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In situ conversion of layered double hydroxide arrays into nanoflowers of Ni_xV_{1-x} -MOF as a highly efficient and stable electrocatalyst for the oxygen evolution reaction[†]

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Through the transformation from layered double hydroxides (LDHs) to metal organic frameworks (MOFs) by a hydrothermal method, we have prepared a promising electrocatalyst (Ni_xV_{1-x}-MOF) for the oxygen evolution reaction (OER). The optimized Ni_{0.9}V_{0.1}-MOF has the best OER performance and only requires an overpotential of 290 mV to drive a current density of 150 mA cm⁻² in alkaline solution.

Nowadays, due to the excess consumption of fossil fuels, the energy crisis and environmental pollution have become two major problems hindering development. Therefore, it is crucial to explore clean and pollution-free energy sources.¹⁻³ Hydrogen, as a sustainable clean energy source, is a promising candidate for replacing traditional fossil fuels.⁴⁻⁶ Water electrolysis offers us an ideal route to produce pure hydrogen.⁷ But the anode reaction, the OER, often involves multiproton-coupled electron transfer steps, causing very sluggish reaction kinetics and high overpotential.8-10 In recent years, the most active OER catalysts are state-of-the-art precious metal catalysts (such as IrO₂ and RuO₂). Unfortunately, the paucity and the high cost of precious metals hinder their widespread application.¹¹ Therefore, exploring high-performance and stable OER electrocatalysts is critical for future development.¹²

Metal organic frameworks (MOFs) have broad prospects in renewable energy conversion, and have massive tunable structures, ultra-high porosity and more active sites.^{12–15}

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Unfortunately, poor conductivity and easy agglomeration are key factors limiting the performance improvement of MOFs.^{16,17} Recently, MOFs with unique microstructures have been obtained by precursor transformation, their catalytic performance and stability are better than those obtained by direct synthesis.^{18,19} Therefore, we speculate that LDH precursors as metal release sources can increase the conductivity of MOFs and optimize the morphology of electrocatalysts. Now therefore, V-based materials have attracted great interest in water splitting application.^{20,21} For example, Ni-V layered double hydroxide (LDH)²⁰ and lepidocrocite VOOH (ref. 21) were reported as competent OER catalysts. We speculate that the introduction of high valence vanadium ions will optimize the electron cloud density of the active center and greatly improve the catalyst performance through the synergistic effect of bimetals.²² In combination with the above discussion, in order to design a highly efficient and stable electrocatalyst, the following conditions may be satisfied: (a) a stable support structure to prevent agglomeration; (b) preparation of excellent precursors to improve conductivity; (c) taking advantage of synergy between metals.

In this communication, we report the use of NiV-layered double hydroxide nanoarrays on a nickel foam (NiV-LDH/NF) as both the precursor and nanoarray template for *in situ* fabrication of highly oriented three-dimensional (3D) MOF nanoflowers (Ni_xV_{1-x}-MOF) (Fig. 1, see the ESI† for preparation details). The as-made Ni_{0.9}V_{0.1}-MOF exhibits



Fig. 1 Schematic illustration for the synthesis of the $Ni_{0.9}V_{0.1}$ -MOF.



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superior activity only demanding an overpotential of 290 mV to drive a current density of 150 mA $\rm cm^{-2}$ in alkaline solution. In addition, such a 3D electrode also presents good long-term electrochemical durability.

Fig. 2a presents the X-ray diffraction (XRD) patterns of the NiV-LDH, Ni-MOF and Ni_{0.9}V_{0.1}-MOF. The NiV-LDH shows characteristic peaks of Ni(OH)₂ (JCPDS no. 38-0715).²³ A single vanadium-based hydroxide shows very low crystallinity. Therefore, no significant change was observed in the X-ray diffraction spectrum after V was incorporated into the structure of Ni(OH)₂, indicating that the NiV-LDH has the same layered structure as Ni(OH)₂.²⁰ The incorporation of V into the Ni-MOF does not result in a significant change in the XRD patterns. After solvothermal treatment, the resulting Ni-MOF and Ni_{0.9}V_{0.1}-MOF both displayed strong diffraction peaks at around 8.9°, 14.9°, 15.7°, and 16.9°, which were indexed to the (200), (001), (201) and (400) planes of respectively (CCDC $Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_2,$ 985792, Cambridge Crystallographic Data Centre), which is a layered Ni-MOF with the C2/m space group.²³⁻²⁵ The other three peaks at about 44.5°, 51.8°, and 76.4° were observed due to the nickel foam substrate (JCPDS no. 04-0850). Two bands at 3598 and 3527 cm⁻¹ in the Fourier transform infrared (FT-IR) spectrum can be assigned to the stretching vibrations of the



