Photoelectrodes Based upon Mo: BiVO₄ Inverse Opals for Photoelectrochemical Water Splitting

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Abstract

BiVO₄ has been regarded as a promising material for photoelectrochemical water splitting, but it suffers from a major challenge on charge collection and utilization. In order to meet this challenge, we design a nanoengineered three-dimensional (3D) ordered macro-mesoporous architecture (a kind of inverse opal) of Mo:BiVO₄ through a controllable colloidal crystal template method with the help of a sandwich solution infiltration method and adjustable post-heating time. Within expectation, a superior photocurrent density is achieved in return for this design. This enhancement originates primarily from effective charge collection and utilization according to the analysis of electrochemical impedance spectroscopy and so on. All the results highlight the great significance of the 3D ordered macro-mesoporous architecture as a promising photoelectrode model for the application in solar conversion. The cooperating amplification effects of nanoengineering from composition regulation and morphology innovation are helpful for creating more purpose-designed photoelectrodes with highly efficient performance.

Keywords: solar water splitting · bismuth vanadate · composition regulation · morphology innovation · template
However, conventional BiVO$_4$ photoelectrodes are prepared through metal–organic decomposition or electrodeposition processes.$^{22-24}$ The disordered geometrical structures would increase the distance that charges must travel, and then charges would suffer from more nonproductive consumption due to increased chances of recombination. Fortunately, nanofabrication offers an opportunity for morphology innovation, enabling high surface reactive junction area and near-unity collection efficiencies. A three-dimensional (3D) ordered macro-mesoporous architecture (a kind of inverse opal) can serve as an efficient candidate for aforementioned requirements of improved charge migration.$^{25-27}$ By coincidence, interconnected periodic macroporous architectures can provide long-range-ordered paths for electron transport throughout the electrode.$^{27}$ Incorporating additional mesoscale pores can further increase the area of electrode/electrolyte junction and electrode/current collector junction. Utilization of holes and transport of electrons can be therefore accelerated. Overall, as shown in Scheme 1, an engineered 3D ordered macro-mesoporous Mo:BiVO$_4$ architecture is expected as a propitious model to meet the challenging point of low charge migration and further optimize the PEC performances of BiVO$_4$.

Inspired by this concept, we realize an innovative design of nanoengineered 3D macro-mesoporous Mo:BiVO$_4$ architecture through a controllable colloidal crystal template method. As a return for this design, superior photocurrent densities are achieved within expectation. This enhancement originates primarily from effective charge migration according to the analysis of PEC performance and electrochemical impedance spectroscopy. In this regard, the synergistic effects of nanoeengineering from composition regulation and morphology innovation show great significance of designing highly efficient photoelectrodes for the application in solar conversion. Morphology innovation is more advantageous for the photoelectrodes with faster charge transport.

RESULTS AND DISCUSSION

The realization of this tentative idea needs feasible and straightforward procedures. Being a technologically facile approach, colloidal crystal template method is chosen here for fabricating the 3D ordered macro-mesoporous scaffold. Scheme 2 outlines the typical procedures of the general solution approach. First, a large-scaled colloidal crystal template is assembled using polystyrene spheres (PSs). Second, interstices in colloidal crystal template are infiltrated with precursor solution that solidifies $\text{in situ}$ to form an intermediate composite structure. Finally, the template is removed through calcination. A 3D ordered macroporous host scaffold can be obtained topologically from the
template with a high degree of periodicity in three dimensions. Compared with single-metal oxide, the principal difficulty for quaternary material is the choice of precursors for infiltration. Some common infiltration (e.g., atomic layer deposition, electrodeposition) possesses many limitations of complex precursors and instruments. Solution infiltration approach offers the possibility for promoting compositional controllability, especially for quaternary materials. On the premise that the wettability and homogeneity can be guaranteed, the precursor solution would be arbitrarily chosen. From the viewpoint of developing an economical route for quaternary material architectures, herein a precursor solution consisting of low-cost metal salts is utilized instead of metal alkoxide.

