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Morphology-controlled synthesis of CoMoO₄ nanoarchitectures anchored on carbon cloth for high-efficiency oxygen oxidation reaction†

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Novel CoMoO₄ nanoarrays with different morphologies are anchored on a carbon cloth *via* a simple hydrothermal method by adjusting the Co/Mo atom ratio. The *in situ* growth and tight immobilization of the CoMoO₄ nanocomposite on the carbon cloth can facilitate the electrolyte infiltration and electrons transfer rate at the contact interface. Therefore, the free-standing electrode of CoMoO₄/carbon cloth with interconnected nanosheets shows superior electrocatalytic activity, and the overpotential of 286 mV is obtained at 15 mA cm⁻² in alkaline solution. Moreover, the catalyst also exhibits a small Tafel slope of 67 mV dec⁻¹ as well as good stability. The relationship between the active material morphology, contact interface and the electrocatalytic performance is also discussed. As the carbon cloth is commercially available, this simple but effective structural controlling method demonstrates a new large-scale practical electrode fabrication technique for high performance OER electrodes and large-scale water splitting.

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1. Introduction

The ever-growing energy demands and environmental issues have triggered a great research interest in the field of clean and sustainable energy sources.¹⁻⁴ As one of the most popular candidates, hydrogen has aroused great attention owing to its high energy conversion efficiency and carbon-/pollution-free nature. Among the large-scale hydrogen production technologies, the electrocatalytic water splitting method shows great advantages due to its high efficiency, easy-scalability and environmental benignity.⁵⁻⁸ However, the anodic oxygen evolution reaction (OER) with multi-electron transfer process, which further hinders the fast reaction kinetics, has been regarded as the bottleneck process of the water splitting.⁹⁻¹¹ RuO₂ and IrO₂ are regarded as the excellent OER catalyst, however, their high cost and low abundance have significantly hindered their practical application.^{12,13} Therefore, design and fabrication of the non-noble-metal alternative electrodes with high

electrocatalytic activity and large-scalable fabrication capability is highly demanded.

Transition metal oxides, as one of the efficient OER catalysts in alkaline solution, have aroused great interests owing to the comparable catalytic activity and environmental friendliness compared with the metal phosphide and sulphides.^{14,15} Among them, Co-based metal oxides composites (Co₃O₄, MnCo₂O₄, CoMoO₄, *etc.*) have been extensively studied due to the natural abundance and good electrocatalytic properties.¹⁶⁻²² Furthermore, the bimetallic CoMoO₄ composite can exhibit much better electrochemical property in comparison with the mono-metallic Co₃O₄ or MoO₃ due to the synergistic interactions between different elements.²³ Moreover, the electrocatalytic activity highly depends on the exposed active sites and electrons transfer efficiency to the active materials, and the active sites is further related to the composition, loading mass, crystallinity and defects, *etc.* Therefore, the morphology design and contact interface control of the active materials are essential for high performance electrocatalysis electrodes.²⁴⁻²⁶ Fabrication of the free-standing composite with active materials coated on the conductive networks is an effective strategy to enhance the electrochemical performance of the electrodes.^{27,28} With the well-designed structure, the electrodes can expose more active sites to the electrolyte, while the engineered contact interface can effectively transfer the electrons from the conductive networks to the active materials.²⁹⁻³¹ Therefore, large-scale fabrication of the hybrid electrodes with high electrocatalytic performance and simple fabrication process is urgently required for the practical application.

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† Electronic supplementary information (ESI) available: SEM images, XRD patterns, XPS spectrums and TEM images of the CoMoO₄/CC composites before and after long term catalytic stability test, and the CV curves of composites collected under different scan rates are listed. See DOI: 10.1039/c8ra09484e

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Herein, the three-dimensional (3D) free-standing CoMoO₄ nanoarchitecture anchored on the carbon cloth (CC) is fabricated *via* a simple one-pot hydrothermal reaction. The CoMoO₄ morphology evolution with the change of the Co/Mo precursor ratio is investigated, the relationship between the materials contact interface and the electrocatalytic performance is also discussed. As an OER electrode, the as-prepared CoMoO₄/CC-2 composite with interconnected nanosheets reveals superior catalytic activity, an overpotential of 286 mV can be obtained at a geometrical catalytic current density of 15 mA cm⁻² in 1.0 M KOH. Moreover, the CoMoO₄/CC-2 electrode shows high long-term OER performance with the activity unchanged for 20 h. As the carbon cloth is commercially available, this simple but effective hydrothermal method demonstrates a new large-scale practical electrode fabrication technique for high performance OER electrodes.

