Ni (II)-Doped Anionic Metal-organic Framework Nanowire Arrays for Enhancing Oxygen Evolution Reaction

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Herein, an anionic metal-organic framework nanowire arrays not only directly grown on Cu foam but also captured Ni (II) ions at ultra-small particles level. The hybrid material exhibited high activity with low overpotential (310 mV at 20 mA cm⁻² in 1.0 M KOH solution) toward oxygen evolution reaction (OER) (1M KOH), with performance comparable to that of the precious metal benchmark. These findings may expand the field of MOFs for scaleup water electrolysis.

The oxygen evolution reaction (OER) plays an important role on the energy storage and conversion applications such as water splitting metal-air batteries.¹⁻³ OER electrocatalysts only exhibited promising catalytic performance in acidic or alkaline conditions due to intrinsic high kinetic barrier (i.e., $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ in base).⁴⁻⁵ Up to now, excellent OER catalysts were mainly focused on inorganic nanoparticles and carbon-based materials,⁶⁻⁸ which still require large overpotentials to realize the desirable current densities. Recently, metal-organic frameworks (MOFs) as a unique of porous functional materials have extensively displayed traditional applications in gas adsorption, catalysis and luminescence,⁹⁻¹² even a few of MOFs exhibited a promising electronic performance.¹³⁻¹⁶ However, MOFs are usually not stable at acid/alkaline environment, which has hastened their usage as the potential OER. In addition, MOFs-derived materials like single atom can exhibited excellent OER activity, but prepare conditions need high hast synthesized conditions.¹⁷⁻²⁰ As a result, to explore chemical stable MOFs that can be directly acted as efficient OER catalysts are highly desirable.

Nanowire arrays in situ grown on the current collectors have been explored as excellent electrodes.²¹⁻²² Because the direct contact of

nanowire arrays with conductive substrates can enhance electrical conductivity, which are beneficial in improving electrocatalytic OER activity. However, most of reported metal oxide nanowires showed low porosity and small surface area. MOFs nanowire arrays with favorable electrical conductivity, for directly electrocatalytic OER is scarcely explored.²³⁻²⁴ Owing to its less activity sites, the apparent electrochemical performance of MOFs in situ growth certain substrates is still unsatisfactory. In general, functional MOFs with rich active sites (e.g., $-\text{NH}_2$ and $-\text{COO}^-$) can enhance close interactions with targeted metal ions.^{13,25-26} So, an ideal strategy is introducing cation like Ni^{2+} and Co^{2+} into the anionic MOFs nanowire arrays can improve the activity to some extent, which have advantages such as self-supported arrays and without any additives. With low price, high redox capability, as well as good stability in alkaline conditions, d¹⁰ transition metal MOFs nanowire array represents a promising candidate to substitute noble-metal based electrocatalysts for efficient OER.

Scheme 1 Illustration of the synthesis process for MOFs with nanowire arrays on Cu foam and doping Ni (II) for OER.

To achieve these goals, we explored an alkaline stable anionic Zn (II) metal-organic framework (JXNU-4) with nanowire arrays,²⁷ which are prepared directly grown on Cu foam via in situ method under solvothermal reaction (denoted as JXUN-NA/CF). The resulting modified JXNU-4 were the anionic MOF structure with rich $-\text{COO}^-$ and $-\text{NH}_2$, which can stabilize the incorporating Ni (II) at ultra-small scale without aggregation. Remarkably, the resulting JXUN-NA/CF with Ni^{2+} dopant exhibited more excellent oxygen evolution activity in comparison to most of the highly active noble-metal/transition-

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metal and nonmetal catalysts reported to date. These findings may open a new opportunity to directly explore metal–organic framework nanowire arrays as electrocatalysts for scaleup water electrolysis.

The growth of JXUN-NA/CF was successfully carried out through the solvothermal reaction with a Cu foam and a mixed solution containing the organic ligands (adeninate and 4,4'-biphenyldicarboxylate) and Zn^{2+} (for details, see the Experimental Section). After synthesis, numerous oriented nanowires with high density homogeneously covered the whole Cu foam (Figure 1a-c). The powder X ray diffraction (PXRD) patterns of JXUN-NA/CF matched well with that of the simulated JXUN-4, suggested the structure remained unchanged.

Fig. 1 (a-c) The SEM images of JXUN-4-NA/CF; (d) PXRD patterns of JXUN-4-NA.