To verify aforementioned tentative steps, Figure 1b shows the typical SEM image of the Mo:BiVO₄ 3D ordered porous architecture, which is the replica translated from the periodic colloidal crystal template using PSs with ~200 nm diameter (Figure 1a). When carefully observing the SEM image, we find that geometrical characteristics are mainly determined by two kinds of pores: one is the macropores surrounded by the skeletal walls with a diameter of ~180 nm; the other is the pores between neighboring macropores with a diameter of 30–50 nm. Commonly, porous materials are classified into several types by their diameters. According to International Union of Pure and Applied Chemistry (IUPAC) notation, a mesoporous material contains pores with diameters between 2 and 50 nm, and a macroporous material is the material that possesses pores with diameters greater than 50 nm. In this sense, we realize the rational design of nanoengineered 3D ordered macro-mesoporous architecture. The XRD and XPS characterizations confirm the pure phase of BiVO₄ after doping. From XPS results, two characteristic peaks located at 232.5 and 235.5 eV arising from 3d⁵/₂ and 3d³/₂ signals are assigned to the +6 oxidation state, suggesting that Mo cations are mainly present as Mo⁶⁺ into the lattice of the V places in BiVO₄.

During all the steps, the colloidal crystal template is always heated for several minutes before infiltration at a temperature that is a little higher than its glass transition temperature (T_g) so as to increase the structural stability and to prevent structural dispersion. This process will also lead to the deformation of neighboring PSs with different extent. Endowed with these interconnected parts, another kind of pore can be introduced into the macroporous host scaffold like a
window between each macropore because of topological transition. The diameter of windows can be tuned easily from macroscale to mesoscale by carefully controlling the contact area between each sphere where the precursor solution cannot reach as long as the complete topological transition can be granted. Since the common precursor solution is not viscid enough to realize a high filling fraction, a key factor enabling our design is the usage of a sandwich infiltration method according to our previous work, as shown in the Experimental Section. It is not necessary to heat the template, and thus the diameter of windows decreased. If the time of post-heating treatment is increased from 0 to 3 min and finally to 10 min (as illustrated in Figures 1a and 2a,b), the deformation caused by heating leads to gradual contact evolution between neighboring PSs from nearly no contact to quasi-point contact to quasi-facet contact, associated with the slightly reduced distance between neighboring spheres from 220 to 200 and 195 nm. The interstices among the PSs become smaller and smaller correspondingly. So after calcination, mesoscale pores (∼90 nm) and larger macropores (∼120 nm) as shown in Figure 2c,d.

To quantify the solar water splitting activity of the 3D macro-mesoporous Mo:BiVO₄ architectures, we employ PEC cells and measure photocurrent densities of the cells. In order to demonstrate our hypothesis of cooperative amplification from nanoengineering, we analyze the PEC performances on various samples: (i) macro-macroporous Mo:BiVO₄ that serves as the reference sample for incorporating the mesoscale pores; (ii) disordered porous Mo:BiVO₄ to show the effects of incorporating the macroporous skeleton and mesoscale windows; (iii) macro-mesoporous BiVO₄ using as a reference sample for composition regulation; (iv) disordered porous BiVO₄ to illustrate cooperative amplification from nanoengineering through composition regulation and morphology innovation. All five architectures are directly fabricated on FTO glasses with the similar calculated maximum photocurrent densities under 1 sun AM 1.5 sunlight. Corresponding characterizations are exhibited in Supporting Information Figures S1–S5. The XRD patterns and XPS peaks indicate that all the Mo-doped and non-doped monoclinic phase BiVO₄ matrix have high crystallinity and purity. All of the measurements here are carried out following optimization of the concentration of doping ions (Mo⁶⁺) for photocurrent density. Since higher or lower concentration will reduce the overall performances, the value is set to 2 atom % at the vanadium sites (BiV₀.₉₈Mo₀.₀₂O₄) according to previous literature and our experiments on optimizing the photocurrent densities.