2. Experimental section

2.1. Synthesis of the CoMoO₄/CC composite

All the materials were purchased from Aladdin Co. The carbon cloth (2 cm × 2 cm, WOS 1009, CeTech Co. Ltd, China) was first washed with ethanol under sonication to remove the impurities, and then pretreated with 0.5 M KMnO₄ for 0.5 h to provide seed crystal.³² The self-supported CoMoO₄ arrays with different morphologies anchored on carbon cloth were synthesized by one-step hydrothermal reaction. In a typical process, *n* mmol Co(NO₃)₂·6H₂O (*n* = 0.3125, 0.625, 1.25, 2.5) and 2.5 mmol Na₂MoO₄·2H₂O were added into 50 mL deionized water and mixed for 15 min to form a homogeneous pink solution. Then, the pretreated carbon cloth and the solution were transferred into a 50 mL autoclave and kept at 140 °C for 4 h. After cooling to room temperature naturally, the obtained samples were washed with DI water and ethanol, then dried at 50 °C for 6 h, and the CoMoO₄ nanostructure anchored on carbon cloth was finally obtained. And the loading mass of the active materials is listed in Table S1 (see ESI†). The commercial IrO₂ electrode was purchased from the Kunshan Yiwanglin Electronic Technology Co., Ltd.

2.2. Material characterization

The microscopic structure and morphology were characterized by scanning electron microscopy (JEOL JSM-7610F Field Emission) and transmission electron microscopy (FEI Tecnai G20). The X-ray diffraction were carried out to ensure the crystal structure (Cu K α radiation). The X-ray photoelectron spectroscopy was conducted on a PHI5000 Versa spectrometer. Raman spectrum were measured by DXRxi spectrometer (Thermo) with 455 nm laser.

2.3. Electrochemical measurements

Three-electrode system was fabricated to tested the electrochemical performance by the electrochemical workstation (CHI 760E). In this system, the free-standing CoMoO₄/CC composite was used as the working electrode directly, and the carbon rod and Ag/AgCl (KCl, saturated) were employed as counter

electrode and reference electrode, respectively. All the operation potentials were calibrated to RHE according to the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$. The linear sweep voltammetry (LSV) was conducted from 0 to 0.6 V (*vs.* Ag/AgCl) at 5 mV s⁻¹ in 1 M KOH (pH = 14). The LSV curves and corresponding Tafel slopes were obtained with *iR* compensation. And the cyclic voltammetry and chronopotentiometric tests were conducted without *iR* compensation. Electrochemical impedance spectroscopy (EIS) measurement was conducted in a frequency ranging from 100 kHz to 0.01 Hz at 5 mV s⁻¹. The current density of the multi-current test starts at 10 mA cm⁻² and ends at 50 mA cm⁻² (5 mA cm⁻² per 500 s without *iR* correction). To measure the electrochemical surface area (ECSA) of all the samples, the *C_{dl}* was calculated according to the cyclic voltammograms curves with different scan rate. The long-term stability of the composite was conducted by the *i-t* curve at a constant working potential of 1.6 V for 20 h.

3. Results and discussion

The crystalline structure of the CoMoO₄/CC-*n* (*n* = 1, 2, 3 and 4) composites is tested by XRD (Fig. 1a). Besides the apparent diffraction peaks of the CC scaffold, the small shoulder peaks located at 23.3°, 25.5°, 26.5°, 28.4° and 33.7° can be indexed to the (021), (201), (002), (-311) and (-222) planes of the CoMoO₄ (JCPDS no. 21-0868), respectively. Moreover, the CoMoO₄/CC-4 composite shows no obvious characteristic peaks of the CoMoO₄, which may be due to the low crystalline degree of the CoMoO₄ structure. Moreover, the XRD pattern of the powder collected from the solution also certifies the existence of the CoMoO₄ crystalline (Fig. S1, see ESI†). The Raman spectroscopy was further applied to illustrate the crystalline and bonding nature of the as-prepared composites (Fig. 1b). The two characteristic peaks located at 1363 cm⁻¹ (D band) and 1588 cm⁻¹ (G band) can be assigned to the carbon cloth. The CoMoO₄/CC-2 composite exhibits good CoMoO₄ crystallinity in comparison with that of the CoMoO₄/CC-*n* (*n* = 1, 3, 4), the three major bands can be observed at 326, 802 and 904 cm⁻¹. The band centred at 326 cm⁻¹ is attributed to the symmetric stretching of the Co–O–Mo bond. The band located at 802 cm⁻¹ is associated with asymmetric stretching modes of O–Mo–O bond while the band at 904 cm⁻¹ corresponds to the symmetric stretching mode of Mo–O bond.^{33,34} The slight variations in the positions of the vibrational modes may be due to the crystal size, morphology and strength of interaction between the ions and the structural order–disorder degree of the composites.³⁵

The XPS is also conducted to confirm the oxidation valence states of the CoMoO₄/CC-2 composite. The full survey spectrum in Fig. 2a indicates the presence of the Mo, Co and O elements in the composite and the unequal atomic ratio of Co/Mo elements are listed in Table S2,† illustrating partial doping of Co element into the CoMoO₄ composite. The deconvolution of the Co 2p spectrum in Fig. 2a shows two peaks, the peaks centred at 781.0 eV and 796.0 eV are related to the Co 2p_{3/2} and Co 2p_{1/2}, respectively, which refer to Co²⁺ species.³⁶ Moreover, the apparent satellite peaks of the Co 2p spectrum also verify the existence of the Co(II). For the Mo 3d spectrum (Fig. 2c), the

