Molecularly well-defined Ni sites at heterogeneous interfaces were derived from the incorporation of Ni\(^{2+}\) ions into heteroatom-doped graphene. The molecular Ni sites on graphene were redox-active. However, they showed poor activity toward oxygen evolution reaction (OER) in KOH aqueous solution. We demonstrated for the first time that the presence of Fe\(^{3+}\) ions in the solution could bond at the vicinity of the Ni sites with a distance of 2.7 Å, generating molecularly sized and heterogeneous Ni-Fe sites anchored on doped graphene. These Ni-Fe sites exhibited markedly improved OER activity. The Pourbaix diagram confirmed the formation of the Ni-Fe sites and revealed that the Ni-Fe sites adsorbed HO\(^{-}\) ions with a bridge geometry, which facilitated the OER electrocatalysis.

**RESULTS**

**Heterogenization of molecular Ni\(^{2+}\) ions**

HG was synthesized from graphene oxides and thiourea in a previously developed hydrothermal method. The as-prepared HG contained sulf oxide groups that could be the main coordination sites for transition metal ions (23). Ni(acac\(_2\)) provided Ni\(^{2+}\) ions, which interacted with HG under mild conditions and were immobilized on HG (denoted as HG-Ni; details are provided in Materials and Methods). The transmission electron microscope (TEM) images showed that the two-dimensional HG-Ni structures contained substantial wrinkles and scrolls, which were
the characteristics of graphene (Fig. 1A and fig. S1). On the graphene layers, the crystal lattices of Ni oxides were not observed. However, energy-dispersive x-ray (EDX) spectroscopy indicated a clear and uniform distribution of Ni, implying that the Ni sites in HG-Ni could be at molecular scales (figs. S2 and S3). The Ni signal was not detected on the HG precursor by EDX.

Figure 1B presents the normalized Ni K-edge x-ray absorption spectroscopy (XAS) data of the Ni(acac)2 precursor and HG-Ni. The inset shows the expanded pre-edge region. The relative intensity of the pre-edge peak is closely related to the local geometry of Ni sites (32, 33). From Ni(acac)2 to HG-Ni, the pre-edge peak of Ni sites only increased slightly, suggesting the similar coordination geometry of Ni sites in Ni(acac)2 and HG-Ni. Because previous single-crystal x-ray diffraction measurements showed that Ni(acac)2 has a distorted octahedral geometry (34), it was thus suggested to retain the distorted octahedral geometry of Ni sites in HG-Ni. Besides, the pre-edge energy shifted very slightly [-0.08 eV, from Ni(acac)2 to HG-Ni], which also reflected the almost equivalent ligand field at the two Ni sites (35). Based on the rising-edge energy, the oxidation state of Ni sites (+2) in HG-Ni was barely altered. In the Fourier-transformed extended x-ray absorption fine structure (EXAFS; Fig. 1C) analysis, the bond length of the inner shell of Ni centers (that is, Ni–O bonds) showed a minor increase. However, the outer shell changed significantly based on the peak at a radial distance ($R'$) of 2.68 Å, confirming the bonding of Ni$^{2+}$ ions with HG (23). The conjugation process was also investigated by density functional theory (DFT) calculations. In a stable model (Fig. 1D), it was found that at the Ni center, four O-donor atoms of two acetylacetonate ligands occupied the equatorial plane. At the axial positions, the Ni center interacted with HG through the O atoms of the doped sulfoxide group, which thus enabled the immobilization of Ni$^{2+}$ ions. The distance between the Ni atom and the O atom of the sulfoxide group was theoretically found to be 2.87 Å, which reflected the newly occurred peak (2.68 Å) in the HG-Ni EXAFS data. In addition, the Fourier transform infrared (FTIR; fig. S4) spectra exhibited a characteristic vibration of Ni(acac)2 at 2990 cm$^{-1}$. This characteristic vibration was caused by its methylene groups. The FTIR signal of the methylene groups on the HG-Ni was also observed at 2973 cm$^{-1}$. This further supported the idea that Ni(acac)2 did not decompose into Ni oxides in the conjugation procedures and that the Ni sites in HG-Ni were molecularly well-defined. The negative shift of the peak position indicated the decreased electron density in the methylene groups. These results might confirm the bonding of Ni$^{2+}$ ions with HG. The electron distribution was thus altered in the neighboring groups of Ni$^{2+}$ ions. From Ni(acac)2 to HG-Ni, we observed a shift of Ni-to-ligand charge transfer band in the ultraviolet (UV)–visible spectra (fig. S5). This also provided support over the change of electron distribution.