Fig. 2 (a) XRD patterns of the NiV-LDH, Ni-MOF, and Ni_{0.9}V_{0.1}-MOF. (b) Fourier transform infrared (FT-IR) spectrum of the Ni_{0.9}V_{0.1}-MOF. (c) SEM image of the Ni_{0.9}V_{0.1}-MOF. (d) EDX elemental mapping images of Ni, V and O for Ni_{0.9}V_{0.1}-MOF nanoflowers. (e) TEM image of a Ni_{0.9}V_{0.1}-MOF nanoflower. (f) SAED pattern of the Ni_{0.9}V_{0.1}-MOF.

OH⁻ groups in the Ni_{0.9}V_{0.1}-MOF (Fig. 2b).^{24,26} The asymmetric and symmetric stretching modes of coordinated -COO⁻ are present as two intense bands at 1580 and 1367 cm⁻¹, respectively, indicating the bidentate coordination of -COO⁻ with two O atoms coordinated to Ni^{2+,23,24,26} Characteristic para-aromatic C-H stretching vibration bands occur at 1503, 1152, 1090, 1023, 827, and 745 cm⁻¹. Furthermore, the band at 549 cm⁻¹ can be assigned to the stretching mode of V-O and Ni-O, suggesting the formation of metal-oxo bonds between the Ni (V) atoms and the carboxylic groups of terephthalic acid.^{20,24,26} The scanning electron microscopy (SEM) images of the hydroxide precursor reveal that nanosheet arrays uniformly grow on the bare nickel foam (Fig. S1[†]). The SEM image of the Ni_{0.9}V_{0.1}-MOF shows that nanoflowers with a rougher surface and a larger pore structure are formed (Fig. 2c). The energy-dispersive X-ray (EDX) elemental mapping images of the Ni_{0.9}V_{0.1}-MOF verify the uniform distribution of the Ni, V, C and O elements (Fig. 2d). In addition, we also measured the element content (Fig. S2[†]). The transmission electron microscopy (TEM) image of the resulting Ni_{0.9}V_{0.1}-MOF further confirms its morphology (Fig. 2e and S3[†]). The high-resolution TEM (HRTEM) image in Fig. S3d[†] shows a lattice fringe spacing of 0.25 nm, which can be ascribed to the (012) plane of Ni(OH)₂. The selected area electron diffraction (SAED) pattern (Fig. 2f) shows discrete spots assigned to the (012) and (102) planes of $Ni(OH)_2$.

The X-ray photoelectron spectroscopy (XPS) survey spectrum of the Ni_{0.9}V_{0.1}-MOF (Fig. S4†) further confirmed the presence of Ni, V, C and O elements. The peaks at 875.1 (Ni $2p_{1/2}$) and 857.2 (Ni $2p_{3/2}$) eV in the Ni 2p region (Fig. 3a) together with two satellites (marked as sat.) at 880.2 and 862.5 eV indicate the presence of Ni^{2+.27} Fig. 3b shows the XPS spectrum of V 2p, further confirming the successful introduction of V instead of simple physical adsorption. The peaks at 524.5 eV and 517.0 eV correspond to V $2p_{1/2}$ and V



Fig. 3 XPS survey spectrum of the $Ni_{0.9}V_{0.1}$ -MOF. XPS spectra in the (a) Ni 2p, (b) V 2p (c) C 1s and (d) O 1s regions for the $Ni_{0.9}V_{0.1}$ -MOF.