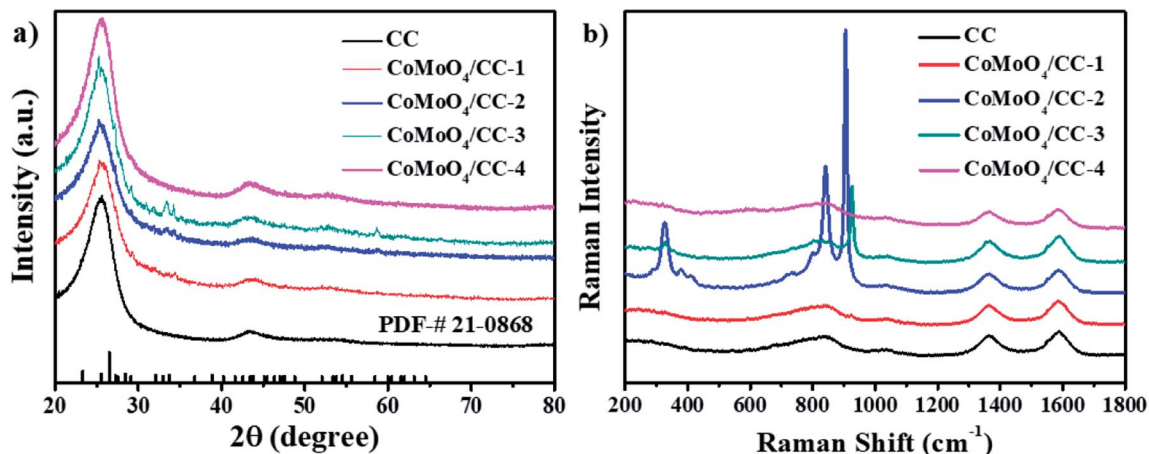


Fig. 1 (a) XRD patterns (b) Raman spectra of the as-prepared CoMoO₄/CC-*n* (*n* = 1, 2, 3 and 4) and raw carbon cloth.

binding energy located at 232.9 eV and 235.3 eV can be specified as Mo d_{5/2} and Mo d_{3/2} of the Mo⁶⁺ species, respectively, which is in line with the valance state of the MoO₄²⁻ precursor.^{18,37} In the O 1s region (Fig. 2d), two peaks around 530.5 eV and 532.1 eV are corresponding to the Mo–O and Co–O, respectively.^{38,39} Therefore, the XPS results demonstrate the successful fabrication of the CoMoO₄ materials on the carbon cloth.

The morphology evolution and the microstructure of the CoMoO₄/CC hybrids are investigated by SEM analysis. As shown in the low-magnification images (Fig. S2†), the hierarchical CoMoO₄ architectures with different morphologies are uniformly and seamlessly anchored on the surface of the carbon cloth, further demonstrating the simple but effective large-scale active material coating strategy. The EDS images of