**Electrochemical investigations**

Cyclic voltammetry (CV) of HG-Ni was conducted in 1 M KOH using common glassware as the electrochemical cell (Fig. 2A and fig. S6). In the initial scan, the HG-Ni showed a pair of redox peaks at 1.3 to 1.4 V [all potentials were quoted against the reversible hydrogen electrode (RHE) unless stated otherwise], corresponding to the typical Ni$^{2+/3+}$ couple (36–38). At higher potentials, HG-Ni delivered an insignificant OER current. Throughout the continuous CV scanning, both the currents of the Ni$^{2+/3+}$ redox and OER first increased and then stabilized.
after 30 cycles. As previously reported, KOH solutions could etch glassware to release trace Fe species, which were reactive to some Ni-based structures, for example, Ni(OH)2 and NiO. To verify whether the Fe species could interact with HG-Ni, CV of HG-Ni was conducted in a purified KOH solution without Fe species in a plastic vessel. The redox currents of Ni2+/3 exhibited little variation, and OER currents remained small during the CV cycles (Fig. 2B). Accordingly, it was inferred that the trace Fe species of KOH solution could cause a structural evolution of HG-Ni and serve as an important determinant to OER activity. We further investigated the influence of the Fe quantity on OER activity by the stepwise addition of FeCl3 to the 1 M KOH solution. As gained from the CV measurements, the addition of FeCl3 clearly improved the OER activity of HG-Ni. With the increase in the content of FeCl3 from 2.4 to 12 μM, the improvement was observed to be significant initially and then gradually turned to be very moderate (Fig. 2C). Therefore, we used 1 M KOH containing 12 μM FeCl3 to study the structure evolution of Ni and Fe sites in the following experiments. Figure 2E presents a typical variation of OER currents on HG-Ni after continuous CV scanning in the 1 M KOH + 12 μM FeCl3 solution (after reaching the steady state, the electrocatalyst on the glassy carbon electrode (GCE) was denoted as HG-NiFe; for comparison, in the case of Fig. 2A, the electrocatalyst at the steady state was denoted as HG-NiFe, which contains much less Fe). CV of HG-NiFe was also conducted in a fresh 1 M KOH solution, and it exhibited little difference compared to the one collected in the KOH/FeCl3 solution (fig. S7), suggesting that the activity comes from the heterogeneous structure. The OER products on HG-NiFe were analyzed by gas chromatography (fig. S8). O2 was the only gaseous product and it was produced with Faradic efficiencies (FEs) of 100% at potentials from 1.54, 1.58, and 1.62 to 1.66 V. In addition, long-term measurement indicated the good stability of HG-NiFe for OER electrocatalysis (fig. S9).

To reduce the influence of metal redox and the capacitance currents of HG-NiFe on OER activity, we conducted linear scanning voltammogram
the TOF was calculated to be 0.53 s−1 in 1 M KOH, and the iR-corrected polarization curve was collected (Fig. 3A). HG-NiFe afforded an OER onset potential of 1.54 V (defined as the potential at 10 mA cm−2), whereas the value was 1.6 V on HG-NiFe0. Correspondingly, the Tafel slope increased from 39 to 59 mV dec−1 (Fig. 3B). The intrinsic OER activity of HG-NiFe was determined by TOFs, which were obtained by normalizing the OER currents with electroactive metal sites (Fig. 3C). At η = 0.35 V, the TOF was calculated to be 0.53 s−1, which was almost 10-fold higher than that of HG-NiFe0. (For HG-Ni, it was difficult to obtain the accurate value of TOF because of the trivial OER currents. However, its TOF should be very low.) The TOF of HG-NiFe was also increased twofold compared to our previously reported molecular Co sites (0.27 s−1) (23).

