Single-atom catalysts (SACs) exhibit intriguing catalytic performance owing to their maximized atom utilizations and unique electronic structures. However, the reported strategies for synthesizing SACs generally have special requirements for either the anchored metals or the supports. Herein, we report a universal approach of electrochemical deposition that is applicable to a wide range of metals and supports for the fabrication of SACs. The depositions were conducted on both cathode and anode, where the different redox reactions endowed the SACs with distinct electronic states. The SACs from cathodic deposition exhibited high activities towards hydrogen evolution reaction, while those from anodic deposition were highly active towards oxygen evolution reaction. When cathodically- and anodically-deposited Ir single atoms on Co$_{0.8}$Fe$_{0.2}$Se$_2$@Ni foam were integrated into a two-electrode cell for overall water splitting, a voltage of 1.39 V was required at 10 mA cm$^{-2}$ in alkaline electrolyte.
Single-atom catalysts (SACs), with uniform isolated metal atoms anchored on supports, have received wide interests in recent years due to their extraordinary catalytic performance towards various reactions such as water splitting, oxygen reduction, CO₂ hydrogenation, and methane conversion. As the supported metals are downsized to the minimum, SACs reach the utmost atom-utilization efficiency. Moreover, the atomically dispersed metal species usually exhibit unique electronic states due to distinctive coordinated environments, strong metal-support interactions, and quantum size effects. In such catalysts, the identical geometric structure of active centers also offers an ideal platform for understanding catalytic mechanisms at the atomic-scale level.

SACs are not readily available since the individual metal atoms incline to diffuse and aggregate into clusters during the synthesis in order to lower surface energy. The last decade has witnessed the development of strategies for fabricating SACs. These strategies include chemical vapor deposition, atomic layer deposition, pyrolysis, wet chemistry methods, photochemical methods, and atom trapping. However, these strategies usually have special requirements for either the atomized metals or the supports. For instance, the pyrolysis method generally yielded carbon-based supports because of the decomposition of metal-organic complexes. Moreover, wet chemistry methods are commonly a trial-and-error process, since no consensus has been reached on the synthetic mechanism. The atom trapping not only required the mobile metal species, but also further varied the concentration of Ir precursors, the number of the supported metals or the supports. For Ir single atoms anchored on supports, have received wide interests in recent years due to their extraordinary catalytic performance.

Here, we report electrochemical deposition as a general strategy to produce SACs. More than 30 different SACs are successfully obtained from cathodic or anodic deposition just by varying metal precursors and supports. Intriguingly, the cathodically and anodically deposited single atoms for the same metal exhibit different electronic states. Moreover, electrocatalytic tests demonstrate that these SACs obtained from cathodic deposition show a great potential for catalyzing hydrogen evolution reaction, while those from anodic deposition are promising candidates for oxygen evolution catalysts. Specially, Ir single atoms on Co₉₉₈Fe₀₀₂Se₂ nanosheets from the cathodic deposition require only an overpotential of 8 mV to reach a current density of 10 mA cm⁻² for alkaline hydrogen evolution reaction. Furthermore, a two-electrode cell assembled by cathodically and anodically deposited Ir single atoms on Co₉ₙ₀Fe₀₀₂Se₂@Ni foam exhibits a voltage of 1.39 V at 10 mA cm⁻² for overall water splitting in alkaline electrolyte.

**Results**

**Synthesis and characterizations of single-atom catalysts.** To demonstrate the synthetic procedure, we take the deposition of Ir single atoms on Co(OH)₃ nanosheets as an example. Specially, we used a standard three-electrode system, where Co(OH)₂ nanosheets were loaded onto a glassy carbon electrode as the working electrode (Supplementary Fig. 1). Soluble metallic salts with a low concentration, 100 μM IrCl₄ in this case, were added into the 1 M KOH electrolyte as the metal precursors. The depositing potential was set from 0.10 to −0.40 V in cathodic deposition and from 1.10 to 1.80 V in anodic deposition for one scanning cycle, with a scanning rate of 5 mV s⁻¹. The scanning cycle was repeated for ten times to obtain C-Ir₁/Co(OH)₂ from the cathode and three times to obtain A-Ir₁/Co(OH)₂ from the anode. Transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns show the absence of Ir-based clusters or nanoparticles in the as-deposited samples (Supplementary Fig. 2). The energy-dispersive X-ray elemental mapping revealed that Ir species of both samples were homogeneously dispersed on the substrates (Supplementary Fig. 3). The aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) images of C-Ir₁/Co(OH)₂ and A-Ir₁/Co(OH)₂ further demonstrated that isolated Ir atoms were uniformly distributed on the substrates (Fig. 1, a, b). The mass loadings of Ir in C-Ir₁/Co(OH)₂ and A-Ir₁/Co(OH)₂ were determined to be 2.0 and 1.2 wt%, respectively, by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Supplementary Table 1).