Successful implementation of our designed approach can produce a photoelectrode with excellent PEC performance. Figure 3a shows linear sweep photovoltammetry measurements to determine the photocurrent density of the five kinds of photoelectrodes. Analysis of the photocurrent densities on various samples allows us to draw the following three conclusions. (i) Upon introduction of molybdenum, photocurrent densities are enhanced significantly across the entire potential range. (ii) All of the three 3D ordered macroporous-based photoelectrodes achieve
Photocurrent densities of a few mA cm\(^{-2}\) under light illumination, which implies that the 3D ordered macroporous architecture is an appropriate model as a photoelectrode for PEC water splitting. As shown in Figure 3b, the superior photocurrent densities can also be observed after illumination for 5 h, which originate from the high stability of 3D ordered macroporous skeletons for keeping such a high performance. (iii) Compared to macro-macroporous photoelectrodes, our macro-mesoporous photoelectrodes show obviously enhanced photocurrent densities over the entire bias range. Typically, at the bias of 1.0 V vs Ag/AgCl, the photocurrent density of the macro-mesoporous photoelectrode is 2.0 mA cm\(^{-2}\), which is 1.5-fold greater than the photocurrent densities of the macro-macroporous photoelectrode. It is expected that, since the macroscale sizes are identical to those photoelectrodes, the smaller mesoscale pores would provide a higher area of electrode/electrolyte junction and more contact area between electrode and current collector. The incident photon-to-electron efficiency (IPCE) mirrors the substantial enhancements of the photocurrent densities across the entire functional wavelength (Figure 3c). The IPCEs of the macro-mesoporous Mo:BiVO\(_4\) photoelectrode reach a high value of \(~40%\) at 1.0 V vs Ag/AgCl. Considering the similar calculated maximum photocurrent density of the five photoelectrodes (i.e., similar absorbed photon flux), we assert that the differences of the photocurrent densities among the five samples can be fully ascribed to the differences in their photon utilization behaviors, which depends on the charge migration (including transfer and surface reactions). To elucidate the detailed effects of incorporating macroporous scaffold/mesoscale windows and doping for charge migration, the internal quantum efficiency, also so-called absorbed photon-to-electron conversion efficiency (APCE), is used to evaluate the capability of actual utilization of the photons more clearly in Figure 3d. These excellent APCE results confirm the synergistic improvement of nanoengineering from composition regulation and morphology innovation for charge migration in PEC water splitting.

In order to explore the details for the enhancement, at least two factors, composition regulation and morphology innovation, should be considered for charge migration carefully. As for composition regulation, depending on the types and degrees of doping (including the formation of solid solutions), changes
in charge migration can be expected. However, the effects of doping may not always be favorable because it will enhance electron-hole recombination, impede charge transport by providing scattering centers, and decrease the width of the depletion layer. Therefore, identifying appropriate dopants and their concentrations are important to increase the overall performances of the photoelectrodes. According to previous literature, various ions\textsuperscript{10,11,16,17} have been introduced into partial sites of V\textsuperscript{5+} in BiVO\textsubscript{4}. Among them, Mo\textsuperscript{6+} ion has been demonstrated as an n-type dopant to enhance BiVO\textsubscript{4} PEC performances, which can be evidenced by the positive slope from Mott–Schottky plots in Figure 4g.

As analyzed in density functional theory calculations (Figure 4a–d), we find that the fundamental reasons for low charge transfer are that the conduction band of BiVO\textsubscript{4} mainly consists of V 3d orbitals. Unfortunately, VO\textsubscript{4} tetrahedra in BiVO\textsubscript{4} are not connected with each other, as shown in Figure 4e.\textsuperscript{34} So free electrons in BiVO\textsubscript{4} have to hop between VO\textsubscript{4} tetrahedra, leading to poor electron mobility. With the help of the substitutional defect of V\textsuperscript{5+} being replaced by Mo\textsuperscript{6+}, the shift of the (004) diffraction peak of BiVO\textsubscript{4} using FTO as the internal standard indicates the extension of c-axis after Mo doping (Figure S6a).\textsuperscript{35–37} Besides, the crystalline symmetry also changes from monoclinic to approximate tetragonal structure like the changes in W:BiVO\textsubscript{4}, evidenced by the (200) and (020) peaks which have been shifted toward one another (Figure S6b).\textsuperscript{24} This crystal deformation caused by larger tetrahedral ionic radii of Mo\textsuperscript{6+} (tetrahedral ionic radii for V\textsuperscript{5+} and Mo\textsuperscript{6+} are 0.35 and 0.41 Å) may help to overcome poor electron mobility in pure BiVO\textsubscript{4} intrinsically.\textsuperscript{11} Another aspect is that Mo\textsuperscript{6+} has one more valence electron than the V\textsuperscript{5+} host atom; hence their substitution into the host lattice can serve as electron donors.\textsuperscript{17} Excess charge carriers may form small and/or large polarons.