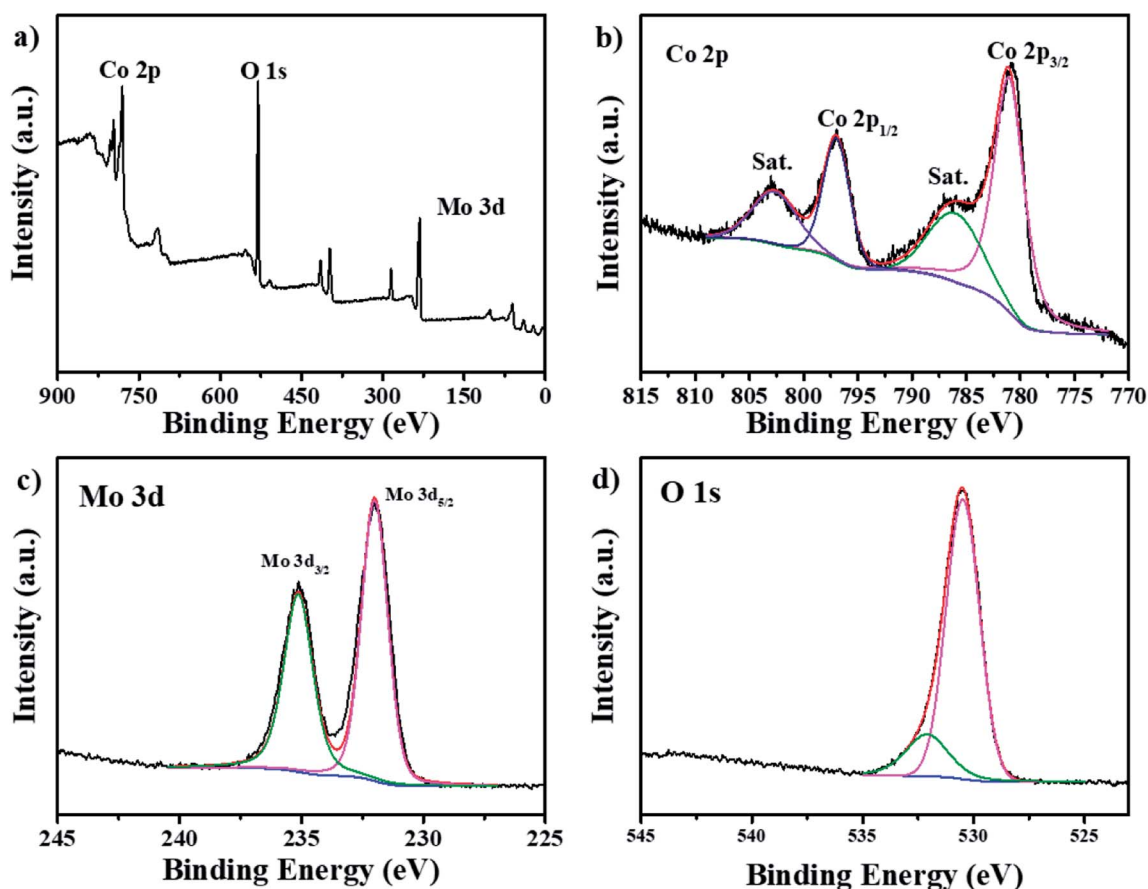


Fig. 2 XPS spectra of (a) full survey, (b) Co 2p, (c) Mo 3d and (d) O 1s of the CoMoO₄/CC-2 electrode.

the CoMoO₄/CC-2 (Fig. 3e) illustrate all the elements (Co, Mo and O) are uniformly dispersed on the CC surface, indicating the uniform distribution of the CoMoO₄ nanosheets. Under higher magnification (Fig. 3), the CoMoO₄ architectures exhibit distinct morphology evolution with the increment of the Co/Mo ratio during hydrothermal process. The CoMoO₄ architecture is constructed by the interconnected nanosheets with high porosity under lower Co/Mo ratio (1 : 8, and 1 : 4) (Fig. 3a and b), while the structure of the nanosheets turns from wrinkled and irregular structure of CoMoO₄/CC-1 to more ideal nanosheets crystals of CoMoO₄/CC-2. Moreover, with higher Co ions concentration, the thickness of the nanosheets increases from less than 10 nm to around 16 nm. Furthermore, the CoMoO₄/CC-3 (Fig. 3c) displays the hybrid CoMoO₄ nanostructure with both nanosheets and nanorods coexisted, while the nanosheets reveal increased plate size and thickness. When the Co/Mo ratio increased to a higher level of 1 : 1 (Fig. 3d), the nanostructure of the CoMoO₄ changed to nanorods arrays vertically aligned on the surface of the carbon

cloth. The morphology evolution with the change of the Co/Mo ratio may be due to the shape-controlled effects of Co²⁺ during hydrothermal reaction: with the increment of the Co²⁺ concentration, the nuclei density of the CoMoO₄ increases at the carbon cloth interface as well as in the solution, which further influences the growth rate and the crystalline structure of the nanostructures. Moreover, the contact interface of these electrodes may differ with the different CoMoO₄ morphology and thickness, the larger contact interface may be beneficial to the electrons transfer rate from the carbon cloth to CoMoO₄, thus influencing the active sites utilization efficiency.⁴⁰

The surface morphology and crystalline feature of the CoMoO₄/CC-2 composite is further confirmed by TEM test. As shown in Fig. 4a, the CoMoO₄ nanosheets exhibit layered and quasi-hexagonal structure, indicating the relatively good crystalline structure of the nanosheets. The high resolution image in Fig. 4b illustrates the formation of mesoporous structures on the CoMoO₄ nanosheets, which may result from the crystal defects of the nanosheets. These defective hexagonal structure

