External and Internal Dual-controls: Tunable Cavity and Ru-O-Co Bond Bridge Synergistically Accelerate the RuCoCu-MOF/CF Nanorods for Urea-assisted Energy-saving Hydrogen Production

Yilin Wang  
Qingdao University of Science and Technology

Yunmei Du  
Qingdao University of Science and Technology

Ziqi Fu  
Qingdao University of Science and Technology

Mengmeng Wang  
Qingdao University of Science and Technology

Yunlei Fu  
Qingdao University of Science and Technology

Bin Li  
Qingdao University of Science and Technology

Lei Wang (✉ inorchemwl@126.com)  
Qingdao University of Science and Technology

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Abstract

Currently, conductive metal-organic frameworks (MOFs) with the merits of porosity and large specific surface area have prodigious development prospects in the field of electrocatalysis. However, the regulation of the cavity of the hollow MOFs and its research on the performance of urea-assisted water splitting are still challenges. Toward this aim, the hollow RuCoCu-MOF/CF nanorods with tunable cavities are directionally constructed by a self-sacrificial template strategy. Benefiting from the innovative morphological control and the unique Ru-O-Co bond bridge, RuCoCu-MOF/CF has superior performances for alkaline hydrogen evolution reaction (HER) and urea oxidation reaction (UOR). Surprisingly, a record-breaking voltage of 1.402 V drives a current density of 10 mA cm$^{-2}$ for urea-assisted overall water splitting under alkaline conditions, greatly promoting the development of energy-efficient hydrogen production technology. This work firstly constructed the MOF-based self-supporting electrode with ultra-high urea-assisted hydrogen production and urea degradation performances via the dual controls of the cavity size and chemical bond bridge. This points out the direction for the development of unique integrated electrodes for both hydrogen production and decontamination.

1. Introduction

With the advocacy and proposal of the "zero-carbon" target strategy, the energy structure adjustment is imminent, requiring the strong development of clean, renewable, and environmentally friendly alternative energy [1–4]. Electrolytic water hydrogen consists of two semi-reactions, cathode hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) [5–7]. However, in the face of the OER process with reasonably high energy consumption, the urea oxidation reaction (UOR) not only has theoretical thermodynamic potential (0.37 V) below OER but alleviates the problem of urea pollution in wastewater, becoming a decent alternative for replacing OER to realize industrial hydrogen production [8–12].

In various types of emerging catalytic materials, the metal-organic frameworks (MOFs) show huge electrocatalytic prospects [13, 14]. MOFs are characterized by their virtues such as a high coordination environment, high porosity, adjustable size, large specific surface area, and abundant structural types, receiving great potential for ideal electrocatalytic functions [15–18]. Compared with the pure one-element metal-based MOF, the synergistic effect between two different metals can change its metal center, and at the same time can significantly enhance the redox reaction and electrocatalytic activity [19–22]. Lou’s group successfully synthesized the CoCu-base conductive MOF nanobox catalyst, the catalytic synergistic effect of Co and Cu bimetallic sites can effectively reduce the reaction energy, promoting an oxygen-reactive kinetic process [23]. Tang’s team successfully synthesized the nanoscale NiCo-MOF-74 catalyst, the geometric structure and electronic structure of the formed active species can be adjusted by adjusting the ratio of Ni and Co in the bimetallic center, and the two-phase structure transition can be regulated by adjusting the phase transition potential of the Ni-O and Co-O parts, thereby optimizing the catalytic activity [24]. However, traditional MOFs and their derivatives are always prepared to be powder electrocatalysts, but the electrode preparation is complicated, and the use of binders will mask active
sites, hinder mass and charge transfer, and block gas permeation, all of these can reduce the catalytic ability of MOFs [25–27]. In order to break down the conventional barriers, researchers are committed to developing a befitting solution, and various MOF-derived materials have been reported one after another [28, 29]. Zhai’s team reported the synthesis of MOF/LDH hetero-nanotree catalysts coupled with single-atom dispersed ruthenium (Ru) sites (CoNiRu-NT), and the grafted MOF nanobranches grown on nickel foam (NF) improved electrical conductivity and provides a larger surface and more accessible channels for charge/mass transport [30]. Xu’s group reported a kind of CoP_x@CNS with porous NF as a template. This ultrastructure is directly used as a self-supporting electrode, showing excellent three-functional electrocatalytic performance to HER, OER, and ORR [31].