**Formation of molecular Ni-Fe dual sites**

The TEM images revealed the graphene structure of HG-NiFe, and the EDX results indicated the uniform distribution of Ni and Fe on the graphene layers (fig. S10). None of the Ni/Fe hydroxides (or oxides) were observed in HG-NiFe (fig. S11). The x-ray diffraction pattern showed only the graphite (002) and (111) facets (fig. S12). We also used ethylenediaminetetraacetic acid (EDTA) disodium to treat the HG-NiFe surface. EDTA is known as a strong ligand for metal cations, which should readily chelate Ni or Fe ions. After the HG-NiFe surface was immersed in 2 mM EDTA solution for 12 hours under ambient environment, the metal redox of HG-NiFe became featureless, as shown by CV measurements, and the surface was OER-inert, indicating that the metal sites were removed from HG. In UV-visible spectra, the resultant EDTA solution exhibited a weak absorption peak at 590 nm, attributed to the ligands coordinating to FeCl3. The Ni-Fe distance in this model was bonded at the neighboring sites of Ni centers in HG-NiFe. The formation of dual Ni-Fe sites was investigated using DFT calculations (fig. S16). Because the formation process was realized in the alkaline solution, we considered that a fraction of acetylacetonate ligands at Ni sites of HG-Ni might be replaced by HO− ions. In a stable model, it was found that the O atoms of HO− ions at Ni sites also served as the ligands coordinating to FeCl3. The Ni-Fe distance in this model was calculated to be 2.73 Å, which was consistent with EXAFS results of Ni and Fe sites. In the OER process, the residual ligands on the Ni-Fe sites (acetylacetonates or chloride ions) could still be labile to provide the open sites for the further adsorption of HO− ions as OER reactants.

**Adsorption of HO− ions at Ni-Fe sites**

We investigated the adsorption of HO− ions, which were the reactants in OER, at the Ni-Fe sites of HG-NiFe. HG-Ni and HG-NiFe0 were also examined as control samples. Despite the immobilized states of Ni-Fe or Ni sites on graphene, their steady redox currents all exhibited linear dependence on the square root of potential scan rates in CVs (5 to 700 mV s−1; figs. S17 to S19). This revealed that the rate-limiting step of metal redox was controlled by the mass diffusion from the electrolyte to the electrode. In alkaline solutions, the redox of Ni-Fe or Ni sites was
typically coupled with the transfer of \( \text{HO}^- \) ions \( \left( \text{26, 29, 37} \right) \). The redox constants \( \left( k_s \right) \) were determined by Laviron’s method \( \left( \text{43} \right) \). It showed that the \( k_s \) of HG-NiFe \( \left( 0.79 \text{ s}^{-1} \right) \) was lower than that of HG-Ni \( \left( 0.92 \text{ s}^{-1} \right) \), because the redox kinetics of the metal sites was determined by the diffusion of \( \text{HO}^- \) ions from electrolytes to electrodes and coupling with the metal sites. The relatively low \( k_s \) of HG-NiFe suggested that the coupling of \( \text{HO}^- \) ions with Ni-Fe sites was slower than that with Ni sites (Fig. 5A). In different KOH solutions with various pH values, the redox potentials of HG-NiFe exhibited linear dependence on pH with a slope of 0.074 \( \text{V pH}^{-1} \), as plotted in the Pourbaix diagram (Fig. 5B). On the basis of the Nernst equation, the linear slope of 0.059 \( \text{V pH}^{-1} \) corresponded to the redox process with a \( \text{HO}^- / \text{H}^+ \) stoichiometry of 1; the 0.118 \( \text{V pH}^{-1} \) corresponded to a \( \text{HO}^- / \text{H}^+ \) stoichiometry of 2. In the present case, the medium value of 0.074 \( \text{V pH}^{-1} \) indicated that the redox process of HG-NiFe involved a \( \text{HO}^- / \text{H}^+ \) stoichiometry of \( 3/2 \). Combining this result with the DFT-derived Ni-Fe model, we proposed that, at each Ni-Fe site in the redox process, two \( \text{HO}^- \) ions were adsorbed with terminal geometry and one \( \text{HO}^- \) ion was adsorbed with bridging geometry. This process is presented in the inset of Fig. 5B. Such a configuration was common for Ni-Fe cluster–based coordination structures, and the Ni-Fe distance \( \left( 2.7 \text{ Å} \right) \) in HG-NiFe was consistent with previous studies, which also involved bridging oxygen-containing ligands \( \left( \text{44–46} \right) \). Furthermore, it was also mentioned in a previous study on hydrous nickel oxides that the redox potentials of dual Ni sites with bridging oxygen-containing ligands exhibited similar linear dependence on pH \( \left( \text{38} \right) \). In contrast, the Pourbaix diagram of HG-Ni showed a linear slope of 0.052 \( \text{V pH}^{-1} \), indicating that each Ni site of HG-Ni interacted with one \( \text{HO}^- \) ion by terminal geometry \( \left( \text{fig. S20} \right) \). We used CO to selectively obstruct the adsorption of \( \text{HO}^- \) ions on HG-NiFe \( \left( \text{fig. S21} \right) \). CO is a \( \pi \) acceptor ligand that can occupy the Ni\(^{2+} \) ions through \( \pi \) back-bonding \( \left( \text{47, 48} \right) \). However, the Fe sites of HG-NiFe were at an oxidation state of +3 and exhibited lower electron density than that of FeCl\(_3\) and FeOOH precursors, the occupation of CO is very difficult \( \left( \text{49} \right) \). After the HG-NiFe surface was immersed into KOH solutions with bubbling CO for 4 hours, the OER currents on the resultant HG-NiFe clearly degraded, suggesting that cooperativity between Ni and Fe sites mainly enabled the high OER activity of HG-NiFe.