According to literature,²⁷ the JXNU-4 was a water stable anionic 3D framework with the uncoordinated carboxylate group and rich $-\text{NH}_2$ lined on the surfaces of one-dimensional (1D) channels, indicating it can potentially be capable of absorbing positively charged ion. The pore of JXNU-4 has the dimensions $9.8\text{\AA} \times 9.8\text{\AA}$, which can accommodate one Ni^{2+} (the ionic radius of a hydrated Ni^{2+} cation is approximately $4\text{\AA}$). Herein, Ni^{2+} were expected to disperse into bulk MOFs, which may realize simultaneous optimization of both porous structures and surface functionalities of the MOF functional catalysts. When fresh JXNU-4 samples are immersed into the Ni^{2+} ions aqueous solution, there will be dynamic interaction between Ni^{2+} ions and functional group like $\text{C}=\text{O}$ and $-\text{NH}_2$. The PXRD patterns showed the hybrid material ($\text{Ni}@\text{JXUN-4}$) kept original crystalline phase with addition of a large amount of Ni^{2+} (Figure S1), as or even were immersed into the strong alkalinity (Figure S1). The fourier transform infrared (FTIR) spectroscopy was also carried out to check whether there was interaction between Ni^{2+} and functional group such as $\text{C}=\text{O}$ groups and $-\text{NH}_2$ in the MOF (Figure 2a). The strong IR adsorption peaks located at $\sim 1349\text{ cm}^{-1}$ can be ascribed to the $\text{C}=\text{O}$ groups' IR adsorption, and the adsorption peaks almost disappeared after the addition of Ni^{2+} , which indicated that the Ni^{2+} had coordinated with COO^- groups on the MOFs. Also, FTIR confirmed that there was weak interaction between the Ni^{2+} and $-\text{NH}_2$. In the FTIR spectra (Figure 2a), the peaks centered at 1012 and 2923 cm^{-1} (i.e., the $\text{C}-\text{N}$ and $\text{N}-\text{H}$ stretching vibrations of the amino group, respectively) decrease in intensity after Ni^{2+} incorporation. This is expected because the $\text{Ni}-\text{N}$

bond formation would weaken the $\text{C}-\text{N}$ and $\text{N}-\text{H}$ bonds due to electron transfer from N to Ni^{2+} .

To determine the chemical state of JXNU-4-Ni photoelectron spectroscopic (XPS) measurements were investigated (Figure 2b). The Ni 2p core-level spectrum with the Ni 2p_{3/2} and Ni 2p_{1/2} peaks at 854.1 and 872.0 eV , respectively, showed the nickel remains the same divalent after the doping into the anionic MOFs.

The transmission electron microscope (TEM) images (Figure 3c) was smooth and selected area electron diffraction (SAED) pattern of $\text{Ni}@\text{JXNU-4}$ displayed that no point- or ring-like picture arose in Figure 2d, indicating that the Ni (II) was no forming aggregation or clustering of the metal nanoparticles during the ion exchange. Meanwhile, high resolution transmission electron microscope (HRTEM) (Figure 2e) exhibited that there was no lattice fringe of crystallized Ni or Ni oxides. From the element mapping and EDS of Ni, Zn, O, C, and N in Figure 2f, we could see that Ni element is also well dispersed into the anionic JXNU-4 frameworks. In addition, inductively coupled plasma atomic emission spectroscopy showed the maximum Fe ion uptake was $5.5\text{ wt. \%}$. Compared to the BET of JXNU-4 ($1250\text{ m}^2\text{ g}^{-1}$),²⁷ Brunauer–Emmett–Teller (BET) surface areas of $\text{Ni}@\text{JXNU-4}$ calculated from the N_2 adsorption data is $12.6\text{ m}^2\text{ g}^{-1}$, which greatly decreased (Figure S2). Therefore, these satisfied results showed the cationic MOF have successfully captured Ni (II) at

ultra-small level.

Fig. 2 (a) FTIR patterns of $\text{Ni}@\text{JXUN-4}$; (b) XPS survey, Ni 2p high resolution spectra of $\text{Ni}@\text{JXUN-4}$ (c) TEM images of $\text{Ni}@\text{JXUN-4}$; (d-e) the corresponding SAED and HRTEM pattern. (f) Element mapping of C, N, O, Zn, and Ni in $\text{Ni}@\text{JXUN-4}$.