In order to optimize the catalytic activity of MOFs materials, morphology engineering design and doping or anchoring of highly active noble metals can be performed, which can increase the number of active centers of MOFs catalysts and improve the intrinsic performance of each active site, respectively [32–36]. In particular, the design of the hollow structure can effectively expose the active sites of the catalytic materials, providing a larger surface for charge/mass transport at the direct interface between the catalyst and the electrolyte, facilitating charge transfer and gas freed [37, 38]. At present, many MOF-based catalysts reported are basically solid nanorod arrays, blocks, solid spheres, and nanosheets [25, 26, 31, 39, 40], while the uniform growth of hollow MOF nanorods on self-supporting electrodes, especially the hollow nanorod materials controllable cavity size are rarely reported. Simultaneously, pure conductive MOFs mainly own HER or OER performances, which lack systematic investigation on urea-assisted water splitting with the merits of high catalytic efficiency and wastewater purification [41, 42].

With these in mind, this work adopts a self-sacrificial template strategy to design and synthesize the hollow RuCoCu-MOF nanorods with controllable cavity size on a copper foam (CF) substrate as a bifunctional catalyst for HER and UOR. The unique hollow nanorod structure endows catalyst with a larger active specific surface area and exposes abundant active sites. And the doping of Ru further enhances the activity of the CoCu-MOF/CF. Notably, the formation of the Ru-O-Co bond bridge as active ingredient provides a channel for the directional flow of electrons from Ru to Co atoms, adjusts their electronic configuration, and further promotes charge/mass transport at the interface between the catalyst and the electrolyte. Meanwhile, these Ru and Co atoms with optimal electronic configuration can synergistically promote the adsorption and dissociation of intermediates, thereby greatly accelerating the dissociation of water and the release of hydrogen. Given the above, this work provides an efficient way to realize the morphology regulation and bond bridge construction of MOFs, and a possibility for MOFs to directly act as an integrated hydrogen production-decontamination electrode.

2. Materials And Methods

2.1 Materials

Sodium hydroxide (NaOH, 97%), Ruthenium chloride anhydrous (RuCl₃·xH₂O), and 2, 3, 6, 7, 10, 11-hexahydroxybenzene (HHTP, ≥ 95%) were purchased from Aladdin. Cobaltous acetate tetrahydrate
(Co(Ac)$_2$·H$_2$O; AR) was acquired from Sinopharm Chemical Reagent. And ammonium persulfate was supplied from Tianjin Yongda Chemical Reagent Co., Ltd.

2.2 Materials synthesis

2.2.1 Synthesis of Cu(OH)$_2$/CF nanorod arrays

Firstly, the copper foam (CF, 1×2 cm$^2$) was washed in acetone, 1 M HCl, and ethanol for 10 minutes, respectively. Then, NaOH required 1 g and 0.2853 g of ammonium persulfate to mix evenly in 20 ml of deionized water to form a clear homogeneous solution. Subsequently, put 4 pieces of cleaned CF into and soaked for 10 min, rinse gently with deionized water and ethanol, and put them in a vacuum to dry to synthesize Cu(OH)$_2$/CF nanorod arrays.

2.2.2 Synthesis of hollow RuCoCu-MOF/CF nanorod arrays

To synthesize hollow RuCoCu-MOF/CF nanorods structure, firstly, 2, 3, 6, 7, 10, 11-hexahydroxybenzene (HHTP; 0.15 mmol) was dissolved in 2.5 ml of DMF, mixed with a solution of Co(Ac)$_2$·H$_2$O (0.15 mmol) and RuCl$_3$·xH$_2$O (X mg, X = 5, 10, and 15) dissolved in 2.5 ml deionized water, and then sonicated for 10 minutes. Subsequently, a piece of the prepared Cu(OH)$_2$/CF was added to the mixed solution to heat to 85 °C for 10 h in the oven (denoted as RuCoCu-MOF/CF-X, X = 5,10, and 15). Similar steps are synthesized by CoCu-MOF/CF, RuCu-MOF/CF, and Cu-MOF/CF, there are no Ru sources, Co sources, and both Ru and Co sources, respectively.

2.3 Materials characterizations

The scanning electron microscopy (SEM, Zeiss sigma 500) was tested to characterize the morphology of the well-prepared catalysts. The transmission electron microscope (TEM), high-resolution TEM (HRTEM), and EDX-mapping were used to further characterize the structure of RuCoCu-MOF/CF and other samples. X-ray photoelectron spectroscopy (XPS) was implemented to get the elemental composition and structure of the measured sample surface by Thermo ESCALAB 250Xi. Powder X-ray diffraction (XRD) was tested on the Rigaku D-MAX 2500/PC (Cu Kα, 2° min$^{-1}$).

