In Situ Growth of MoS$_2$ Nanosheet Arrays and TS$_2$ (T = Fe, Co, and Ni) Nanocubes onto Molybdate for Efficient Oxygen Evolution Reaction and Improved Hydrogen Evolution Reaction

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ABSTRACT: Rationally designing efficient and low-price bifunctional electrocatalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are vitally important to bring solar/electrical-to-hydrogen energy conversion processes into reality. Herein, we report on a synthetic method that leads to an in situ growth of ultrathin MoS$_2$ nanosheets and transition metal disulfide nanocubes onto the surface of Fe$_{1/3}$Co$_{1/3}$Ni$_{1/3}$MoO$_4$ nanorods for the first time. Such hybrids are found to serve as a bifunctional electrocatalyst with high activities for OER and HER, as represented by an impressive anodic and cathodic current density of 10 mA cm$^{-2}$ at 1.53 and $-0.25$ V, respectively. More importantly, the performance for OER is even better than that of IrO$_2$, the conventional noble metal electrocatalyst. These striking observations were interpreted in terms of the combination of strongly synergistic effect of multimetal components, large amount of exposed active site, and super-aerophobia. The present methodology has been confirmed universal for synthesizing other molybdate solid solutions, which would open up new possibilities for designing novel non-noble bifunctional electrocatalysts for OER and HER.

INTRODUCTION

Electrochemical water splitting is widely considered as a promising and sustainable route for hydrogen production because electrical energy can be supplied from renewable energy resources such as wind turbines, hydropower, photovoltaic cells, and so forth. Enhancing electrocatalytic activities of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the half reactions of water splitting, is vital for solving environment and energy issues, particularly for OER. At present, IrO$_2$ and Pt/C are popularly used as the electrocatalysts for OER and HER, which however have the demerits such as high cost, scarcity of noble metals, and monofunction. All these drawbacks make both IrO$_2$ and Pt/C unsuitable in wide applications. Hence, developing bifunctional electrocatalysts with an attractive price and quality becomes more and more important in a clean energy field.

Until now, many strategies have been tried for the development of efficient bifunctional electrocatalysts with improved OER and HER activities. These strategies can be primarily divided into several categories: the first one is to enhance the synergistic effect between interfaces in multimetal components. $^{10}$ The second one is to increase the number of active sites. $^{11-13}$ Xie and co-workers prepared defect-rich MoS$_2$ and Ni(OH)$_2$ nanosheets and achieved significantly improved HER and OER performances when compared to the defect-poor samples. The third one is to design superaerophobic electrodes that can accelerate gas evolution behavior and improve electrocatalytic performance at high reaction rates. $^{14,15}$ Jiang and co-workers fabricated a 3D-nanostructured Cu film for hydrazine fuel cells. $^{14}$ Given that all these strategies could improve the activity of OER and HER to some extent, we wonder whether remarkable catalytic activity can be obtained when we unify all these strategies in a material system.

Heterostructures, integrating distinct components with different functionalities in one system, give a chance to answer the above question because of their strong synergistic effect. However, most reported heterostructures were only two components as of now, which is not enough to settle this problem. Motivated by this, we attempted to initiate a strategy,

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in which MoS₂ nanosheet arrays and transition metal disulfide nanocubes (TS₂, T = Fe, Co, and Ni) were grown in situ onto the surface of transition metal molybdate solid solution. This novel strategy is expected to show merits of strong synergistic effect, large amount of exposed active sites, and super-aerophenia.

To this end, for the first time, we report a synthetic method that leads to a highly efficient MoS₂–TS₂–transition metal molybdate electrocatalyst for OER and HER. The obtained material could be considered as an integrator of ultrathin MoS₂ nanosheet arrays, TS₂ nanocubes, and transition metal molybdate solid solution nanorods. We show that the integrator exhibits a high electrocatalytic activity toward both OER and HER, thanks to its special composition and structure. Most notably, by modulating the transition metal composition, an anodic current density of 10 mA cm⁻² is achieved, which is better than those of IrO₂ and commercial noble metal electrocatalysts. Furthermore, the catalyst also achieved a cathodic current density of 10 mA cm⁻² only at ~0.25 V (vs RHE), which is superior to that of the MoS₂ catalyst.