To study the electrocatalytic performance of the anionic MOFs for OER electrocatalytic application, JXUN-4-NA/CF samples were obtained by growing crystals on conductive Cu foam to prepare electrodes under solvothermal system. The obtained electrodes JXUN-4-NA/CF were immersed in Ni^{2+} solution (hereafter, $\text{Ni}@\text{JXUN-4-NA/CF}$), which can directly use for the working electrodes under strong alkaline solution (1.0 M KOH) in a three-electrode system. As shown in Figure 3a, the linear sweep voltammetry (LSV) curves displayed the catalytic performance of $\text{Ni}@\text{JXUN-4-NA/CF}$, JXUN-4-NA/CF RuO_2/CF and CF. The overpotentials of $\text{Ni}@\text{JXUN-4-NA/CF}$

reached 310 mV (at 20 mA cm⁻²), which compares favorably to the activity of other Ni-based OER catalysts such as Ni(OH)₂ (~372 mV), NiCo₂O₄ (~391 mV), and NiCo-LDH (~393 mV) at the same current density.²⁸⁻³⁰ In contrast, JXUN-NA/CF exhibited very poor electrocatalytic OER activities (Figure 3a). It also should be noted that the catalytic performance of Ni@JXUN-4-NA/CF is comparable to or even superior to recently reported MOF-based electrocatalysts and precious metals benchmark (RuO₂/CF, 458 mV at 20 mA cm⁻²) (Figure 3a Table S1). As seen in Fig. 3b, Tafel plot slopes of Ni@JXUN-4-NA/CF is 102 mV dec⁻¹ is much lower than that of CF, JXUN-4-NA/CF and RuO₂/CF, showing its more favorable catalytic kinetics for the OER on Ni@JXUN-4-NA/CF. After performing OER stability tests, the chronoamperometric response for the Ni@JXUN-4-NA/CF displays a small current attenuation due to the aggregation and peeling of electroactive species during oxygen gas evolution (Figure S3). Luckily, the main absorption peaks (e.g., ~1349 cm⁻¹, ~1700 cm⁻¹ and ~2923 cm⁻¹) were all preserved (Figure S4). This demonstrates that the JXUN-4 structure was unchanged after OER. What's more, the PXRD and LSV of Ni@JXUN-4-NA/CF showed negligible changes (Figure S1, S5). These results showed that Ni doping MOF nanowire array architectures directly anchored on a conductive substrate are conducive to high structural stability for OER under extremely alkaline solution.

Fig. 3 (a) OER polarization and (b) Tafel plots of JXUN-4-NA based electrocatalysts, Cu foam and RuO₂ cast on Cu foam. (c) OER polarization curves of Ni@JXUN-4-NA/CF electrocatalysts with different Ni²⁺ concentrations. (d) EIS of Ni@JXUN-4-NA/CF and JXUN-4-NA/CF electrodes (Inset: the magnification of EIS).

To gain the further understand for the superior OER activity, we investigated JXUN-4 based electrocatalysts by comparing with the following control samples. Firstly, compared with those of the bulk JXUN-4 catalysts with Ni²⁺ dopant (denoted as Ni@JXUN-4), the Ni@JXUN-4-NA morphology was itself beneficial for enhancing the OER activity, because these nanowire arrays have grown uniformly on the Cu substrate with good size distribution; which largely contributing to more active sites were exposed in electrolyte. The bulk JXUN-4-based electrocatalyst such as Ni@JXUN-4/CF showed an overpotential of 441 mV at 20 mA cm⁻², which is obvious more than that of Ni@JXUN-4-NA/CF (Figure S6). Second, Ni is generally looked

as the active center for OER.^{12,16,31} This effect is more obviously enhancing with increasing Ni²⁺ immersed concentration in the JXUN-4-NA/CF (Figure 3c). Ni@JXUN-4-NA/CF should be more effective in accelerating charge-transfer due to exposing more active sites Ni (II) ions in comparison to JXUN-4-NA/CF. Further, the electrochemical impedance spectrum (EIS) analysis confirmed that the function of Ni(II) in enhancing OER perform is through decreasing the charge transfer impedance in comparison with JXUN-4-NA/CF without Ni²⁺ dopant (Figure 3d). Finally, the electrochemical active surface area (ECSA) has been evaluated by the double layer capacitance (C_{dl}) for Ni@JXUN-4-NA/CF and JXUN-4-NA/CF (Figure S7). The C_{dl} of Ni@JXUN-4-NA/CF is 1.80 mF cm⁻², which is larger than that of JXUN-4-NA/CF (C_{dl} = 1.08 mF cm⁻²), indicating that more ECSA is created in Ni@JXUN-4-NA/C. Therefore, nanowire array morphology and active sites Ni (II) played important roles in enhancing OER activities.

In conclusion, we developed an anionic metal-organic framework nanowire arrays directly grown on Cu foil under hydrothermal reaction, which can capture and stabilize Ni (II) at ultra-small particles level without forming aggregation of the bulk metal nanoparticles. The strategy for growth of MOFs on conductive substrates can improve mass/charge transfer and enable high-current operation. The substantial dopant of Ni (II) resulted in increasing activity sites, which enhanced OER activities in comparison with that of (benchmark) RuO₂. This work will help open new opportunities for exploring a range of stable and cheap MOF-based nanowire arrays to replace of noble-metal for sustainable energy research.

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