2.4 Electrochemical measurements

All of the electrochemical measurements (HER, OER, UOR, and urea-assisted water splitting (HER UOR)) were implemented by the electrochemical workstation Gamry Instruments Reference 3000. The HER and OER tests were in 1 M KOH electrolyte at 25 °C, the electrolyte of UOR and HER UOR were prepared by 1 M KOH containing 0.5 M urea. And the electrolysis devices (HER, OER, and UOR) were made by the traditional simple three-electrode system, including the working electrode (the as-prepared self-supporting electrode), counter electrode (carbon rod), and the reference electrode (KCl-saturated Ag/AgCl electrode). Besides, the HER UOR adopted a two-electrode system, and the cathode and anode of the electrolytic cell device were prepared electrodes. All the measured potentials have been converted to reversible hydrogen electrodes (RHE), and the relevant formula is:
$$E(\text{RHE}) = E_{\text{Ag/AgCl}} + 0.198 \text{ V} + 0.0592 \times \text{pH}$$

The electrochemical properties were initially measured by Linear sweep voltammograms (LSVs) at the sweeping rate of 10 mV s$^{-1}$, and all of the LSV curves were iR-compensation. The frequency window range of electrochemical impedance spectroscopy (EIS) was 0.1 ~ 105 Hz, and the applied voltages of HER and UOR were −1.219 V and 0.5 V, respectively. Cyclic voltammetry (CV) tests set the scanning speeds to 40, 80, 120, 160, and 200 mV s$^{-1}$. Moreover, to explore the stability and durability of RuCoCu-MOF/CF, the IT tests were carried out, as well as the comparison of LSV curves before and after 4000 cycles of CV testing.

3. Results & Discussion

3.1 Synthesis and characterizations

As seen in Scheme 1, the well-designed RuCoCu-MOF catalysts with hollow nanorod structure were constructed on CF (RuCoCu-MOF/CF) via a facile self-sacrificial template method. Firstly, Cu(OH)$_2$ nanorod arrays with a diameter of about 135 nm (Fig. S1) were in situ grown on CF by surface chemical oxidation. Then during the hydrothermal process, these Cu(OH)$_2$ nanorods as self-sacrificial templates continuously released Cu ions, which further underwent a coordination reaction with 2, 3, 6, 7, 10, 11-hexahydroxybenzene (HHTP). And finally, the hollow conductive RuCoCu-MOF nanorods array composed of small cubes was formed with the assistance of Ru and Co salts (Fig. S2).

The diffraction peaks of as-prepared Cu-MOF powder (peeled from Cu-MOF/CF) and simulated Cu-MOF are well-matched in Fig. S3, indicating that the pristine Cu-MOF is successfully fabricated [43]. Strikingly, Fig. 1a shows that both the synthesized CoCu-MOF and RuCoCu-MOF have the same characteristic peaks as Cu-MOF. While the diffraction peaks of the as-prepared CoCu-MOF and RuCoCu-MOF shifts to a lower angle compared with that of Cu-MOF, confirming that a small amount of Co atoms replaces the Cu metal center to coordinate with HHTP to form CoCu-MOF. Moreover, the reduced peak intensity of RuCoCu-MOF may be due to the incorporation of Ru atoms into the interior of the CoCu-MOF without destroying the crystal structure of the CoCu-MOF [25]. Figure 1b shows the Fourier transform infrared spectroscopy (FTIR) spectra of the HHTP, Cu-MOF, CoCu-MOF, and RuCoCu-MOF. The broad peak at 3420 cm$^{-1}$ belongs to O-H bonds due to the presence of water, the peak at 1641 cm$^{-1}$ is the characteristic absorption peak of the aromatic ring, and the peaks of 1641 and 1450 cm$^{-1}$ both belong to the asymmetric vibration of O = C-O. More importantly, the characteristic peak of Cu-O also appears at 573 cm$^{-1}$, certifying the existence of the Cu-MOF host in the RuCoCu-MOF sample [44, 45]. As revealed by Figs. 1c-d, RuCoCu-MOF/CF still maintains the nanorod morphology, but the surface of RuCoCu-MOF/CF becomes rougher and the diameter of nanorods increased to 280 nm. Meanwhile, as displayed in Figs. 1e-f, the RuCoCu-MOF nanorod peeled from RuCoCu-MOF/CF consists of many ultra-small cubes with a width of 18 nm, which interior is a cavity with a diameter of about 75 nm. This unique structure of hollow nanorod endues the well-constructed RuCoCu-MOF/CF electrode with a large specific surface area and abundant active sites,
providing a large surface for mass and charge transfer in the direct interface microenvironment of catalyst and electrolyte, which plays a positive significance in improving the catalyst activity [46]. Further magnification of the small cubes on the surface of the RuCoCu-MOF nanorod (Fig. 1f) demonstrates that all lattice spacing is 1.82 nm, which belongs to the (100) plane of the CoCu-MOF. Furthermore, the elemental mapping images (in Fig. 1g) reveal that the Cu, Co, Ru, C, and O elements are uniformly dispersed on the RuCoCu-MOF catalyst. Besides, both relevant energy dispersive spectroscopy (EDS) (Fig. S4) and the inductively coupled plasma atomic emission spectroscopy (ICP-AES) of RuCoCu-MOF/CF (Table S1) verify the low content of Ru and Co elements.