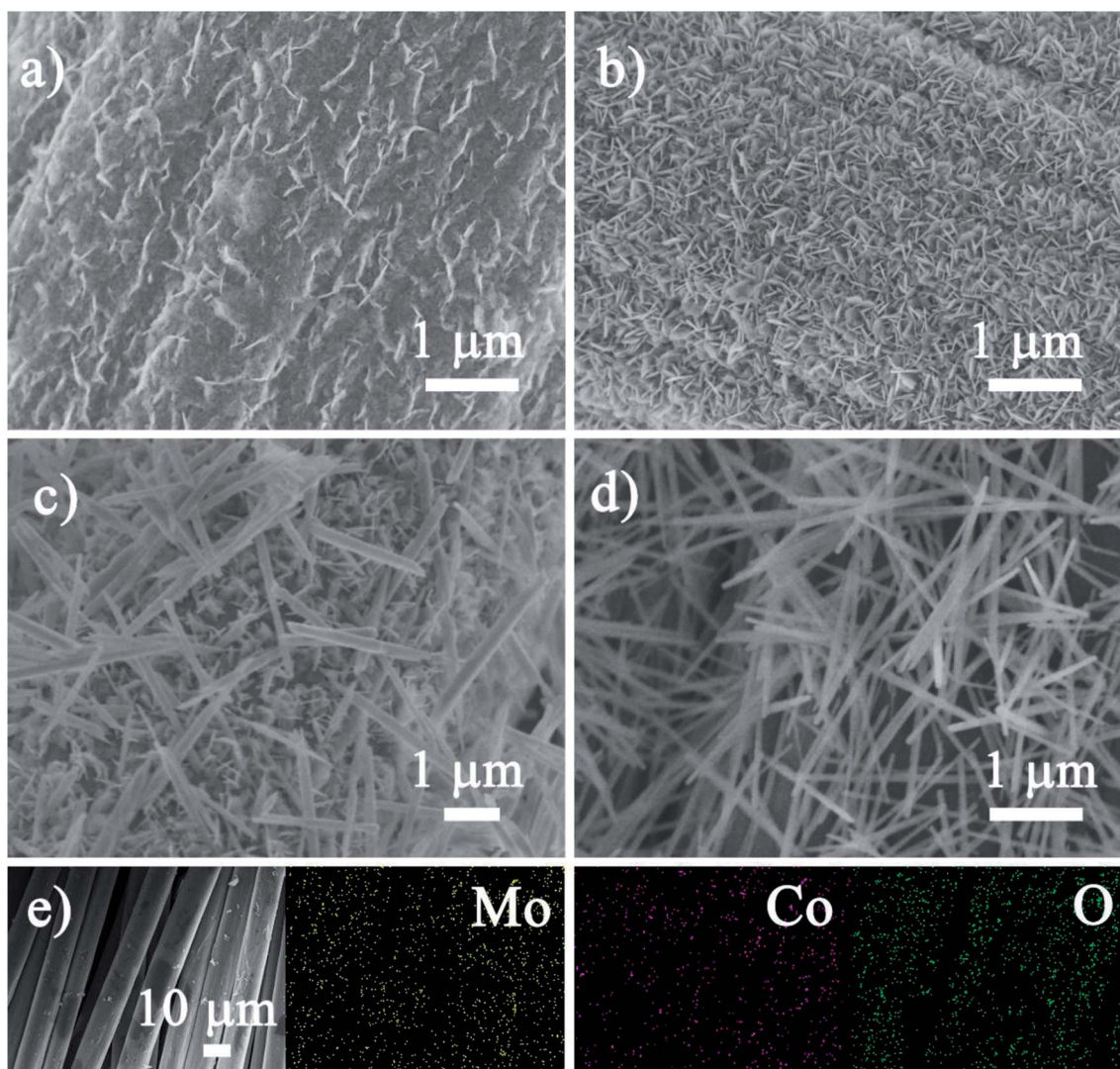


Fig. 3 SEM images of the (a) CoMoO₄/CC-1, (b) CoMoO₄/CC-2 and (c) CoMoO₄/CC-3 and (d) CoMoO₄/CC-4, (e) the SEM image and corresponding elemental mapping of Mo, Co and O of the CoMoO₄/CC-2.