Finally, during the in situ formation of Ni-Fe sites by CV measurements (Fig. 2E), it is possible that pristine molecular Ni sites of HG-Ni could aggregate into Ni hydroxides and interacted with Fe species to form Ni-Fe hydroxides at OER potentials, therefore losing the feature of molecular dispersion. To further exclude such a possibility, we presented the CV result of HG-Ni in the KOH/FeCl\(_3\) solution in the absence of OER polarization \( \left( \text{fig. S22A} \right) \). The metal redox exhibited a similar variation to that presented in Fig. 2E. After reaching the steady state, the LSV of the electrode was collected at a scan rate of 5 \( \text{mV s}^{-1} \), affording an OER onset potential of 1.55 \( \text{V} \) and a TOF of 0.57 \( \text{s}^{-1} \) at \( \eta = 0.35 \text{ V} \) (Fig. S22B). Moreover, the redox currents of the metal sites exhibited linear dependence on the square root of potential scan rates, indicating that the diffusion of \( \text{HO}^- \) ions was the rate-limiting step, and \( k_s \) was calculated to be 0.75 \( \text{s}^{-1} \) \( \left( \text{fig. S23} \right) \). All these OER results were consistent with those collected on HG-NiFe.

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**Fig. 4. Formation of molecular Ni-Fe sites.** (A) Normalized Ni K-edge XAS data of HG-Ni and HG-NiFe. The inset presents the pre-edge region. (B) Fourier-transformed EXAFS curves at Ni K-edge. (C) Normalized Fe K-edge XAS data of HG-NiFe, FeOOH, and FeCl\(_3\). (D) Fourier-transformed EXAFS curves at Fe K-edge.
DISCUSSION

In summary, we have reported that Ni\(^{2+}\) ions were incorporated into HG under mild conditions to form heterogeneous and molecularly well-defined Ni sites for OER in alkaline aqueous solutions. The molecular Ni sites on graphene were intrinsically not OER-active. However, they could interact with Fe species in KOH solutions to form Ni-Fe sites. This structural variation resulted in a significant enhancement on OER activity. The structure of Ni-Fe sites was investigated by various techniques. The results showed that they maintained molecular dispersion on graphene, and the Ni-Fe distance was revealed to be 2.7 Å. We also proposed that the adsorption configuration with HO\(^-\) ions was tuned from pristine Ni sites to Ni-Fe sites. HO\(^-\) ions were bridged with the Ni-Fe sites before OER. These results demonstrated a novel, molecularly well-defined and heterogeneous structure catalyst for OER which might also serve as a platform to gain further insights into the OER mechanism.