To systematically study the effect of the introduction of different metals on the MOF growth mechanism and electrocatalytic activity, Cu-MOF/CF and CoCu-MOF/CF counterparts were prepared by the same method. Figures 2a-b and Fig. S5 show that the as-prepared Cu-MOF/CF is also a nanorod array structure with an enlarged diameter of ~360 nm, but its inner hollow cavity is only ~52 nm in diameter. Besides, the nanocubes that make up the pure Cu-MOF/CF nanorod become larger in size (~35 nm), smaller in quantity, and more disordered in distribution than the well-defined RuCoCu-MOF/CF. Like RuCoCu-MOF/CF and Cu-MOF/CF, the integrated CoCu-MOF/CF (Figs. 2c-d and Figs. S6a-e) also has a hollow nanorod structure. However, the diameter of its nanocubes is slightly larger than that of RuCoCu-MOF/CF, and nanocubes in CoCu-MOF/CF is measured to be ~310 nm, ~65 nm, and ~30 nm, respectively. Meanwhile, Fig. S6f displays that the lattice fringes spacing of CoCu-MOF is 1.80 nm, which completely identifies with the lattice spacing of the (100) plane of Cu-MOF, profoundly disclosing that Co atoms also participate in the coordination with HHTP to form CoCu-MOF. It is worth noting that under the action of the Co and Ru, the nanocubes in CoCu-MOF/CF and RuCoCu-MOF/CF (Figs. 2e-f) are both uniformly arranged along the nanorods, indicating that the adding of Ru and Co exerts a certain regulatory effect on the nucleation-growth of Cu-MOF crystals.

All in all, with the introduction of Co and Ru atoms, the diameter of the hollow nanorods becomes smaller, while the diameter of the cavity becomes larger. Simultaneously, the RuCoCu-MOF nanocubes become smaller and denser. Based on the above analysis, a plausible explanation can be made to reveal the effect of heterometallic doping on the structural evolution of hollow nanorods and the potential advantages of RuCoCu-MOF/CF that result from this. Specifically, the formation of the hollow nanorod structure mainly involves two processes, one is the dissolution process of Cu(OH)\textsubscript{2} nanowires, and the other is the coordination process of metal ions and organic ligands (Fig. 2g). With the addition of Ru and Co salts, the dissolution rate of Cu\textsuperscript{2+} in the nanowires increases and is faster than its coordination process, which promotes a large amount of Cu\textsuperscript{2+} to diffuse out to a certain distance to form MOF crystals with the HHTP, and thus making the diameter of MOF cavity larger. Notably, the above coordination process has a huge impact on the size and number of MOF nanocubes. This is because the metal-ligand coordination reaction mainly involves the formation process and growth process of the crystal nucleus. Among them, Ru and Co atoms can act as mediators to promote the rapid formation of the Cu-MOF crystal nucleus. When the formation speed of the Cu-MOF crystal nucleus is much faster than its growth speed, small and ample RuCoCu-MOF nanocubes are formed. This distinct nanostructure not only
enlarges its specific surface area but also expedites electrolyte transport at the interfacial microenvironment.

Additionally, Raman spectroscopy (Fig. S7) confirms that the D peak and the G peak in RuCoCu-MOF compared with CoCu-MOF are enhanced and weakened, respectively. And the value of I_D/I_G decreases in the sequence of RuCoCu-MOF > CoCu-MOF > Cu-MOF, indicating that the introduction of heteroatom, especially Ru atom, is conducive to improving the graphitization extents of the material and the conductivity of RuCoCu-MOF [36, 45, 47]. In contrast, RuCoCu-MOF/CF-5 and RuCoCu-MOF/CF-15 were synthesized by changing the doping amount of Ru (Figs. S8-S10). Strikingly, the amount of Ru doping has little effect on their nanorod morphology and crystal structure, but they are all slightly enlarged in size, which is not favorable for the exposure of active sites.