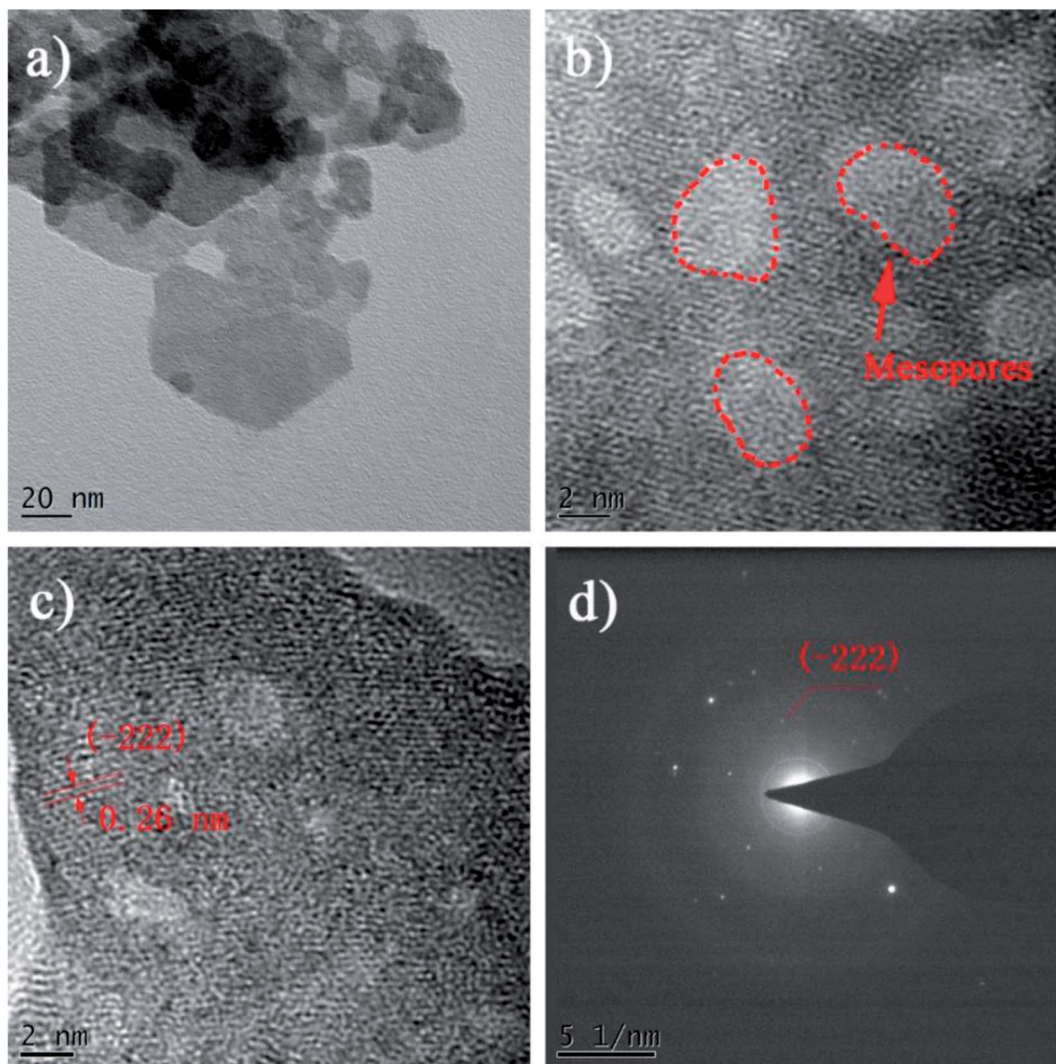


Fig. 4 TEM images of the CoMoO₄/CC-2 composite, (a) the CoMoO₄ nanosheets, (b and c) the high-resolution image of the CoMoO₄ nanosheets and (d) the SAED pattern acquired from CoMoO₄ nanosheets.

and porous defects can provide sufficient active sites for the electrocatalytic reaction.^{41,42} Moreover, Fig. 4c reveals the defective polycrystalline structure of the as-prepared CoMoO₄ nanosheets, and the lattice fringe of 0.26 nm can be related to the (−222) plane of CoMoO₄. Moreover, the crystalline structure is further confirmed by the selected area electron diffraction (SAED) pattern (Fig. 4d), the (−222) plane is in line with the XRD results. Similar crystalline structure can also be observed from the TEM images of the CoMoO₄/CC-3 composite (Fig. S3, see ESI[†]). Therefore, the CoMoO₄/CC composites may act as the high-performance electrocatalytic electrode: the interconnected porous CoMoO₄ nanocrystals with sufficient defects can provide sufficient active sites for electrochemical conversion reaction, while the 3D conductive struts and the tightly contact interface can facilitate the electrons transfer rate to ensure the utilization efficiency of the active sites.

The three-electrode system is carried out to investigate the electrocatalytic OER performance of the composites. The LSV curves collected under 5 mV s^{−1} are shown in Fig. 5a. The

CoMoO₄/CC-2 electrode shows an overpotential of 286 mV at 15 mA cm^{−2}, which is better than that of the CoMoO₄/CC-1 (307 mV), CoMoO₄/CC-3 (294 mV), CoMoO₄/CC-4 (398 mV), CC scaffold and commercial IrO₂ (339 mV). Moreover, this value is also better than or comparable with that of the state-of-the-art electrocatalysts (Table S3, see ESI[†]). Furthermore, the overpotential of the CoMoO₄/CC-2 is still lower than that of the other CoMoO₄/CC-*n* (*n* = 1, 3, 4) electrodes under higher response current density (Fig. 5b). Moreover, The Tafel slopes are calculated to be 71, 67, 74, 73, 122 and 82 mV dec^{−1} for CoMoO₄/CC-1, CoMoO₄/CC-2, CoMoO₄/CC-3, CoMoO₄/CC-4, CC and commercial IrO₂, respectively (Fig. 5c). The earlier overpotential and smaller Tafel slope of the CoMoO₄/CC-2 composite can be attributed to the improvement of the electrons transfer rate at the contact interface and increased active sites utilization efficiency.²⁸ To gain insights into the activity improvement mechanism, the EIS results are presented in Fig. 5d. The CoMoO₄/CC-2 electrode exhibits similar charge transfer resistance with that of the other composites in high