### EXPERIMENTAL SECTION

**Preparation of Materials.** All chemical reagents used were of analytical grade without further treatment.

**Synthesis of 1D Porous TMoO₄ (T = Ni, Co, and Fe) Nanorods.** Porous TMoO₄ nanorods were synthesized via pyrolysis of the TMoO₄·H₂O precursor in air atmosphere. The synthetic procedure could be briefly described as follows: 3 mmol sodium molybdate was dissolved in 30 mL of deionized water under vigorous stirring to get solution A. Transition metal nitrate or sulfate (3 mmol) was dissolved in 30 mL of deionized water under vigorous stirring to get solution B. Then, solution B was dropped into solution A under vigorous stirring. Finally, the resulting suspension solution was kept for heating at 150 °C for 12 h and cooled down naturally. The resultant powder was collected after centrifugation and washed several times with deionized water and ethanol and subsequently dried at 60 °C. To fabricate TMoO₄ nanorods, the dried powder was moved to an alumina crucible and then heated to 500 °C at a heating rate of 1 °C/min and maintained at 500 °C for 2 h. The whole procedure was conducted under a constant N₂ gas flow to maintain an inert atmosphere. For convenience, the product was marked as TMO (T = Ni, Co, and Fe).

**Synthesis of 1D Porous TMoO₄ (T = Ni/Co, Ni/Fe, or Ni/Co/Fe) Nanorods.** The procedure for preparing 1D TMoO₄ nanorods was similar to that for TMoO₄ except for solution B of TMoO₄ that contained given ratios of transition metal salts (Ni/Co = 1:1, Ni/Fe = 8:2, and Fe/Co/Ni = 1:1:1). The obtained sample was named TMO, for example, Ni₅Co₅MoO₄ was marked as NCMS (see Table 1 for details).

**Synthesis of 1D and 2D Hybrids MoS₂/TMO.** MoS₂/TS₂/TMO hybrids were prepared via a simple low-temperature hydrothermal process. In a typical procedure, 150 mg of TMO or TMO nanorods and certain amount of L-cysteine (0.12, 0.25, 0.36, and 0.48 g) were dispersed in 60 mL of deionized water in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C for 18 h and then naturally cooled to room temperature. The resulting product was collected by a filter and washed by deionized water thoroughly. Finally, the black powder was dried under vacuum. For convenience, the powder was marked as TMS. T symbolizes transition metal, M is the initial letter of molybdenum, and S represents sulfidation.

**Synthesis of MoS₂ nanosheets and Reference Samples.** CoS₂ and NiS₂ nanosheets were also prepared via a hydrothermal process. In a typical procedure, 1 mmol sodium molybdate and 5 mmol thiourea were dissolved in 60 mL of deionized water in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 300 °C for 18 h. Reference samples CoS₂ and NiS₂ were synthesized using a similar procedure, except that Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O was used to substitute Na₂MoO₄.

**Physical Characterization.** X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku Miniflex apparatus equipped with a Cu Ka radiation source (λ = 1.5418 Å). Field-emission scanning electron microscopy (SEM) images and energy dispersive spectrometer (EDS) mapping data were performed on JSM-6700F. Transmission electron microscopy (TEM) measurements were carried out on Tecnai G2 S-TWIN F20. Scanning transmission electron microscopy (STEM) measurements were performed on JEOL-2100F. Specific surface areas of the samples were measured with the Brunauer–Emmett–Teller equation, and pore size distributions were calculated via Barrett–Joynt–Halenda formula by a surface area analyzer ASAP 2020 (Micromeritics). X-ray absorption fine structure data were collected at the 1W1B station in Beijing synchrotron radiation facility.

**Electrochemical Characterization.** In a typical procedure to prepare the working electrode, each of the sample was dispersed in 1 mL of mix solution (containing 450 μL of H₂O, 500 μL of ethanol, and 50 μL of 5% Nafton) via ultrasonic dispersion for 30 min to obtain a homogeneous ink. Then, 10 μL of ink was loaded onto a glassy carbon electrode (GCE) of 5 mm in diameter (loading amount: 0.20 mg cm⁻²). Prior to the coating of the catalyst, the GCE was polished with an Al₂O₃ paste (50 nm) and washed ultrasonically with deionized water. Then, the catalyst-modified GCE was dried at room temperature.

