodes for onsite applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF) (NRF-2017R1A2B4008117). This work was also supported by the Korea Research Fellowship Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2016H1D3A1909289) for an outstanding overseas young researcher. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2018R1A6A1A03024334).

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