X-ray photoelectron spectroscopy (XPS) was carried out to acquire further insight into the surface chemical state and composition of RuCoCu-MOF/CF, CoCu-MOF/CF, and Cu-MOF/CF. The survey spectrum (Fig. S11) confirms the presence of Ru, Cu, Co, Ru, C, and O elements for RuCoCu-MOF/CF, and further proves the successful preparation of the RuCoCu-MOF/CF catalyst. In the Cu 2p spectrum (Fig. 3a), two peaks at 932.40 eV and 952.22 eV can be assigned to Cu 2p_{3/2} and Cu 2p_{1/2} of Cu^0, respectively, which is mainly due to the existence of the copper foam substrate. The peaks at 934.53 eV and 954.16 eV are ascribed to Cu^{2+} 2p_{3/2} and Cu^{2+} 2p_{1/2}, respectively. Other peaks at 943.79 and 963.09 eV are attributed to satellite peaks. As seen in Fig. 3b, the Co 2p spectrum of RuCoCu-MOF/CF displays two pairs of peaks. The first pair at 782.17 eV and 797.70 eV are allotted to the Co 2p_{3/2} and Co 2p_{1/2} of Co^{2+} species, and the other pair of peaks at 787.13 eV and 803.19 eV belong to satellite peaks. Strikingly, the binding energy ascribed to Co^{2+} in RuCoCu-MOF/CF shifts toward lower binding energy compared to CoCu-MOF/CF, indicating that Co^{δ+} in RuCoCu-MOF/CF has more negative charges, which is favorable for promoting the desorption of H_2. As shown in Fig. 3c, the peaks of RuCoCu-MOF/CF at 462.63 eV and 484.95 eV are attributed to the Ru 3p_{3/2} and Ru 3p_{1/2} orbitals of Ru^0, respectively. And the signals at 465.83 eV and 488.50 eV are indexed to the Ru-O bond [48]. Notably, the binding energy belonging to the Ru-O bond in RuCoCu-MOF/CF is higher than the pure RuO_2 [26], demonstrating that the Ru species has more positive charges and it has a strong electron interaction with Co species. Additionally, the O 1s spectrum (Fig. 3d) of RuCoCu-MOF/CF exhibits a strong peak at 530.57 eV belonging to the Ru-O-Co bond, illustrating Co and Ru atoms for electron transport through the Ru-O-Co bridge [49, 50]. Overall, the Ru dopant in the RuCoCu-MOF exists in the form of Ru-O-Co bonds, and electrons flow directionally from Ru atom to Co atom through the metal-oxygen bridge. This bond-induced effect effectively optimizes the electronic configuration of RuCoCu-MOF, thereby significantly expediting the electrocatalytic reaction kinetics, and enhancing the catalytic performance [48, 51].

### 3.2 Electrocatalytic performance of HER and UOR

To reveal the excellent electrocatalytic activity of the well-designed RuCoCu-MOF/CF self-supported electrodes, the HER test was primarily evaluated at room temperature of 25℃ in the usual three-electrode
system with N$_2$-saturated 1.0 M KOH. As a comparison, commercial Pt/C, CoCu-MOF/CF, RuCu-MOF, Cu-MOF, and Cu(OH)$_2$/CF were tested. Figure 4a exhibits that the RuCoCu-MOF/CF catalyst only acquire a low overpotential of 11.6 mV to drive the current density of 10 mA cm$^{-2}$, which is completely lower than CoCu-MOF/CF (44.1 mV), RuCu-MOF/CF (81.1 mV), Cu-MOF/CF (84.8 mV), and Cu(OH)$_2$/CF (350.7 mV), reflecting that the RuCoCu-MOF/CF presents optimal HER activity. It also exceeds that of commercial Pt/C/CF catalyst (25.6 mV at 10 mA cm$^{-2}$), suggesting that the ultra-low amount of Ru doped CoCu-MOF possesses superior HER activity surpassing that of noble metal catalysts. And the HER activity of RuCoCu-MOF/CF is still better than other counterparts (Fig. 4b) at the higher current density of 100 mA cm$^{-2}$. The above results confirm that the HER activity of the pure Cu-MOF is mediocre, while the doping of Ru has little effect on the activity of the pristine Cu-MOF, as the addition of Ru during the synthesis process is not conducive to the maintenance of the hollow rod structure of the Cu-MOF (Fig. S12). But the introduction of Co activates HER performance and promotes a significant increase in the current density of the catalyst, and further the doping of Ru further improves its HER activity, which is mainly due to the movement of electrons from Ru to Co and Cu atom, optimizing the electronic structure of the catalyst. Simultaneously, motivated by the bond-inducing effect caused by the formed Ru-O-Co bridge, the Ru sites and the optimized Co sites can synergistically favor the adsorption and dissociation of the intermediates, as well as the interfacial mass/charge transfer between the catalyst and the solution, thereby greatly accelerating the water dissociation and the release of hydrogen. Above all, the electrochemical test results confirms that the formation of the Cu-O bond and Ru-O-Cu bond bridge does not improve the properties of the catalysts. But the formation of the Co-O bond optimizes the catalytic activity of CoCu-MOF/CF. Especially the Ru-O-Co bond bridge, as the most active catalytic component of the catalyst, makes the performance of RuCoCu-MOF/CF the best. Notably, the Tafel plot can reflect the kinetics of the HER. Figure 4c shows that RuCoCu-MOF/CF has the lowest Tafel slope (84.1 mV dec$^{-1}$), which is better than commercial Pt/C/CF (106.2 mV dec$^{-1}$) and other comparative catalysts, indicating that RuCoCu-MOF/CF owns the accelerated HER kinetics and its HER process follows the Volmer-Heyrovsky mechanism. In addition, the electric double-layer capacitance ($C_{dl}$) was calculated based on the cyclic voltammetry (CV) curves at different scan rates (Fig. S13), which was then used to evaluate the electrochemical surface area (ECSA) of the catalysts. As summarized in Fig. 4d, RuCoCu-MOF/CF exhibits the highest value of $C_{dl}$ (58.2 mF cm$^{-2}$), indicating that it has the largest electrochemical area to expose more active sites, which is stimulated by its hollow structure, as well as the small and dense nanocubes. The LSV curve of HER was normalized by ECSA value (Fig. S14), and the well-designed RuCoCu-MOF/CF still had the best catalytic activity compared with other comparative samples, proving the trace Ru-doped RuCoCu-MOF/CF has the most excellent HER intrinsic activity. Remarkably, the Nyquist plot (Fig. 4e) indicates that the charge transfer resistance ($R_{ct}$) of RuCoCu-MOF/CF is the smallest among these samples, which also benefited from the constitution of the Ru-O-Co bridge, facilitating the quick charge transfer of RuCoCu-MOF catalyst. In fact, the electrocatalytic properties of RuCoCu-MOF/CF-X (X = 5, 10, 15) with different Ru dosages were also monitored (Fig. S15), the RuCoCu-MOF/CF catalyst with 10 mg Ru dosage has the best catalytic activity, demonstrating that the doping of an appropriate amount of Ru can optimize its catalytic properties. At the same time, under the I-T test
(Fig. 4f), it can be found that there is almost no change in the current density under the 48-hour test, which means that RuCoCu-MOF/CF has excellent stability, and promotes the industrial application of the catalyst for a longer period of time. Additionally, the SEM images and XPS patterns (Fig. S16 and Fig. S17) after the HER test are not much different from those before the reaction, and the excellent durability and stability are attributed to the strong Ru-O-Co bonding and the firm MOF structure after the crystal growth ends. As reflected in Fig. 4g and Table S2, compared with some representative noble metal-doped MOFs catalysts reported so far, the RuCoCu-MOF/CF exhibits the lowest overpotential at η_{10} among them as an outstanding electrocatalyst towards alkaline HER.