MATERIALS AND METHODS

**Chemicals**

Graphite powders, thiourea, KOH, K\(_2\)S\(_2\)O\(_8\), P\(_2\)O\(_5\), KMnO\(_4\), Ni(acac)\(_2\), Fe(acac)\(_3\), and FeCl\(_3\)·H\(_2\)O were purchased from Sigma-Aldrich and used as received. Other reagents and solvents were of analytical or high-performance liquid chromatography grade and used without further purification. All aqueous solutions were prepared with Millipore water with a resistivity of 18 megohm·cm.

**Synthesis of HG-Ni**

Graphene oxides (GOs) were synthesized following a modified Hummers’ method, as previously established (23). An aqueous suspension of GO (1 mg ml\(^{-1}\), 10 ml) was mixed with thiourea at a mass ratio of 1:50 (GO/thiourea), followed by sealing in a Teflon-lined stainless autoclave at 150°C for 3 hours to obtain HG. Afterward, the as-obtained HG (6 to 7 mg; dispersed in 10 ml of N,N-dimethylformamide (DMF) was mixed with 0.1 M Ni(acac)\(_2\) (dissolved in 10 ml of DMF) at 80°C for 12 hours (1 atm) to form HG-Ni. The resultant HG-Ni was dispersed and stored in isopropanol with a concentration of 1 mg ml\(^{-1}\). In a control experiment, we used the same procedure to synthesize an HG-Fe sample. In particular, HG (6 to 7 mg; in 10 ml of DMF) was mixed with 0.1 M Fe(acac)\(_3\) (dissolved in 10 ml of DMF) at 80°C for 12 hours (1 atm).

**Electrochemical measurements**

All electrochemical measurements were performed on an Autolab PGSTAT302 potentiostat at ambient environment (23°C ± 1°C, 1 atm). Electrocatalysts were casted onto rotating GCEs (4 mm in diameter; typically loaded with 10 μl of 1 mg ml\(^{-1}\) of HG-Ni) as working electrodes and attached to a Pine Instruments MSR rotator. An Ag/AgCl wire (placed in saturated KCl solution that was periodically refreshed to counteract the contamination from electrolytes) was used as the reference electrode, and a Pt foil was used as the counter electrode. The potential of the Ag/AgCl reference electrode was converted to a RHE scale following the equation:

$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH}$

(KOH solutions) V. The alternating current (ac) impedance measurement for Ni-Fe sites was performed at $\eta = -0.35$ V from 10\(^{-2}\) to -0.1 Hz with an ac voltage of 5 mV. The gaseous products of OER were analyzed by gas chromatography. Typically, the OER measurement was conducted in 1 M KOH in an H-type cell with the cathode (Pt foil) and the anode (HG-Ni-Fe\(_x\) or HG-NiFe\(_x\)-coated carbon papers, and the anodic chamber contained a Ag/AgCl reference electrode) separated by a membrane. During electrolysis, helium was continuously sparged into the anodic chamber with a flow rate of 20 standard cubic centimeters per minute. The gaseous product from the anode was measured in real time by in-line gas chromatography. On HG-NiFe, O\(_2\) was the only product and it was produced with FEs of 100% at potentials from 1.54, 1.58, 1.62, to 1.66 V. On HG-NiFe\(_x\), the FEs for O\(_2\) production were also 100% at 1.62, 1.66, and 1.70 V.