To determine the electronic structures and coordination environment of Ir atoms in the as-deposited SACs, we performed X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurements. Figure 1c shows the Ir L₃-edge XANES spectra of C-Ir₁/Co(OH)₂ and A-Ir₁/Co(OH)₂. The white line intensity for C-Ir₁/Co(OH)₂ lay between that for IrCl₃ and IrO₂, indicating that the oxidation state of Ir was between +3 and +4. By comparison, the white line intensity for A-Ir₁/Co(OH)₂ was higher than that for IrO₂, yielding a higher oxidation state of Ir than +4. The oxidation states of Ir in both samples were also confirmed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 4). As shown in the EXAFS spectra of C-Ir₁/Co(OH)₂, two peaks appeared at 1.97 Å and 2.32 Å, which were contributed to the first coordination shell of Ir-O and Ir-Cl, respectively (Fig. 1d). The fitting results indicated a coordination number (CN) of 3.3 for Ir-O contribution and 3.1 for Ir-Cl contribution (Supplementary Fig. 5 and Supplementary Table 2). No other typical peaks for Ir-Cl contribution at 2.71 Å were observed, revealing the atomic dispersion of Ir atoms throughout the whole C-Ir₁/Co(OH)₂. In the EXAFS spectra of A-Ir₁/Co(OH)₂, only one prominent peak showed at 2.01 Å for Ir-O contribution (Fig. 1d). The fitting results indicated a CN of 5.8 for Ir-O contribution (Supplementary Fig. 5 and Supplementary Table 2). The absence of peaks for Ir-Cl contribution also confirmed the atomically dispersed Ir in A-Ir₁/Co(OH)₂.

**Synthetic mechanism.** We propose a typical schematic for cathodic and anodic deposition of Ir species in KOH electrolyte according to the above results. For the cathodic deposition, iridium cations were driven towards the cathode by the applied electric field and deposited on the supports (Fig. 2a). Based on the CN of 3.1 for Ir-Cl contribution, we suppose that the cations were IrCl₄⁺. According to the CN of 3.3 for Ir-O contribution, IrCl₄⁺ cations were proposed to coordinate with three O atoms on Co (OH)₂. Moreover, the deposition of IrCl₄⁺ was accompanied with a reduction of Ir ions under the negative electric field, giving rise to the oxidation state of Ir in C-Ir₁/Co(OH)₂ lower than +4. For the anodic deposition, iridium anions are driven by the electric field towards the anode (Fig. 2b). The iridium anions were likely derived from the combination of Ir₄⁺ in the precursors with OH⁻ in the electrolyte. Ultraviolet–Visible (UV) adsorption spectrum of the 1 M KOH electrolyte containing 100 μM IrCl₄ showed a prominent peak at 318 cm⁻¹, corresponding to the adsorption of Ir(OH)₄⁺ ( Supplementary Fig. 6)¹¹. This suggested that Ir(OH)₄⁺ acts as the depositing species for anodic deposition, which is in accordance with the EXAFS result of A-Ir₁/Co(OH)₂ with a CN of 5.8 from Ir-O contribution. Meanwhile, this anodic deposition was coupled with an oxidation process of the anions, resulting in the oxidation state of Ir in A-Ir₁/Co(OH)₂ higher than +4.

To get an insight into the deposition mechanism of SACs, we further varied the concentration of Ir precursors, the number of scanning cycles, and the scanning rate. Cathodic depositions were
**Fig. 1** Structural characterizations of Ir single atoms on Co(OH)₂ nanosheets. a, b HAADF-STEM images of C-Ir₁/Co(OH)₂ (a) and A-Ir₁/Co(OH)₂ (b). Singly dispersed Ir atoms are indicated by yellow circles. c, d Normalized XANES (c) and EXAFS (d) spectra at the Ir L₃-edge for C-Ir₁/Co(OH)₂ and A-Ir₁/Co(OH)₂. Ir powder, IrCl₃, and IrO₂ were used as references.