The UOR catalytic activity of RuCoCu-MOF/CF was also evaluated in an electrolyte solution consisting of 1.0 M KOH and 0.5 M urea. As summarized in Fig. 5a, RuCoCu-MOF/CF has an ultra-low onset potential of 1.32 V (vs. RHE) for UOR, after which the current gradually increases. And the current density of 10 and 100 mA cm^{-2} can be yielded for RuCoCu-MOF/CF by applying only a potential of 1.35 and 1.50 V, respectively. Noticeably, the UOR overpotential at the same current density (100 mA cm^{-2}) is 136 mV lower than OER at 1.0 M KOH. In addition, the current density of RuCoCu-MOF/CF for UOR is 0.24 times to 0.83 times higher than that of CoCu-MOF/CF, RuCu-MOF/CF, Cu-MOF/CF, and Cu(OH)_{2}/CF at the applied voltage of 1.51 V (Fig. 5b). The excellent UOR properties of RuCoCu-MOF/CF can be displayed in Fig. 5c. The superior UOR activity of RuCoCu-MOF/CF is mainly attributed to the hollow nanorod array exposing more active area and the interfacial bond-induced effect motivated by the as-formed Ru-O-Co bond. Simultaneously, in comparison to the UOR property of RuCoCu-MOF/CF-X (X = 5, 10, 15), the UOR activity of RuCoCu-MOF/CF is still the best when the Ru input is 10 mg (Fig. S18). The Tafel slope can be used to reflect the UOR kinetics of catalysts, as shown in Fig. 5d, the Tafel slope of the RuCoCu-MOF/CF catalyst (106.7 mV dec^{-1}) is much lower than that of other counterparts, indicating that the RuCoCu-MOF/CF catalyst has a fast electron transfer rate and optimal UOR kinetics. Moreover, the CV curves and C_{dl} measurements show (Fig. S19 and Fig. 5e) that the as-prepared RuCoCu-MOF/CF has the largest C_{dl} value (74.2 mF cm^{-2}), which is much higher than that of CoCu-MOF/CF (26.3 mF cm^{-2}), RuCo-MOF/CF (18.9 mF cm^{-2}), and Cu-MOF/CF (17.5 mF cm^{-2}), verifying that RuCoCu-MOF/CF has a larger ECSA. Besides, ECSA-normalized LSV curves of UOR (Fig. S20) show that RuCoCu-MOF/CF still has the most outstanding UOR intrinsic activity. Electrochemical impedance spectroscopy (EIS, Fig. S21) analysis further confirms that RuCoCu-MOF/CF owns minimal charge transfer resistance for UOR, which largely contributes to its brilliant activity. At the same time, RuCoCu-MOF/CF also showed super UOR stability within 48 hours of the I-T test (Fig. 5f). Moreover, after the UOR stability test, the SEM image of RuCoCu-MOF/CF (Fig. S22) shows a slight change in morphology, the hollow rod structure is slightly thickened, and the small cubes are also slightly larger and rounder, which may originate from the metal is partially oxidized in solution, resulting in an oxide layer on the surface during the process of UOR. It can be seen from the XPS spectrum (Fig. S23) after UOR treatment that the peak positions are almost unchanged before and after the reaction, but the oxidation peaks of Cu and Co are significantly enhanced, and the peaks of Ru-O bonds are also prominently reinforced, indicating that the metal is oxidized in RuCoCu-MOF/CF, and the Co species is more easily converted to the active phase Co-O (or Co-OOH) [52], and the O
1s spectrum can see the enhancement of Ru-O-Co bonds, and the Ru-O-Co bridge plays a great role in the catalytic UOR activity. Surprisingly, the UOR activity of RuCoCu-MOF/CF is comparable to or even better than that of the major UOR catalysts reported so far (Fig. 5g and Table S3).