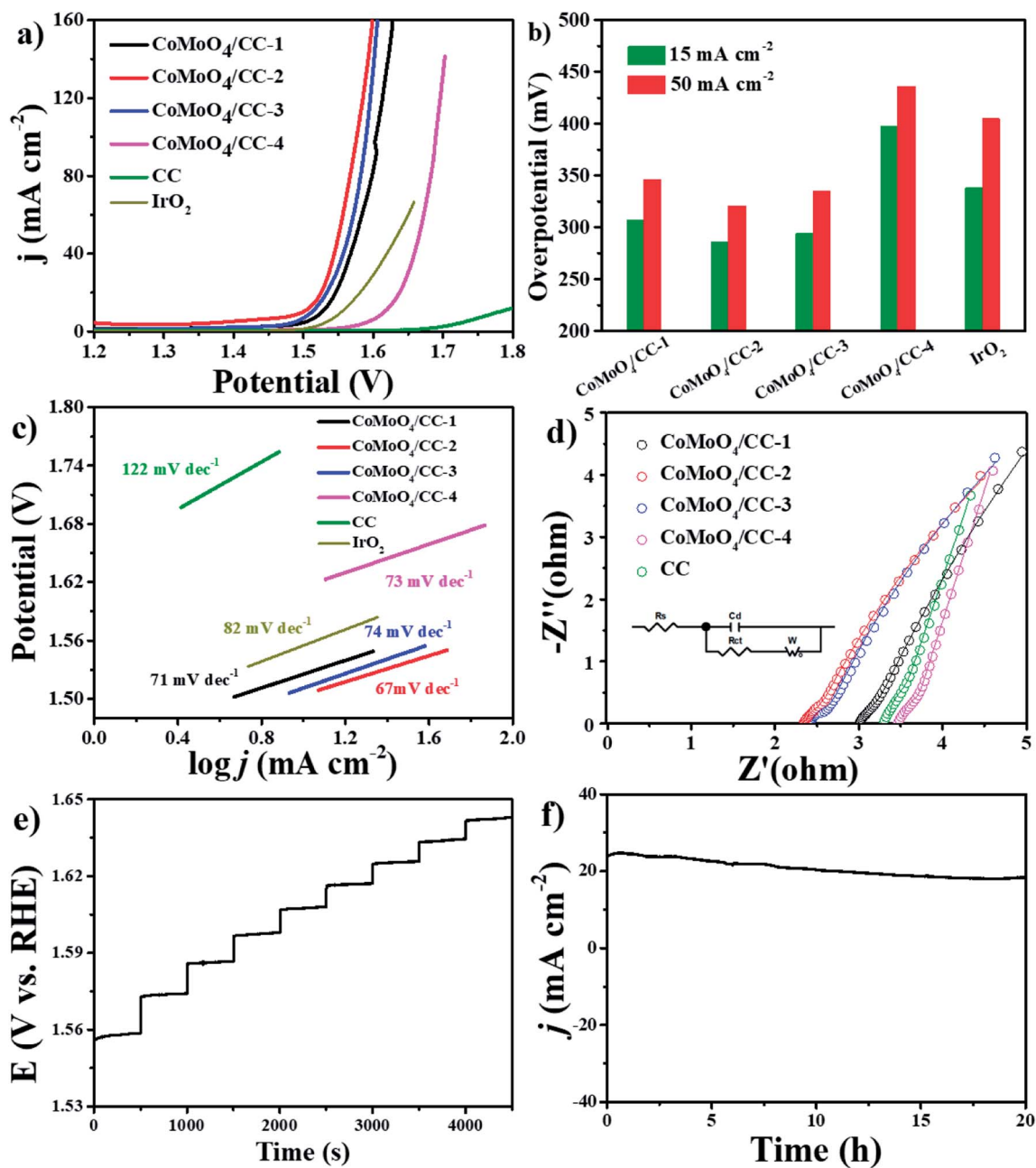


Fig. 5 (a) LSV curves, (b) comparative overpotential (c) Tafel curves (d) EIS curves of the $\text{CoMoO}_4/\text{CC}-n$ ($n = 1, 2, 3$ and 4) electrodes. (e) Multi-current process of $\text{CoMoO}_4/\text{CC}-2$. The current density started at 10 mA cm^{-2} and ended at 50 mA cm^{-2} , with an increment of 5 mA cm^{-2} per 500 s without iR correction. (f) $i-t$ curves of $\text{CoMoO}_4/\text{CC}-2$ composite.

frequency region, while the contact interface conductivity is improved clearly with the R_s 2.2Ω from the equivalent circuit, which is in accordance with OER catalytic performance. The multi-current responding curve in Fig. 5e reveals the potential stabilized at 1.558 V under 10 mA cm^{-2} and similar results remain unchanged at all other steps, illustrating the good conductivity, mass transportation property and mechanical robustness of the 3D $\text{CoMoO}_4/\text{CC}-2$ electrode.^{43,44} Moreover, the long-term stability of the $\text{CoMoO}_4/\text{CC}-2$ composites is evaluated by applying a constant potential (1.6 V vs. RHE) on the electrode for 20 h (Fig. 5f). The constant response current density during

the period indicates good electrocatalytic stability of the $\text{CoMoO}_4/\text{CC}-2$ composites.⁴⁵ Furthermore, the SEM, XRD, XPS and TEM results of the $\text{CoMoO}_4/\text{CC}-2$ electrode after the long-term catalytic test also reveal the superior structural and crystalline stability of the nanosheets (Fig. 6 and S4–S6, see ESI†).