Figure 4. Calculated (a) electronic band structure, (b) electronic density of states; charge density contour plots projected along a (001) plane are shown for the two bands of (c) conduction band minimum and (d) valence band maximum at the A point (plotted from –0.1 (blue) to 0.1 (red) e\textsuperscript{−} Å\textsuperscript{−3}). (e) Atomic supercell structures of monoclinic scheelite BiVO\textsubscript{4} from which the 2 × 1 × 2 tunneled structure and the interconnected VO\textsubscript{4} tetrahedra can be observed clearly. (f) Bode phase plots of electrochemical impedance spectra of macro-mesoporous BiVO\textsubscript{4} before and after introduction of molybdenum. (g) Mott–Schottky plots of macro-mesoporous BiVO\textsubscript{4} before and after introduction of molybdenum.
(e.g., an electron with associated polarization field extending short or long distance) involving a sizable lattice distortion around the reduced V⁶⁺ ion; the former polarons localize at the atomic scale, and the latter polarons are extended over several lattice sites. For Mo-doped cases, the excess electron residing at the V⁶⁺ site may undergo migration to an adjacent V⁴⁺ (or Mo⁶⁺) site, and a higher concentration of polarons would lead to a larger overlap between them, thereby lowering the activation energy for polaron hopping, resulting in enhanced charge carrier mobility and reduced resistance.

Outwardly, from the Bode phase plots for different BiVO₄ photoelectrodes at the open-circuit voltage (VOC) of the PEC cells, the characteristic maximum frequency peaks (f_max) decrease obviously after doping. Generally speaking, there is no current passing through the external circuit at VOC; meanwhile, all the electrons injected into the conduction band must be the reacted electrode/electrolyte interface. Thus, the lifetime of electrons for recombination with a time constant (τn) is correlated with f_max as this equation:³⁸

\[ \tau_n = 1/(2\pi f_{\text{max}}) \]

As presented in Figure 4f, the maximum frequency value decreases with incorporating mesoscale pores and doping from ~2.2 to ~1 Hz, indicating that Mo:BiVO₄ possesses a 2-fold improved lifetime of electrons than that of undoped BiVO₄. Therefore, a low recombination rate is highly desired to achieve high charge collection efficiency, eventually leading to high solar conversion efficiency. Additional evidence comes from the slope of the linear part in the Mott–Schottky curves in Figure 4g; we can obtain carrier density to the photoelectrode. A steady-state photocurrent (I_{ss}) is achieved once the charge generation and recombination rates reach equilibrium. With all else being fundamentally equal, low recombination rates would give rise to long transient decay times. To know more details, we examine the transient decay time τ via a logarithmic plot of the parameter D, given by the equation:³⁹,⁴⁰

\[ D = (l_t - l_{ss})/(ln - l_{ss}) \]

where l_t is the photocurrent at time t (s) and l_{ss} is the steady-state photocurrent. The transient time constant (τ) is defined as the time at which ln D = −1.³⁹,⁴⁰ The method allows a qualitative comparison of the electron lifetime within these photoelectrodes. Figure 5a compares the logarithmic plots of the photocurrent density transient decay D and τ of these photoelectrodes at 1.0 V vs Ag/AgCl. Both 3D macroporous-based photoelectrodes possess longer τ than disordered photoelectrode (1.1 s), indicating that the 3D macroporous skeleton plays a positive role in suppressing charge recombination and improving charge migration. Looking over the curves of normalized plots of photocurrent–time dependence, we find that τ has an obvious
improvement to 3.0 s after introducing mesoscale windows into the macropore skeleton. With a view to the few influences originating from similar carrier density and flat voltage, as shown in Figures 4g and 57, the trend between r and morphology inspires us to further examine the resistance of three films to obtain more insight into charge transport within the films and the electrical contact with the current collector. As shown in Figure 5b, the resulting symmetrical and linear appearance indicates the Ohmic contacts between the film and the substrate. The macro-mesoporous architecture possesses the smallest resistance for charge transfer, resulting in facile charge transport.