3.3 Urea-assisted water splitting performance

In view of the excellent HER and UOR performance of RuCoCu-MOF/CF electrodes, an energy-efficient electrolyzer device was constructed by coupling RuCoCu-MOF/CF self-supporting electrodes (Fig. 6a). As shown in Fig. 6b, the as-prepared RuCoCu-MOF/CF electrode for HER||UOR electrolyzer only needs a voltage of 1.402 V to reach a current density of 10 mA cm\(^{-2}\), which is the catalyst with the best performance in the alkaline overall water splitting system that has been reported so far (Fig. 6c and Table S4). At the same time, this excellent value also represents the highest performance of overall water splitting under alkaline conditions. Moreover, the electrolyzer composed of RuCoCu-MOF/CF-X (X = 5, 10, 15) still showed the best HER||UOR properties with a feed amount of 10 mg Ru (Fig. S24). The excellent properties of RuCoCu-MOF/CF in HER||UOR system benefit from the hollow nanorods with controllable cavity size composed of nanocubes and the bond-induced effect of the unique Ru-O-Co bridge, optimizing the atomic structure of Ru and Co, and promoting the formation of highly-active sites for HER and UOR. The LSV curve after 4000 CV cycles is demonstrated in Fig. 6d, the LSV curve after 4000 CV cycles has almost no change from the initial curve, and the properties of RuCoCu-MOF/CF remained basically unchanged under 48h IT test (Fig. 6e), indicating that RuCoCu-MOF/CF has outstanding stability and durability, and the RuCoCu-MOF/CF electrode is expected to be an excellent candidate for the HER||UOR energy-saving system. Interestingly, urea-assisted overall water splitting can not only improve the energy-saving effect, but also purify urea-rich wastewater without the need for a more complicated process. As shown in Fig. S25, when the voltage is set to 1.55 V, urea with a concentration of 300 mg/L can be degraded to less than 100 mg/L within 3.5 hours. Therefore, this HER||UOR coupled energy-saving system can accelerate the development of the relationship between water and energy to a sustainable hydrogen economy, and has outstanding potential for practical application.

4. Conclusions

In summary, this work adopts self-sacrificial template strategy to delicately design and synthesize RuCoCu-MOF/CF with a cavity-tunable hollow nanorod structure composed of nanocubes on the CF substrate for HER-coupled UOR. Surprisingly, the RuCoCu-MOF electrocatalyst only needs a voltage of 1.402 V to reach a current density of 10 mA cm\(^{-2}\) in the energy-efficient HER||UOR electrolyzer, this excellent value represents the highest performance of overall water splitting under alkaline conditions. Besides, RuCoCu-MOF/CF has the ultra-low overpotential of 11.6 mV at \(\eta_{10}\) for HER, which is 2.21 times better than that of commercial Pt/C/CF. Simultaneously, the ultra-low onset potential of 1.32 V is also displayed in the RuCoCu-MOF/CF for UOR, significantly outperforming most of the UOR catalysts that have been developed. Notably, the prominent HER and UOR properties of RuCoCu-MOF/CF are mainly due to the following points: 1) The co-introduction of Ru and Co atoms balances the dissolution-coordination
and nucleation-growth processes during the formation of conductive MOFs, resulting in the distinct cavity-tunable hollow RuCoCu-MOF nanorods composed of abundant nanocubes; 2) the doping of trace amounts of Ru further enhances the activity of RuCoCu-MOF/CF and optimizes the intrinsic properties of each active site; 3) the bond-induced effect excited by the Ru-O-Co bridge as the most active catalytic component accelerates the direct interfacial mass and charge transfer between the catalyst and the electrolyte, and promotes the adsorption of intermediates together with water dissociation. This work innovatively proposes an “external and internal dual-controls” strategy for the cavity size and chemical bond bridge, and lays a foundation for the preparation of MOF-based self-supporting electrodes to achieve the efficient hydrogen production and purification of urea-rich wastewater in the future.