To estimate the ECSA of the electrodes and understand the relationship between the active material crystal structure and OER activity, the CV tests are conducted in the region of 1.276 to 1.376 V vs. RHE under different scan rates (Fig. 7a and S7†). As the response current density should only be relevant to the electrical double layer surface area (C_{dl}), thus the ECSA of the

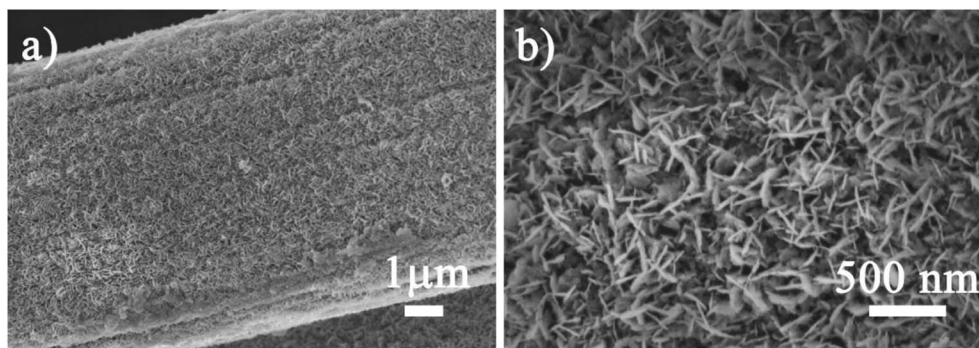


Fig. 6 (a) The low-magnification and (b) low-magnification SEM images of the CoMoO₄/CC-2 electrode after long-term catalytic stability test.

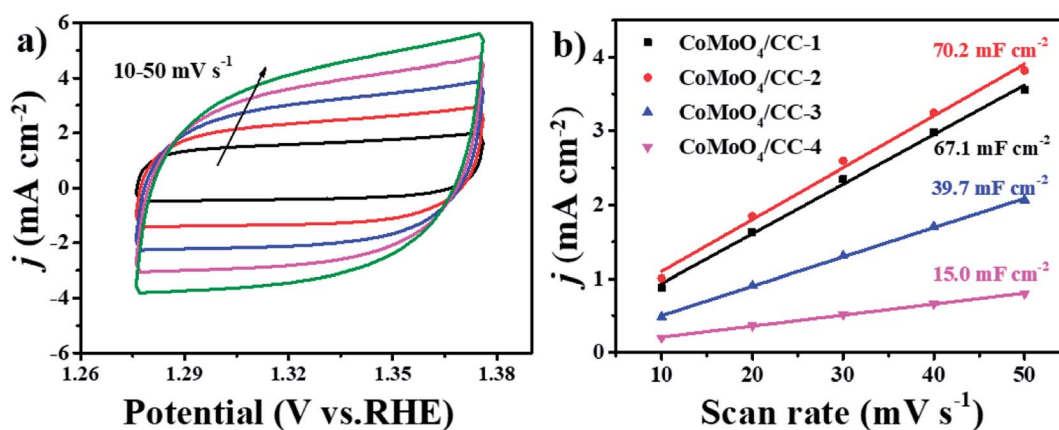


Fig. 7 (a) CV curves of the CoMoO₄/CC-2 at different scan rates from 10 to 50 mV s⁻¹, (b) estimated C_{dl} and relative electrochemically active surface area of the CoMoO₄/CC-*n* electrodes.

electrodes can be calculated.⁴⁶ The CoMoO₄/CC-2 sample shows a highest C_{dl} of 70.2 mF cm⁻² (Fig. 7b), which is larger than those of the CoMoO₄/CC-1 (67.1 mF cm⁻²), CoMoO₄/CC-3 (39.7 mF cm⁻²) and CoMoO₄/CC-4 (15.0 mF cm⁻²). The highest C_{dl} of the CoMoO₄/CC-2 hybrid suggests the enlarged electrocatalytic surface area, thus active sites utilization efficiency of the active material in the catalytic process is also largely increased.^{47,48}

4. Conclusion

In summary, the three-dimensional (3D) free-standing CoMoO₄ nanoarrays with different morphologies anchored on the carbon cloth were synthesized *via* a one-pot hydrothermal method without post heat treatment. The CoMoO₄ morphology evolution with the change of the Co/Mo precursor ratio and the materials contact interface is investigated. As the OER electrode, the CoMoO₄/CC-2 composite with interconnected nano-sheets reveals superior catalytic activity, the overpotential of 286 mV at 15 mA cm⁻² and Tafel slope of 67 mV dec⁻¹ can be obtained. Moreover, the CoMoO₄/CC-2 electrode shows high long-term electrochemical and structural stability. As the carbon cloth is commercially available, this simple but effective morphology controlling method can act as a new large-scale practical electrode fabrication technique for large-scale water splitting.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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