As seen from the photocurrent densities and the electrochemical impedance measurements, 3D ordered macro-mesoporous MoBiVO4 provides multiple beneficial effects: First, interconnected 3D ordered macroporous architectures can provide long-range-ordered paths for electron transport throughout the electrode. In common, photoactivity of BiVO4 is limited by its rapid charge recombination upon excitation, the suppression of which contributes to improving the overall photocurrent generation and catalytic reaction. Charge recombination is always promoted by the existence of many grain boundaries among particles as well as poor contact with the FTO surface. With respect to macro-mesoporous architectures, it can be imagined that the thick wall forms within the interstitial space, which ensures high electrode/electrolyte area to reduce the interface transfer resistance. When in contact with the electrolyte, band bending forms at the junction and extends to the rest of the coating, giving rise to the depletion region where charges yielded by incident photons are separated. Photogenerated electrons are readily transported away, and the photogenerated holes are transferred to the electrolyte for chemical reactions. Considering the fact that the surface reaction is directly related to the surface area and the macro-mesoporous structure possesses open-edge geometry plus a high surface-to-volume ratio, the locations of active sites can be maximized; in other words, the surface reaction is accelerated. Moreover, the open-edge geometry is beneficial for improving the efficiency in elimination of produced O2 from the pores. A part of the O2 generated in the disordered pores cannot eliminate from the pore and consequently decreases the photocurrent. This is more significant for photoelectrodes to retain photocurrent after long-time illumination. Third, partially substituting V5+ with Mo6+ can increase the charge carrier concentration for the host lattice intrinsically, leading to higher electrical conductivity than bare BiVO4 photoelectrodes. Overall, we can understand the synergistic effects of composition regulation and morphology innovation more clearly from the enhancement factors of the solar-to-hydrogen conversion efficiencies ($\eta_{\text{STH}}$; see Figure S8 for details) and IPCE in Figure 6, which are defined as the ratio of the efficiencies of various BiVO4-based films to that of the BiVO4-disordered porous film. At the bias of 0.6 V vs Ag/AgCl, the $\eta_{\text{STH}}$ enhancement factor (Figure 6a) for MoBiVO4 macro-mesoporous film is 6.9, while the factors for BiVO4 macro-mesoporous film and MoBiVO4-disordered porous film are 3.4 and 1.7. The synergistic effect is obviously larger than simple composition regulation or simple morphology innovation. Moreover, the $\eta_{\text{STH}}$ enhancement factor between MoBiVO4...
macro-mesoporous film and MoBiVO$_4$-disordered porous film is 4.1, which is larger than the factor between BiVO$_4$ macro-mesoporous BiVO$_4$-disordered porous film (3.4). The IPCE enhancement factors and $\eta_{STH}$ enhancement factors at other biases all mirror the substantial enhancement, indicating that the influences of morphology innovation are more advantageous for the photoelectrodes with faster charge transport.

**CONCLUSION**

In conclusion, three-dimensional ordered macro-mesoporous MoBiVO$_4$ architectures are fabricated for PEC water splitting. With the help of a modified solution infiltration method and adjustable post-heating time, we can realize the incorporation of additional mesoscale pores into a periodic macroporous host scaffold. Three-dimensional ordered macro-mesoporous architecture possesses a more compact space occupation of materials through a larger interstitial space, which minimizes the inner resistance of charge transport and the contact resistance at the electrode/electrolyte and electrode/current collector junction. The efficiency in elimination of produced O$_2$ is also increased. Then the approach of precursor infiltration facilitates the composition regulation, so we can further substitute V$^{5+}$ with Mo$^{6+}$ to further optimize the charge migration of BiVO$_4$. The superior PEC performances and the analysis of EIS further prove that the charge migration is optimized. All of the results highlight the synergistic effect of nanomechanics and nanomorphology innovation. This approach is helpful for creating more purpose-designed photoelectrodes with highly efficient performance.