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 $2p_{3/2}$, respectively. The peaks of V $2p_{3/2}$ can be decomposed into three components at 516.2 eV, 517.0 eV, and 517.8 eV, which are V³⁺, V⁴⁺, and V⁵⁺, respectively.²⁸ The C 1s region (Fig. 3c) can be deconvoluted into three surface components: two peaks at 285.4 and 284.2 eV correspond to the benzoic rings of terephthalic acid linkers, and the peak at 288.2 eV arises from the conjugative effect of the terephthalic acid ligand.²³ In the O 1s region, the signals at binding energies (BEs) of 531.5 and 530.0 eV are representative of oxygen atoms in OH⁻ groups and O²⁻ in transition metal (oxy) hydroxides, respectively. The signal at BE = 532.7 eV suggests the presence of a carbonate group in the material.²⁹ All the above stated analyses verify the successful preparation of the highly oriented Ni_{0.9}V_{0.1}-MOF.

We further investigated the water oxidation activity of the Ni_{0.9}V_{0.1}-MOF via the linear sweep voltammetry (LSV) technique using a typical three electrode system with a scan rate of 5 mV s⁻¹ in 1.0 M KOH aqueous electrolyte. The OER performances of the NF, RuO2/NF, NiV-LDH and Ni-MOF were also measured under the same conditions for comparison. To reflect the intrinsic behavior of the catalysts, all experimental data were corrected with ohmic potential drop (iR) losses resulting from the solution resistance. From the LSV curves (Fig. 4a), we observe that RuO₂/NF exhibits excellent OER activity and only needs an overpotential of 260 mV to achieve a current density of 150 mA cm⁻². It's worth noting that the overpotential of the Ni_{0.9}V_{0.1}-MOF is 290 mV at the same current density, 90 mV less than that of the Ni-MOF. This also proves that the Ni_{0.9}V_{0.1}-MOF has a better catalytic performance than the Ni-MOF. In addition, this performance is better than those of a Co-MOF ($\eta_{50mVcm^{-2}}$ = 311 mV),³⁰ NiFe-MOF-74 rhombic crystals ($\eta_{100\text{mVcm}^{-2}}$ = 390 mV),³¹ and other non-noble metal OER catalysts in alkaline media (Table S1[†]). The reaction kinetics of the OER can be



Fig. 4 (a) Linear sweep voltammetry (LSV) curves of the bare NF, NiV-LDH, Ni-MOF, Ni_{0.9}V_{0.1}-MOF and RuO₂/NF with a scan rate of 5 mV s⁻¹. (b) Tafel plots of the NiV-LDH, Ni-MOF, Ni_{0.9}V_{0.1}-MOF and RuO₂/NF. (c) Corresponding capacitive current densities at 0.974 V vs. RHE as a function of scan rate for the Ni-MOF and Ni_{0.9}V_{0.1}-MOF in 1.0 M KOH. (d) Nyquist plots of the Ni-MOF and Ni_{0.9}V_{0.1}-MOF recorded in 1.0 M KOH solution.

estimated by the Tafel equation: $\eta = b \log j + a$, where *b* is the Tafel slope and *j* is the current density. Fig. 4b shows the Tafel plots of the RuO₂/NF, NiV-LDH, Ni-MOF and Ni_{0.9}V_{0.1}-MOF, and the Tafel values are calculated to be 11.8, 28.9, 39.8 and 22.3 mV dec⁻¹, respectively, implying superior OER catalytic kinetics on the Ni_{0.9}V_{0.1}-MOF. Different V/Ni ratios also affect the oxidation activity of water. And overpotentials of 420 and 310 mV are needed to afford 150 mA cm⁻² (Fig. S5a†) along with larger Tafel slopes of 32.1 and 31.4 mV dec⁻¹ (Fig. S5b†) for the Ni_{0.95}V_{0.05}-MOF and Ni_{0.8}V_{0.2}-MOF, respectively. In order to further emphasize the superiority of synthesizing MOFs from NiV-LDH precursors (Fig. S6†), we have experimentally demonstrated that the materials synthesized from these precursors performed significantly better than the materials synthesized in one step.