**Fig. 2** Electrochemical deposition mechanism. a, b Schematic of cathodic (a) and anodic (b) deposition of Ir species. The yellow, green, red, and white spheres represent Ir, Cl, O, and H atoms, respectively. A standard three-electrode system was used, with Co(OH)₂ nanosheets loaded on a glassy carbon electrode as the working electrode (WE), a carbon rod as the counter electrode (CE), and an Ag/AgCl electrode as the reference electrode (RE). c, d Ir mass loadings as a function of Ir concentration in the 1 M KOH electrolyte for cathodic (c) and anodic (d) deposition. The scanning cycle number was kept at ten for cathodic deposition and three for anodic deposition. The color gradient from yellow to white indicates the transition from single atoms to clusters with increasing Ir concentration. The inset images correspond to the HAADF-STEM images of the samples obtained at a certain concentration. The areas in white circles indicate the agglomerations of single atoms to form clusters.
conducted in 1 M KOH electrolytes via changing the Ir concentration from 50 to 300 μM for ten scanning cycles. As shown in Fig. 2c, the mass loadings of Ir species constantly increased with the growing Ir concentration. When the Ir concentration was increased to 150 μM, Ir single atoms were still obtained at a mass loading of 3.5%. When the concentration was further raised to 200 μM, Ir clusters appeared at a mass loading of 4.7%. As such, for the formation of SACs, there exists an upper limit of mass loadings between 3.5% and 4.7%. When we changed the scanning cycles at the Ir concentration of 100 μM, the upper limit of mass loadings lay between 3.3% and 3.9% for the formation of SACs (Supplementary Fig. 7a). Moreover, the Ir mass loadings increased with decreasing scanning rate, where the upper limit of mass loadings lay between 2.6% and 3.6% for the formation of SACs (Supplementary Fig. 8a). This upper limit was roughly consistent with those obtained via varying the Ir concentration and the scanning cycles. For the anodic depositions, similar phenomena were also observed, whenever the Ir concentration, the scanning cycle, and the scanning rate were changed (Fig. 2c and Supplementary Figs. 7b and 8b). These electrochemical deposition processes resemble the molecular mechanism of nucleation in the solution-phase synthesis, where the support can be regarded as the solvent. In this case, the upper limit of mass loading for SACs corresponds to the level of minimum supersaturation on the support. When the mass loadings of metal on the support exceed the minimum supersaturation level, singly dispersed metal atoms start to nucleate into clusters. Therefore, the formation of SACs strongly relies on controlling the mass loading below the level of minimum supersaturation. Moreover, since the isolated single atoms are usually anchored to the support through defects or strong metal-support interaction, the value of minimum supersaturation might be relevant to the number of depositing sites such as vacancies, edges, or steps.

To test the generality of this method for synthesizing SACs, we replaced the Ir precursor with other precursors of 4d and 5d metals, including Ru, Rh, Pd, Ag, Pt, and Au. HAADF-STEM images illustrated that all these metal species were successfully deposited and atomically dispersed on Co(OH)2 nanosheets under similar depositing conditions (Fig. 3, a, b). The atomic dispersion of metal species was further supported by in-situ diffuse reflectance infrared Fourier transform (DRIFT) experiments using CO as a probe molecule (Supplementary Fig. 9). Besides, the cathodic and anodic deposition of the same precursor resulted in different oxidation states of the deposited species (Supplementary Fig. 10). To further extend the applicability of this method, we utilized the same depositing method and obtained SACs comprising of other 3d and 4d transitional metals on nitrogen-doped carbon (N-C) support as well (Supplementary Fig. 11). We also deposited Ir single atoms onto other supports following the same procedure of synthesizing Ir1/Co(OH)2. These supports include MnO2 nanosheets, MoS2 nanosheets, Co0.8Fe0.2Se2 nanosheets, and N-C (Supplementary Fig. 12). Likewise, the Ir single atoms were successfully deposited on these supports.
through the cathodic or anodic deposition (Fig. 3, c, d). The absence of metal-metal bond in the EXAFS spectra further confirmed the atomic dispersion of these single atoms, in good agreement with the HAADF-STEM results (Supplementary Fig. 13). To be noted, due to the applied oxidative potential, the surface of these substrates underwent reconstructions during the anodic deposition process. The Co(OH)2, MnO2, MoS2, and Co0.8Fe0.2Se2 substrate was partially transferred to oxyhydroxides, amorphous phase, oxides, and oxyhydroxides, respectively, leading to vague lattice fringes in the HAADF-STEM images (Supplementary Fig. 2d and Supplementary Fig. 14). In addition, we have also applied this deposition method in acid electrolyte. Ir single atoms were successfully obtained from both cathodic and anodic deposition in 0.5 M H2SO4 (Supplementary Fig. 15).