Electrochemical measurements were performed in a typical three-electrode cell using a CHI 760E workstation at room temperature. OER and HER were tested under different conditions. For OER, a graphite rod and Hg/HgO electrode were used as the counter electrode and the reference electrode, respectively. Linear scan voltammetry (LSV) was carried out at a scan rate of 5 mV s⁻¹ in 1 M KOH, and all data were revised by Ohmic potential drop (iR) correction. The potentials were displayed versus RHE by RHE calibration: E (RHE) = E (Hg/HgO) + 0.098 + 0.059 × pH. The stability tests were performed in 1 M KOH at room temperature by potential

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**Table 1. Names and Abbreviations of All Samples in This Work**

| transition metal or ratio | TMoO₄·H₂O (TMH) | TMoO₄ (TMO) | MoS₂–TMO or TMO (TMS) |
|--------------------------|-----------------|-------------|-----------------------|
| Co                       | CMH             | CMO         | CMS                   |
| Ni                       | NMH             | NMo         | CMS                   |
| Fe/Co/Ni = 1:1:1         | FCNMH           | FCNM0       | FCNMS                 |
| Ni/Fe = 4:1              | NFNMH           | NFMO        | NFMS                  |
| Ni/Co = 1:1              | NCNMH           | NCMO        | NCMS                  |

"T, F, C, N, and M represent transition metals, Fe, Co, Ni, and Mo, respectively; H represents hydration, O represents oxide, and S represents sulfidation."
cycling between 1.2S and 1.7 V (vs RHE) at a sweep rate of 50 mV s$^{-1}$ for 3000 cycles. Cyclic voltammetry (CV) measurements with different scan rates (40, 80, 120, 160, and 200 mV s$^{-1}$) were used to determine the electrochemical double layer capacitances (EDLC, $C_d$). The electrochemical impedance spectroscopy (EIS) measurements were carried out at an overpotential of 300 mV in the frequency range of $10^{-2}$ to $10^6$ Hz. Prior to all the above measurements, oxygen was bubbled into the electrolyte for 30 min.

For HER, a graphite rod and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. LSV was carried out at a scan rate of 5 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$, and all results were revised by iR correction. The potentials were displayed versus RHE by RHE calibration: $E$ (RHE) = $E$ (SCE) + 0.241 + 0.059 × pH. Prior to all the above measurements, nitrogen was bubbled into the electrolyte for 30 min.

## RESULTS AND DISCUSSION

MoS$_2$–T$_S$–TMoO$_x$ hybrids were initiated to be prepared via a two-step method (shown in Figure 1). In step 1, transition metal molybdate hydrates were pyrolyzed under an inert atmosphere to release H$_2$O, and then porous transition metal molybdate hydrates were pyrolyzed under an inert electrode, respectively. LSV was carried out at a scan rate of 5 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$, and all results were revised by iR correction. The potentials were displayed versus RHE by RHE calibration: $E$ (RHE) = $E$ (SCE) + 0.241 + 0.059 × pH. Prior to all the above measurements, nitrogen was bubbled into the electrolyte for 30 min.

Figure 1. Schematic illustration for the preparation of TMS hybrids via a two-step method.

Metal molybdate hydrates were pyrolyzed under an inert atmosphere to release H$_2$O, and then porous transition metal molybdate nanorods were obtained. In step 2, porous TMO nanorods were sulfided by l-Cys in a hydrothermal environment. During the sulfidation procedure, S$^{2-}$ anions dissociated from l-Cys might react quickly with metal ions (transition metal or Mo ions) on the surface to form a thin layer metal disulfide. This thin layer metal disulfide could play a key role in obstructing further reaction between inner metal ions and outside S$^{2-}$.

By optimizing the experiment parameter (Figures S1 and S2), we chose to add 0.36 g of l-Cys in the synthesis of our catalysts. Composition, pore size distributions, and specific surface area of the as-synthesized samples were measured by XRD patterns and nitrogen adsorption–desorption (Figures S3 and S4).