**Removal of Fe species from KOH solutions**

KOH solutions (in this case, the Fe content in the raw KOH solution was detected by inductively coupled plasma measurements, but it suggested that the Fe content should be at a trace level) were purified following a previously reported approach (36). Briefly, 2 g of Ni(NO\(_3\))\(_2\)·6H\(_2\)O was mixed with 20 ml of 1 M KOH in polypropylene centrifuge tubes to achieve Ni(OH)\(_2\) solids, followed by washing with Millipore water and 1 M KOH successively. Afterward, 40 ml of 1 M KOH was added to mix with the Ni(OH)\(_2\) solids in the polypropylene centrifuge tubes for 4 to 5 hours. In the electrolychemical measurement, the purified 1 M KOH was stored in a plastic beaker.

**Procedures to obtain HG-NiFe**

In a typical experiment, 10 μl of HG-Ni (1 mg ml\(^{-1}\)) was casted onto GCE. The CV of HG-Ni/GCE was performed in 30 ml of 1 M KOH at a scan rate of 50 mV s\(^{-1}\). During this process, 200 μl of FeCl\(_3\) aqueous solution (1.8 mM in water) was injected stepwise into the KOH solution. The CV polarization curve can reach steady state after 30 cycles. In a control experiment, 10 μl of HG suspension (1 mg ml\(^{-1}\)) was casted on HG-Ni, HG-NiFe, and HG-NiFe\(_x\). The resultant HG-NiFe was dispersed and stored in isopropanol with a concentration of 1 mg ml\(^{-1}\). Afterward, the as-obtained HG (6 to 7 mg; dissolved in 10 ml of DMF) was mixed with 0.1 M Ni(acac)\(_2\) (dissolved in 10 ml of DMF) at 80°C for 12 hours (1 atm).

![Fig. 5. Adsorption of HO\(^-\) ions at Ni-Fe sites. (A) $k$ of metal redox in HG-Ni, HG-NiFe, and HG-NiFe. (B) Pourbaix diagram, formal potentials of redox versus pH values of KOH solutions. The inset shows the proposed configuration for the adsorption of HO\(^-\) ions onto Ni-Fe sites before OER.](image-url)
GCE and underwent the same procedure to investigate the interacting sites of HG-Ni with the Fe species.

**Calculation of TOFs**

\[
\text{TOF} = (J \times A) / (4 \times F \times m)
\]

where \( J \) is the OER current density, which was achieved from LSV with a low scan rate of 5 mV s\(^{-1}\) to minimize the influence of the currents from metal redox and electrode capacitance; \( A \) is the geometrical surface area of the electrode; \( F \) is the Faraday constant; and \( m \) is the amount of electroactive Ni or Ni-Fe sites, which was obtained from integrating the charge amount of metal redox peaks.

**Laviron equation**

\[
E_c = E_{1/2} - (RT/\alpha n F) \times \ln(\alpha n F/RTk_\alpha) - (RT/\alpha n F) \times \ln(n)
\]

where \( E_c \) is the reduction potential of metal redox, \( E_{1/2} \) is the formal potential of metal redox, \( R \) is the universal gas constant, \( T \) is the temperature in kelvin, \( n \) is the number of electrons transferred, \( \alpha \) is the transfer coefficient, \( k_\alpha \) is the rate constant of metal redox, and \( n \) is the scan rate in the CV measurements.

**Computational method**

Our calculations were performed based on DFT implemented in the QUANTUM-ESPRESSO package (50). Structural relaxation was performed by using spin-polarized scalar relativistic ultrasoft pseudopotentials and an exchange correlation functional in the form of a Perdew-Burke-Ernzerhof functional with the van der Waals interaction by the empirical effects.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/3/eaap7970/DC1.