To prove the enhanced OER activity of the Ni-MOF after the introduction of vanadium, the electrochemically active surface area (ECSA) was investigated, as a larger ECSA indicates more electrochemically active sites.^{32,33} The ECSA can be converted from the electrochemical double layer capacitance $(C_{\rm dl})$ by the equation:^{32,33} ECSA = $C_{\rm dl}/C_{\rm s}$, where $C_{\rm s}$ representing the specific capacitance is 0.04 mF cm⁻². Then the C_{dl} was determined to estimate the ECSA based on the cyclic voltammograms (CVs) at different scan rates (Fig. S7[†]).³³ As observed in Fig. 4c, the C_{d1} values for the Ni-MOF and $Ni_{0.9}V_{0.1}$ -MOF were calculated to be 4.2 mF cm⁻² and 5.1 mF cm⁻², respectively. Therefore, the Ni_{0.9}V_{0.1}-MOF has a larger ECSA of 127.5 cm^{-2} compared to the Ni-MOF (ECSA = 105 cm⁻²), showing more active sites and enhanced OER activity after V introduction.³² The results from EIS tests, as shown in Fig. 4d, reveal that V introduction can promote the electrical conductivity, which is beneficial for enhancing the catalytic performance. Fig. S8† shows the multi-step chronopotentiometric curve for the Ni_{0.9}V_{0.1}-MOF. The increasing current density from 80 to 280 mA cm⁻² (20 mA cm⁻² per 500 s) indicates the excellent transport properties, conductivity, and mechanical robustness of the Ni_{0.9}V_{0.1}-MOF electrode. We also applied turnover frequency (TOF), related to the surface concentration of active sites,34 to further investigate the enhanced OER activity of the Ni-MOF after V introduction.13 As presented in Fig. S9,† compared with the Ni-MOF (TOF_{Ni-MOF} = 0.05 mol O_2 per s), the Ni_{0.9}V_{0.1}-MOF showed a larger TOF value (0.138 mol O₂ per s) at an overpotential of 400 mV, which further demonstrates the enhanced OER activity of the Ni_{0.9}V_{0.1}-MOF.¹³ Furthermore, the TOF value of the Ni_{0.9}V_{0.1}-MOF (0.138 mol O₂ per s, η = 400 mV) is also superior to those of most reported nonnoble-metal water oxidation catalysts, such as benzoate- $Co(OH)_2$ (0.111 mol O₂ per s, $\eta = 380$ mV),³⁵ CuCo₂S₄ (0.069 mol O₂ per s, $\eta = 300$ mV),³⁴ and NiCo₂O₄@Ni-Co-B (0.019 mol O₂ per s, $\eta = 500$ mV),³⁶ adequately confirming the superior electrocatalytic activity of the Ni_{0.9}V_{0.1}-MOF.

Durability is also a crucial factor for electrocatalysts. As shown in Fig. S10,† the LSV curves of the $Ni_{0.9}V_{0.1}$ -MOF after 500 even 2000 cyclic voltammetry (CV) cycles exhibit no obvious change compared to its initial performance,

demonstrating the good stability of the Ni_{0.9}V_{0.1}-MOF (Fig. S10a and b†). Furthermore, we measured the time dependent current density curve of the Ni_{0.9}V_{0.1}-MOF at a fixed overpotential of 120 mV and found that this catalyst presents good electrochemical durability, with its catalytic activity being maintained for at least 60 h (Fig. S10c†).

Conclusions

In summary, we have demonstrated a facile approach to prepare three-dimensional Ni_xV_{1-x} -MOFs *via* a simple hydrothermal process. The $Ni_{0.9}V_{0.1}$ -MOF only demands an overpotential of 290 mV to drive a current density of 150 mA cm⁻² in alkaline solutions. In addition, its catalytic activity can be maintained for at least 60 h at a high current density of 120 mA cm⁻². Thus, the $Ni_{0.9}V_{0.1}$ -MOF demonstrates high catalytic activity and stability, which proves the superiority of this catalyst. This work opens up a new avenue towards developing highly active multicomponent noble-metal-free MOF electrocatalysts.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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