Declarations

Author contribution Yilin Wang designed and conducted all the experiments, made the formal analysis, and wrote the original draft; Yunmei Du contributed to the analysis, supervision, and editing; Ziqi Fu and Mengmeng Wang analyzed the data and offered helpful suggestions; Yunlei Fu contributed to the software; Bin Li contributed to the software and sources; Li Wang contributed to the supervision, editing and sources. All authors contributed to the general discussion.

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Conflict of interest The authors declare no competing interests.

Supplementary Information The online version contains supplementary material available at......

References


Scheme

Scheme 1 is available in the Supplementary Files section.

Figures
Figure 1

(a) XRD pattern and (b) FT-IR spectra of RuCoCu-MOF, CoCu-MOF, Cu-MOF, and HHTP, (c-d) SEM images of RuCoCu-MOF/CF, (e) TEM images of RuCoCu-MOF/CF, (f) high-resolution TEM images of RuCoCu-MOF/CF, and (g) EDX elemental mapping images of RuCoCu-MOF/CF.
Figure 2

(a) SEM image and (b) TEM image of Cu-MOF/CF, (c) SEM image and (d) TEM image of CoCu-MOF/CF, (e) SEM image and (f) TEM image of RuCoCu-MOF/CF of RuCoCu-MOF/CF, and (g) schematic illustration of the heterometallic doping on the structural evolution of hollow MOF/CF nanorods.
Figure 3

XPS spectra of (a) Cu 2p, (b) Co 2p, (c) Ru 3p, and (d) O 1s in RuCoCu-MOF/CF, CoCu-MOF/CF, and Cu-MOF/CF.
Figure 4

HER performances of RuCoCu-MOF/CF, CoCu-MOF/CF, RuCu-MOF/CF, Cu-MOF/CF, Cu(OH)2/CF, and Pt/C in 1.0 M KOH: (a) the polarization curves with iR-compensation, (b) the histogram of overpotentials at 10 and 100 mA cm\(^{-2}\), (c) their corresponding Tafel plots, (d) the Cdl measurements of RuCoCu-MOF/CF, CoCu-MOF/CF, RuCu-MOF/CF, and Cu-MOF/CF, (e) their Nyquist plots, (f) the chronoamperometry tests of RuCoCu-MOF/CF at 85.3 mV, and (g) histogram of \(\eta_{10}\) during HER for the as-prepared RuCoCu-MOF/CF catalyst and the recently reported noble metal-doped MOFs electrocatalyst.
Figure 5

UOR performance of RuCoCu-MOF/CF, CoCu-MOF/CF, RuCu-MOF/CF, Cu-MOF/CF, Cu(OH)2/CF in 1.0 M KOH and 0.5 M urea: (a) the polarization curves of RuCoCu-MOF/CF with iR-compensation compared with the OER of 1.0 M KOH, (b) the polarization curves with iR-compensation, (c) the histogram of overpotentials at 10 and 100 mA cm\(^{-2}\), (d) their corresponding Tafel plots, (e) the Cdl measurements of RuCoCu-MOF/CF, CoCu-MOF/CF, RuCu-MOF/CF, and Cu-MOF/CF, (f) the chronoamperometry tests of RuCoCu-MOF/CF at 1.47 V, and (g) histogram of \(\eta_{10}\) during UOR for the as-prepared RuCoCu-MOF/CF catalyst and the recently reported advanced UOR electrocatalyst.
Figure 6

Urea-assisted water splitting tests in 1.0 M KOH + 0.5 M urea. (a) Schematic illustration of the energy-efficient electrolyzer device composed of RuCoCu-MOF/CF||RuCoCu-MOF/CF, (b) the LSV curves of RuCoCu-MOF/CF||RuCoCu-MOF/CF, CoCu-MOF/CF||CoCu-MOF/CF, RuCu-MOF/CF||RuCu-MOF/CF, Cu-MOF/CF||Cu-MOF/CF, and Cu(OH)2/CF||Cu(OH)2/CF with iR-compensation, (c) histogram of $\eta_{10}$ during HER||UOR for the as-prepared RuCoCu-MOF/CF catalyst and the recently reported MOF-material.
electrocatalyst under the alkaline conditions, (d) the LSV curves of RuCoCu-MOF/CF||RuCoCu-MOF/CF before (black) and after (red) 4,000 CV cycles, (e) the stability tests of RuCoCu-MOF/CF|| RuCoCu-MOF/CF at 1.48 V.

Supplementary Files

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- SupplementaryMaterials.docx
- scheme1.png