**REFERENCES AND NOTES**

1. I. Roger, M. A. Shipman, M. D. Symes, Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. Nat. Rev. Chem. 1, 0003 (2017).
2. B. M. Hunter, H. B. Gray, A. M. Müller, Earth-abundant heterogeneous water oxidation catalysts. Chem. Rev. 116, 14120–14136 (2016).
3. C. Liu, N. P. Dasgupta, P. Yang, Semiconductor nanowires for artificial photosynthesis. Chem. Mater. 26, 415–422 (2014).
4. Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, Synthesis and activities of rutile IrO\(_2\) and RuO\(_2\) nanoparticles for oxygen evolution in acid and alkaline solutions. J. Phys. Chem. Lett. 3, 399–404 (2012).
5. J. Rossmeissl, Z.-W. Qu, H. Zhu, G.-J. Kresse, J. K. Nørskov, Electrolysis of water on oxide surfaces. J. Electroanal. Chem. 607, 83–89 (2007).
6. J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, Molecular catalysts for water oxidation. Chem. Rev. 115, 12974–13005 (2015).
7. E. Mirzakulova, R. Khatmullin, J. Walpita, T. Corrigan, N. M. Varjas-Vargas-Barbosa, S. Vyas, S. Gottikall, S. F. Manzer, C. M. Hadad, K. D. Glusac, Electrode-assisted catalytic water oxidation by a flavin derivative. Nat. Chem. 4, 794–801 (2012).
8. M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, Artificial photosynthesis: Molecular systems for catalytic water oxidation. Chem. Rev. 114, 11863–12001 (2014).
9. E. Y. Tsui, R. Tran, J. Yano, T. Agapie, Redox-inactive metals modulate the reduction potential in heterometallic manganese–oxide clusters. Nat. Chem. 5, 293–299 (2013).
10. S. Bang, Y.-M. Lee, S. Hong, K.-B. Cho, Y. Nishida, M. S. Seo, R. Sarangi, S. Fukuzumi, W. Nam, Redox-inactive metal ions modulate the reactivity and oxygen release of mononuclear non-haem iron(III)–peroxo complexes. Nat. Chem. 6, 934–940 (2014).
11. T. Fukushima, W. Dirsdell, J. Yano, Y. Suresndranath, Graphite-conjugated pyrazines as molecularly tunable heterogeneous electrocatalysts. J. Am. Chem. Soc. 137, 10926–10929 (2015).
12. C. M. Araujo, M. D. Doherty, J. S. Konzynski, D. R. Luca, A. Ustiyansky, H. Grade, E. Lobkovsky, G. L. Solovechik, R. H. Crabtree, V. S. Batista, Tuning redox potentials of bis(μ-imino)pyridine cobalt complexes: An experimental and theoretical study involving solvent and ligand effects. Dalton Trans. 41, 3562–3573 (2012).
13. D. J. Cole-Hamilton, Homogeneous catalysis—New approaches to catalyst separation, recovery, and recycling. Science 299, 1702–1706 (2003).
14. A. Choplin, F. Quignard, From supported homogeneous catalysts to heterogeneous molecular catalysts. Coord. Chem. Rev. 178–180 (Pt. 2), 1679–1702 (1998).
15. J. R. McKone, N. S. Lewis, H. B. Gray, Will solar-driven water-splitting devices see the light of day? Chem. Mater. 26, 407–414 (2014).
16. S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, D. Kim, Covalent organic frameworks comprising cobalt porphyrins for catalytic CO\(_2\) reduction in water. Science 349, 1208–1213 (2015).
17. E. S. Andreiadis, P.-A. Jacques, P. D. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pécaut, S. Palacin, M. Fontecave, V. Artero, Molecular engineering of a cobalt-based electrocatalytic nanomaterial for H\(_2\) evolution under fully aqueous conditions. Nat. Chem. 5, 48–53 (2013).
18. A. Le Goff, V. Artero, B. Jousselme, P. D. Tran, M. Fontecave, From hydrogenses to noble-metal-free catalytic nanomaterials for H\(_2\) production and uptake. Science 326, 1384–1387 (2009).
19. J. D. Blakemore, A. Gupta, J. J. Warren, B. S. Brunschwig, H. B. Gray, Noncovalent immobilization of electrocatalysts on carbon electrodes for fuel production. J. Am. Chem. Soc. 135, 18288–18291 (2013).
20. P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave, V. Artero, Noncovalent modification of carbon nanotubes with pyrene-functionalized nickel complexes: Carbon monoxide tolerant catalysts for hydrogen evolution and uptake. Angew. Chem. Int. Ed. 50, 1371–1374 (2011).
21. X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang, H. Wang, Highly selective and active CO\(_2\) reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. Nat. Commun. 8, 14675 (2017).
22. K. Elouarzaki, A. Le Goff, M. Holzinger, J. Thery, S. Cosnier, Electrocatitlatic oxidation of glucose by rhodan avinorhoin-functionalized MWCNT electrodes: Application to a fully molecular catalyst-based glucose/O\(_2\) fuel cell. J. Am. Chem. Soc. 134, 14078–14085 (2012).
23. J. Wang, X. Ge, Z. Liu, L. Thia, Y. Yan, W. Xiao, X. Wang, Heterogeneous electrocatalyst with molecular cobalt ions serving as the center of active sites. J. Am. Chem. Soc. 139, 1878–1884 (2017).
24. J. Y. C. Chen, L. Dang, H. Liang, W. Li, B. J. Gerken, S. Jin, E. E. Alp, S. S. Stahl, Operando analysis of NiFe and Fe oxhydroxide electrocatalysts for water oxidation: Detection of Fe\(^{IV}\) by Mössbauer spectroscopy. J. Am. Chem. Soc. 137, 15090–15093 (2015).
35. R. Sarangi, X-ray absorption near-edge spectroscopy in bioinorganic chemistry: electrochemical evolution of oxygen.