Therefore, the electrochemical deposition is a universal method that is applicable to a wide range of metals and supports for the fabrication of SACs.

Catalytic properties towards water splitting. Based on the library of obtained SACs, we searched for efficient catalysts towards water splitting, one of the most promising reactions for renewable hydrogen production. This chemical process consists of two half-reactions, including hydrogen evolution (HER) and oxygen evolution (OER) reactions. The polarization curves of cathodically deposited SACs for HER and anodically deposited SACs for OER were recorded in 1 M KOH electrolyte (Fig. 4, a, b). The commercial Pt/C and IrO2 were used as references for HER and OER, respectively. The overpotentials at 10 mA cm−2 for HER (c) and OER (d) are shown. Strikingly, C-Ir1/Co0.8Fe0.2Se2@Ni foam delivered an overpotential of 8 mV at a current density of 10 mA cm−2, comparable to the state-of-the-art HER catalysts in alkaline media (Supplementary Table 3). Towards OER, A-Rh1/Co(OH)2, A-Ag1/Co(OH)2, A-Ir1/Co(OH)2, and A-Ir1/Co0.8Fe0.2Se2 exhibited higher activities towards HER relative to the commercial Pt/C (Fig. 4c). Chronopotentiometric curves of Ir1/Co0.8Fe0.2Se2@Ni foam for overall water splitting at 10, 100, and 500 mA cm−2 for 100 h.
only needed an overpotential as low as 230 mV to reach 10 mA cm$^{-2}$, which was 135 mV lower than that of IrO$_2$ (Fig. 4d). The prominent HER and OER activity of Ir single atoms on Co$_{0.8}$Fe$_{0.2}$Se$_2$ might originate from highly efficient charge transfer ability of the support and strong metal-support interaction (Supplementary Fig. 17)23-28.

Inspired by the high activities of as-deposited SACs towards HER and OER, we assembled C-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$ and A-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$ into a two-electrode cell for overall water splitting. The Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$ electrolyzer only needed a cell voltage of 1.48 V to reach a current density of 10 mA cm$^{-2}$ and maintained the performance over 30 h (Supplementary Fig. 18). In order to improve the overall water splitting activity, the Co$_{0.8}$Fe$_{0.2}$Se$_2$ nanosheets were further in-situ grown on Ni foam (denoted as Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam) to replace the glassy carbon electrode for more catalyst loading, higher conductivity, and better adhesion of the catalysts (Supplementary Fig. 19)29. Consequently, the overpotential needed to reach 10 mA cm$^{-2}$ was further decreased to 4 mV for C-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam during HER, and to 140 mV for A-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam during OER, respectively (Supplementary Fig. 20, a, d). After 20 h of reaction, C-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam and A-Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam were assembled into a two-electrode cell (denoted as Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam) for overall water splitting (Supplementary Fig. 21a). Figure 4e shows the polarization curves for the Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam electrolyzer in comparison with the Pt/C-IrO$_2$ coupled electrolyzer. For Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam, only a cell voltage of 1.39 V was required to reach a current density of 10 mA cm$^{-2}$, substantially lower than that (1.57 V) for the Pt/C-IrO$_2$ electrolyzer (Supplementary Fig. 21b). Moreover, the Faradaic efficiency of the two-electrode cell was estimated to be >99% towards both HER and OER, indicating that the current density only derived from water splitting (Supplementary Fig. 21, c, d). Notably, Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam readily drove the cell to a current density as high as 500 mA cm$^{-2}$ at a voltage of only 1.62 V, which benefits for practical application in industry30. To the best of our knowledge, Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam outperformed all the reported electrocatalysts for overall water splitting in alkaline electrolyte up to date (Supplementary Table 4). Furthermore, Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam electrolyzer maintained its performance for over 100 h at a wide range of current densities in the long-term durability tests (Fig. 4f). Structural characterizations showed that Ir$_1$/Co$_{0.8}$Fe$_{0.2}$Se$_2$/Ni foam showed no obvious change after the durability tests (Supplementary Fig. 22). The synthesis of N-C was based on a previously reported method31. Typically, Zn(NO$_3$)$_2$·6H$_2$O (1.68 g) was dissolved in 80 mL of methanol. A mixture of 2-methylimidazole (3.70 g) and methanol (80 mL) was added into the above solution under vigorous stirring for 2 h. The products were separated by centrifugation and washed three times with methanol. Then the as-obtained products were washed with methanol and ethanol for several times. The final products were dried at 40 °C under vacuum overnight.