SEM images in Figure 2 illustrate the evolution process from precursors (NCMH, NFNM, and FCNMMH) to the corresponding sulfide samples (NCMS, NFMS, and FCNMS). After calcinations at 500 °C, NCMO, NFMO, and FCNMO maintained the nanorod morphology of their precursors, probably due to the slow heating rate. The diameter of NCMO is about 500–1000 nm, whereas the diameter for NFMO and FCNMO is about 0.5–2 μm. By comparing the data in Figure S5, it is found that sizes of NCMO, NFMO, and FCNMO are clearly larger than those of CMO and NMO.

That is to say, the size of a nanorod can be tuned by doping a transition metal. Figure 2c,fi shows the morphologies of NCMS, NFMS, and FCNMS, respectively. Obviously, after sulfuration, NCMS, NFMS, and FCNMS still showed a rodlike morphology. Moreover, an ultrathin nanosheet array and some cubes (white circle in Figure 2c,fi) were grown onto the surface of molybdate. It is reasonable that the nanosheet array is MoS$_2$, whereas the nanocube is T$_S$ (T = Fe, Co, and Ni), as deduced by the layered structure characters of MoS$_2$ and cubic phase structure of T$_S$. The composition of T$_S$ was further verified by STEM and corresponding EDX element mapping (Figure S7).

The morphology and structure of FCNMS, NCMS, and NFMS were further investigated by TEM and HRTEM (Figures 3 and S6). The TEM image (Figure 3a) shows that the ultrathin nanosheets were wrapped onto an FCNMO nanorod, showing a thickness of less than 5 nm, and that the nanocubes have a lateral size of about 200 nm. Careful data examination indicates that the nanosheets appeared to be stacked loosely and partially curved. The edges were approximately about 5–6 layers. The interlayer distance of nanosheets is about 0.63 nm, which can be indexed to the (002) plane of MoS$_2$. Further, HRTEM of nanocubes shows a lattice distance of 0.25 nm, corresponding to the (210) plane of T$_S$.

EDS mapping was used to examine the dispersion of elements for samples FCNMS, NFMS, and NCMS (Figures 4 and S8). After sulfidation, S element is evenly dispersed onto the sample surface. Moreover, it is found that the O element is still uniformly dispersed in the core of FCNMS, which demonstrates a core–shell structure of FCNMS (core FCNMO and shell MoS$_2$/T$_S$). Also as shown in Figure S8, Co, Ni, Mo, O, S and Ni, Fe, Mo, O, S were uniformly dispersed on nanorods of NCMS and NFMS, respectively.

It is worth noting that CMS and NMS could not maintain the rod morphology (Figure S5). There are two possible reasons. First, CMO and NMO nanorods are too thin to maintain the rodlike morphology. Comparatively, once doping other transition metal ions into CMO and NMO, such as FCNMO, the nanorods became thicker (Figures 2 and S5), which may be in favor of maintaining the rod morphology. Second, doping transition metals may change the exposed crystal plane of precursors and thus be conducive to epitaxial growth of MoS$_2$. To verify this, TEM and HRTEM were used to monitor the exposed plane for FCNMO (Figure 5a, b).

TEM analysis in Figure 5a demonstrates the rod characteristic of FCNMO, consistent with the observations by SEM (Figure 2). The distance between lattice fringes marked in Figure 5b is about 0.67 nm, corresponding to the plane (001) of monoclinic CoMoO$_4$ (JCPDF no. 21-0868). Similarly, the lattice distance for NCMO and NFMO was 0.65 nm (Figure S9), very closer to 0.62 nm for the plane (110) of NiMoO$_4$ (JCPDF no. 33-0948). The measured lattice fringes for three samples NCMO, NFMO, and FCNMO matched well with that of 0.63 nm for the plane (002) of MoS$_2$ nanosheets (Figure 3b). Comparatively, CMO and NMO exhibited a lattice spacing of 0.28 and 0.34 nm, respectively (Figure S10), which could be assigned to the planes (201) and (130). Hence, doping transition metals into molybdate is beneficial for the exposure of planes (001) and (110). Previous literature has established that the well-matched lattice distance could facilitate the epitaxial growth of two different materials. Accordingly, the mechanism of sulfidation can be illustrated in Figure 5c. That is,
during the sulfidation procedure, $S^{2-}$ anions dissociated from L-Cys may react quickly with surface Mo atoms to form MoS$_2$ nanosheets. Then, these MoS$_2$ nanosheets would grow along the plane (001) of FCNMO because the lattice distance of 0.63 nm for the plane (002) of MoS$_2$ is closer to that of 0.67 nm for the plane (001) of FCNMO. On the other side, a part of transition metals (Fe, Co, and Ni) would react with $S^{2-}$ to generate the TS$_2$ nanocubes on the surface of molybdate.