36. L. Trotochaud, S. L. Young, J. K. Ranney, S. W. Boettcher, Nickel electrocatalysts for hydrogen production.

37. M. W. Louie, A. T. Bell, An investigation of thin-film Ni–Fe water splitting electrocatalysts.

38. S. A. Wilson, J. Chen, S. Hong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, Identification of highly active Fe sites in NiFeOOH for electrocatalytic water splitting.

39. B. Mei, A. A. Permyakova, R. Frydendal, D. Bae, T. Pedersen, P. Malacrida, O. Hansen, An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation.

40. M. E. G. Lyons, R. L. Doyle, M. P. Brandon, Redox switching and oxygen evolution at iron electrodes for efficient oxygen evolution at high current densities.

41. S. A. Wilson, J. Chen, S. Hong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, Identification of highly active Fe sites in NiFeOOH for electrocatalytic water splitting.

42. M. Wilke, F. Farges, P. E. Petit, E. Brown Gordon Jr., F. Martin, Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study.

43. E. Laviron, The use of linear potential sweep voltammetry and of a.c. voltammetry for the study of the surface electrochemical reaction of strongly adsorbed systems and of redox modified electrodes.

44. B. E. Barton, C. M. Whaley, T. B. Rauchfuss, D. L. Gray, Nickel–iron dithiolate hydrides relevant to the [NiFe]-hydrogenase active site.

45. S. Canaguier, V. Artero, M. Fontecave, Modelling NiFe hydrogenases: Nickel-based electrocatalysts for hydrogen production.

46. X. Engelmann, S. Yao, E. R. Farquhar, T. Szilvási, U. Kuhlmann, P. Hildebrandt, M. Driess, Coordination of Fe in minerals: An Fe K-XANES spectroscopic study.

47. J.-H. Jeoung, H. Dubbek, Carbon dioxide activation at the Ni,Fe-cluster of anaerobic carbon monoxide dehydrogenase.

48. H. Ogata, Y. Mizouchi, N. Muzuno, K. Miki, S.-i. Adachi, N. Yasuoka, T. Yagi, O. Yamauchi, S. Hirotà, Y. Higuchi, Structural studies of the carbon monoxide complex of [NiFe] hydrogenase from Desulfovibrio vulgaris Miyazaki F: Suggestion for the initial activation site for dihydrogen.

49. J. Li, B. C. Noll, E. C. Schulz, W. R. Scheidt, Comparison of cyanide and carbon monoxide as ligands in iron(III) porphyrinates.

50. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Coccocioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scuseria, A. P. Seitsonen, A. Smogunov, P. Uram, R. M. Wentzcovitch.

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