Methods

Synthesis of Co(OH)$_2$ nanosheets. Co(OH)$_2$ nanosheets were synthesized using a modified co-precipitation method31. In a typical procedure, CoCl$_2$·6H$_2$O (2 mmol), NaCl (10 mmol), and hexamethylenetetramine (12 mmol) were dissolved in a mixture of deionized water (200 mL) and ethanol (20 mL). The solution was magnetically stirred at 90 °C for 2 h, and cooled down to room temperature. The as-obtained products were washed three times with deionized water and ethanol. The final products were dried at 40 °C under vacuum overnight.

Synthesis of MnO$_2$ nanosheets. In the synthesis of MnO$_2$ nanosheets, 0.04 g of MnCl$_2$·4H$_2$O was dissolved in 10 mL of ethanolamine under vigorous stirring at room temperature, followed by adding 10 mL of deionized water. Then, the mixture was stirred at room temperature for 24 h. The obtained precipitates were washed with deionized water and ethanol. The final products were dried at 40 °C under vacuum overnight.

Synthesis of Co$_{0.8}$Fe$_{0.2}$Se$_2$ nanosheets. The synthesis of Co$_{0.8}$Fe$_{0.2}$Se$_2$ nanosheets was based on the selenization of cobalt-iron hydrides34. First, CoCl$_2$·6H$_2$O (1.6 mmol), FeCl$_3$ (0.4 mmol), NaCl (10 mmol), and hexamethylenetetramine (12 mmol) were dissolved in a mixture of deionized water (200 mL) and ethanol (20 mL). The solution was magnetically stirred at 90 °C for 2 h, and cooled down to room temperature. The as-obtained products were washed three times with deionized water and ethanol. Next, the products were dispersed in a mixture of Se (3.75 mmol), NaOH (7.5 mmol), hydrazine (0.14 mL), and DMF (25 mL) for selenization. The mixed solution was finally transferred into a 50-mL autoclave. After keeping at 180 °C for 1 h, the as-obtained Co$_{0.8}$Fe$_{0.2}$Se$_2$ nanosheets were obtained. The molar ratio of CoFe was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a value of 0.78:0.22. The growth of Co$_{0.8}$Fe$_{0.2}$Se$_2$ nanosheets on Ni foam followed a two-step procedure. In the first stage, cobalt-iron hydrides were in-situ grown on Ni foam. Typically, CoCl$_2$·6H$_2$O (1.6 mmol), FeCl$_3$ (0.4 mmol), NaCl (10 mmol), and hexamethylenetetramine (12 mmol) were dissolved in a mixture of deionized water (200 mL) and ethanol (20 mL). Then, acid-treated Ni foam (1 cm × 2 cm) was added into the mixture. Next, cobalt-iron hydrides were in-situ grown on Ni foam under magnetic stirring at 90 °C for 2 h. In the second step, the as-obtained product was further selenized. Typically, the cobalt-iron hydrides@Ni foam was transferred into a 50-mL autoclave containing a mixture of Se (3.75 mmol), NaOH (7.5 mmol), hydrazine (0.14 mL), and DMF (25 mL) for selenization. The autoclave was kept at 180 °C for 1 h and then cooled down to room temperature. The final product was
washed with ethanol for three times and dried for later use. The mass loadings of Co0.8Fe0.2Se2 nanosheets on Ni foam was determined to be 1 mg cm⁻² by ICP-AES.