XANES were measured to examine the valence states of Mo ions in FCNMS. As shown in Figure 6a, the absorption edge of FCNMS shifted toward lower energies relative to that of FCNMO, indicating that partial Mo$^{6+}$ ions in FCNMO were reduced and reacted with $S^{2-}$ to generate MoS$_2$ nanosheets. The amount of reduced Mo ions can be estimated by linear combination fitting from Mo K-edge XANES of FCNMS, FCNMO, and MoS$_2$. The data fit result was shown in Figure S11, where about 52% of Mo$^{6+}$ ions were reduced to Mo$^{4+}$. Hence, the average valence of Mo ions in FCNMS is about 4.96 (Figure 6b).

Electrocatalytic activity of FCNMS for OER was studied using a typical three-electrode electrochemical cell in 1 M KOH. Figure 7a compares their polarization curves (sample loading was set at 0.2 mg cm$^{-2}$) with a scan rate of 5 mV s$^{-1}$. FCNMS and FCNMO achieved a current density of 10 mA cm$^{-2}$ (a current density for 12% efficiency of a solar to fuel conversion device) at 1.53 and 1.56 V, respectively. Further, FCNMS exhibited a large anodic current density of 206 mA cm$^{-2}$ at 1.7 V, about 2 times larger than that of FCNMO. Apparently, the catalytic performance of FCNMO is substantially enhanced after sulfuration. More importantly, the catalytic activity of FCNMS is even better than that of IrO$_2$, a benchmark noble metal electrocatalyst for OER. Such a performance observed for FCNMS is also better than the previous reports for most of the transition metal-based OER catalysts.$^{6,14,19-25}$

To understand better the electrocatalytic performance of the sample FCNMS, one has to take FCNMO, CoS$_2$, NiS$_2$, mixture of FCNMO and CoS$_2$, and mixture of FCNMO and NiS$_2$ as the contrast samples. As shown in Figure 7a, the catalytic activity of FCNMS is superior to that of other samples, indicating the presence of a strong interaction between TS$_2$ and FCNMO. The data in Figure 7a show that the activities of mixtures of FCNMO and TS$_2$ (T = Co or Ni), CoS$_2$, and NiS$_2$ do not surpass those of FCNMO. Therefore, it could be reasonable that the molybdate solid solution plays a dominant role in the catalytic reaction of the FCNMS composite. In addition, to gain

Figure 2. SEM images for precursors (a) NCMH, (d) NFMH, and (g) FCNMH; for unsulphide (b) NCMO, (e) NFMO, and (h) FCNMO; and for sulfide (c) NCMS, (f) NFMS, and (i) FCNMS. White cycles in (c,f,i) are assigned to TS$_2$. 

Figure 3. (a) TEM and (b,c) HRTEM of FCNMS.
insights into the oxygen evolution activity, Tafel plots of various catalysts were compared as shown in Figure 7b. The Tafel slope of FCNMS hybrids is 48 mV dec\(^{-1}\), much closer to the value obtained for IrO\(_2\), but apparently lower than those for FCNMO, CoS\(_2\), and NiS\(_2\), implying that FCNMS hybrids can give rise to a high OER rate in practical applications.\(^{26,27}\)

The EDLC were measured to compare the active area of electrocatalysts (Figure S12). The values of \(C_{dl}\) for FCNMS are 3.43 mF cm\(^{-2}\), slightly larger than those for other samples, which further indicates that the BET surface area is not a primary factor to catalysis. EIS data of the samples are comparatively studied, as shown in Figure 7c to understand the electrode reaction kinetics. The equivalent electric circuit of the cell and the fitting results are shown in Figure S13 and Table S1, respectively. The larger semicircle in the low-frequency region corresponds to the electrical models of the anodes. \(R_{ct,2}\) is related to the electrocatalytic kinetics, with a smaller value representing a faster reaction rate.\(^{28}\) The smallest \(R_{ct,2}\) for FCNMS indicates a faster charge transport among all the studied counterparts.