**EXPERIMENTAL SECTION**

Fabrication of PS Colloidal Crystal Templates. FTO glass was cleaned under sonication by sequentially immersing in ethanol, acetone, and distilled water, and then treated with the H$_2$SO$_4$/H$_2$O$_2$/H$_2$O (3:1:1, volume ratio) solution for a few seconds to make them uniformly hydrophilic. The well-ordered colloidal crystal templates comprising polystyrene spheres (PSs) arranged on a face-centered cubic lattice were fabricated using the methods of vertical deposition. The substrates were immersed vertically in the 0.5 wt % polystyrene latex at 60 °C. The drying of the sample at very low speed in the presence of moisture prevented the occurrence of cracking on the sample. Then the templates consisting of 200 nm PSs were heated at 110 °C for 0, 3, and 10 min.

Fabrication of MoBiVO$_4$ Films. In a typical procedure, Bi(NO$_3$)$_3$·5H$_2$O (0.5 mmol), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (0.0014 mmol), and NH$_4$VO$_3$ (0.0014 mmol) were dissolved in distilled water. Then the mixed solution was diluted with 10 mL of ethanol. The disordered porous film was prepared by drop-coating and calcination at 500 °C for 2 h with the ramping rate of 2 °C min$^{-1}$. Bi(NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$/(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were dissolved in distilled water as the precursor solution using the same atomic ratio.

Characterization. The X-ray diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm). The field emission scanning electron microscopy images were performed by a JEOL JSM-6700F field emission scanning electron microscope (15 kV). The solid-state current–voltage ($I–V$) measurements in the dark were measured on an electrochemical station (CHI660B, Shanghai Chenhua Limited, China). Silver paste was used to make connections from the current–voltage testing system to the bottom FTO substrate, and the top MoBiVO$_4$ layer is in a double-probe configuration and set as voltage bias mode. The distance between the electrodes and between electrode and the edge of the film were both kept the same.

![Figure 6](image-url). Enhancement factors of (a) solar-to-hydrogen conversion efficiencies (η$_{STH}$) and (b) IPCEs at 1.0 V vs Ag/AgCl, which are defined as the ratio of the efficiencies of various BiVO$_4$-based films to that of the BiVO$_4$-disordered porous film.
Photoelectrochemical Measurement. Photoelectrochemical test systems were composed of a standard three-electrode configuration. The Mo/BiVO₄ films with a Pt counter electrode and a Ag/AgCl reference electrode were immersed in a degassed 0.5 mol L⁻¹ Na₂SO₄ buffer at pH 6.6, which had been purged with nitrogen for 15 min prior to the measurement. The photoelectrochemical characterizations, electrochemical impedance measurements, and open-circuit voltage decay were measured on an electrochemical station (CHI660B, Shanghai Chenhua Limited, China) under illumination using a 300 W Xe lamp under illumination from the back (glass) side of the film. The monochromatic light was filtered by filter plates for different wavelengths with a bandwidth of 10 nm and transmittance of 80%, and the monochromatic light power density was measured by a UV-vis radiometer with an accuracy of 1 μW cm⁻². The potential was swept at a sweep rate of 10 mV s⁻¹. The measured potentials vs Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: 

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \text{pH} + 0.1976$$

Absorbed photon-to-electron conversion efficiency can be expressed as APCE = IPEC/I° − 10⁻³, where A is the absorption of the film at a specific wavelength. The solar-to-hydrogen conversion efficiencies (ηₛ) are estimated from the Gibb’s free energy, $\eta_S = J / (\lambda_n - \lambda_v) = V_{\text{rev}} / J = \eta_{\text{light}}$, which accounts for the thermodynamic losses associated with application of an external anodic bias and assumes 100% faradic efficiency. $V_{\text{light}}$ is the external anodic bias; $J$ is photocurrent density (mA cm⁻²) at $V_{\text{light}}$; $V_{\text{rev}}$ is the standard reversible potential which is 1.23 V vs RHE; and $I$ is the light intensity of light source (mW cm⁻²).

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Figure S1–5 represent typical characterization of macro-macroporous Mo/BiVO₄ architecture, disordered porous Mo/BiVO₄ architecture, macro-mesoporous BiVO₄ architecture, and disordered porous BiVO₄ architecture. Figure S6 is XRD data from representative BiVO₄ films. Figure S7 is Mott–Schottky plots of Mo:BiVO₄ macro-macroporous film and disordered porous film. Figure S8 is the solar-to-hydrogen conversion efficiencies of various BiVO₄-based films. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


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