**Synthesis of SACs.** Electrochemical depositions of single-atom M (M = Ir, Ru, Rh, Pd, Ag, Pt, Au, Fe, Co, Ni, Zn, V, Cr, Mn, and Cu) on supports were conducted using a linear sweep voltammetry method. The depositions were conducted in a standard three-electrode system. A carbon rod was used as the counter electrode. An Ag/AgCl electrode was used as the reference electrode. The SACs were deposited on the working electrode. The as-prepared Co(OH)₂ nanosheets, MnO₂ nanosheets, Mn₂O₃ nanorods, and Co₃O₄ nanowires were first mixed with sodium carboxymethylated active carbon. Then the mixture was loaded onto the glassy carbon electrode by Nafion with a yield loading of 0.28 mg cm⁻² as the working electrodes. N-C was loaded onto the glassy carbon electrode by Nafion with a yield loading of 0.56 mg cm⁻² as the working electrode. Co₃O₄/Se-Ni foam was directly used as the working electrode. The electrocatalytic current was measured after 15 s and fixed for further analysis of the electrochemical behavior of Ir single atoms. The Ir was also loaded in acid medium using 0.5 M H₂SO₄ containing 100 μM IrCl₄ as the precursors, the electrolyte, and N-C as the support.

**XAFS measurements.** XAFS spectra at Ir L₃-edge were obtained at the BL14W1 beam line of Shanghai Synchrotron Radiation Facility operated at 3.5 GeV under “top-up” mode with a constant current of 220 mA. The XAFS data of C-Ir(CO)₃ and A-Ir(CO)₃ were recorded under fluorescence mode with a 32-element Ge solid-state detector. The energy was calibrated according to the absorption edge of pure Ir powder. Athena and Artemis codes were used to extract the data and fit the profiles. For the XANES part, the experimental absorption coefficients as a function of energy (μ(E)) were processed by background subtraction and normalization procedures. We refer to this process as “normalized absorption”.

For the EXAFS part, the Fourier-transformed data in R space were analyzed by applying the first shell approximation or metallic Ir model for the Ir-O bond-length. The passive electron factors, S₂, were determined by fitting the experimental Ir powder data and fixing the Ir-Or-Ir coordination number (CN) to be 12. The determined factors were fixed for further analysis of the measured samples. Other parameters such as CN, bond distance (R), and Debye-Waller (D. W) factor around the adsorbed atoms were allowed to vary during the fitting process. XAFS spectra of other SACs were obtained at the 1W1B beam line of Beijing Synchrotron Radiation Facility.

**In-situ DRIFT.** In-situ diffuse reflectance infrared Fourier transform (DRIFT) experiments of CO adsorption were conducted on a Fourier transform infrared spectrometer (TENSOR II Sample Compartment RT-DLaTGS). The DRIFT experiments of CO adsorption were conducted on a Fourier transform infrared spectrometer (TENSOR II Sample Compartment RT-DLaTGS). The DRIFT experiments of CO adsorption were conducted on a Fourier transform infrared spectrometer (TENSOR II Sample Compartment RT-DLaTGS).

**Electrochemical measurements.** An electrochemical workstation (CHI 660E, Shanghai CH Instruments) was used to measure the electrocatalytic properties of the samples. HER and OER electrocatalysis were measured in a standard three-electrode system at room temperature. The glassy carbon electrode loaded with the as-obtained catalysts was used as the working electrode. A carbon rod was used as the counter electrode. An Ag/AgCl electrode was used as the reference electrode. The polarization curves were obtained using a linear sweep voltammetry method. All potentials unless specially mentioned in this work were measured against the Ag/AgCl electrode and converted to reversible hydrogen electrode (RHE) scale by E (vs. RHE) = E (vs. Ag/AgCl) + 0.194 V + 0.059 pH V, where 0.194 V was obtained by calibrating the Ag/AgCl electrode against the RHE in 0.5 M H₂SO₄. The calibration was carried out using a three-electrode system at room temperature. The glassy carbon electrode loaded with the as-obtained catalysts was used as the working electrode. A carbon rod was used as the counter electrode. An Ag/AgCl electrode was used as the reference electrode. The polarization curves were recorded from 0.0 to −0.40 V with a sweeping rate of 5 mV s⁻¹ in hydrogen-saturated 1 M KOH electrolyte. The polarization curves were recorded from 1.10 to 1.80 V with a sweeping rate of 5 mV s⁻¹ in oxygen-saturated 1 M KOH electrolyte. The data that support the findings of this study are available from the corresponding author on reasonable request.
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Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to S.Z. or J.Z.

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