Figure 4. Elemental mapping images of FCNMS sample: (a) SEM image, the mapping of (b) Fe (cyan), (c) Co (purple), (d) Ni (blue), (e) Mo (yellow), (f) O (red), and (g) S (green), and (h) the mixed image of all elements.

Figure 5. (a) TEM and (b) HRTEM images of FCNMO, (c) schematic diagram for the growth mechanism of FCNMS. The gold and blue arrows in (c) mean that the transition metals (Fe\(^{2+}\), Co\(^{2+}\), and Ni\(^{2+}\)) and molybdate ions in FCNMO were sulfided to TS\(_2\) and MoS\(_2\), respectively.

Figure 6. (a) Normalized Mo K-edge XANES of FCNMS, FCNMO, and MoS\(_2\) and (b) average valence states of Mo ions in FCNMS, FCNMO, and MoS\(_2\).
stability of FCNMS-modified electrodes was tested by continuous cycling for 3000 cycles (Figure 7d). After cycling for 3000 times, the polarization curve was slightly decreased in the anodic current. Although the overpotential at about 10 mA cm$^{-2}$ was slightly increased from 300 to 318 mV, FCNMS still achieved a current density of 187 mA cm$^{-2}$ at 1.7 V (vs RHE), and about 91% activity was maintained. Additionally, the current-time plots at a fixed potential were also collected, and the anodic current almost maintained a constant value around 10 mA cm$^{-2}$ over 10 h, further confirming an excellent stability of the FCNMS-modified electrode.

Meanwhile, the effect of catalyst loading on the OER activity was examined (Figure S14), which indicated that the measured activities were in the regime of intrinsic kinetics. The above results clearly demonstrate that FCNMS possesses an excellent catalytic performance for OER. This observation could be attributed to their distinctive structural advantages: (i) the synergistic effect of multimetal components and strong interaction between FCNMO and TS$_2$ in FCNMS, (ii) the mesoporous structure of FCNMS gives more active sites for the catalytic reaction, as reported elsewhere; and (iii) the nanosheet array on the surface of nanorods is suitable for desorption of the gas products, thus giving a much improved electrocatalytic performance. It is worth noting that NFMS and NCMS (the vulcanized products of NFMO and NCMO) also exhibited a distinctly improved OER activity (as shown in Figure S15). To further illustrate the advantage of our catalysts, we compared the overpotentials of FCNMS and NFMS at 10 mA cm$^{-2}$ with the overpotential of the recently reported electocatalyst (as shown in Figure S16). FCNMS has shown the lowest overpotential, demonstrating a best OER performance.

In addition to the marvelous OER activity, FCNMS has a possibility to show good catalytic activity for HER because a large amount of MoS$_2$ have exposure edges that could become the active sites for HER. Figure 8a exhibits the polarization curves of various samples for HER. All the vulcanized samples exhibit a better HER activity than MoS$_2$. Especially, FCNMS achieved a cathode current density of 10 mA cm$^{-2}$ at −0.25 V (vs RHE), superior to that of other samples. Moreover, FCNMS also shows the smallest Tafel slope of 74 mV dec$^{-1}$ among all samples, indicating the fastest HER rate.

**CONCLUSIONS**

In summary, a universal synthetic route has been reported for in situ growth of ultrathin MoS$_2$ nanosheet arrays and transition metal disulfide nanocubes onto the surface of molybdate solid solutions. Such MoS$_2$–TS$_2$–TMoO$_x$ hybrids have shown merits of strong synergistic effect among components,
mesoporous property, and superaerophobia. These merits allow these hybrids to show an impressive anodic and cathodic current density of 10 mA cm$^{-2}$ at 1.53 and $-0.25$ V (vs RHE), respectively. The findings reported in this work mark an important step toward the development of non-noble metal electrocatalysts for OER and HER with high efficiency.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.omega.7b01965. XRD, SEM, BET, TEM, HRTEM, EDS mapping, STEM, XANES curves fitting result, EDLC, and polarization curves for OER (PDF)

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**Notes**

The authors declare no competing financial interest.

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