



Review

Advances in regulating the electron spin effect toward electrocatalysis applications

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HIGHLIGHTS

- This article reviews the recent advancements on the spin effect toward electrocatalysis applications.
- The methods for spin manipulation of catalysts and the related catalytic mechanisms are thoroughly discussed.
- The key directions for the future development of spin effects in the field of electrocatalysis are described.

GRAPHICAL ABSTRACT



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ABSTRACT

Building highly reactive electrocatalysts is of great significance for addressing the energy crisis and developing green energy. Electrocatalytic reactions occur at the interface of catalysts, where the physicochemical properties of the catalyst surface play a dominant role. In particular, the electron spin behavior on the catalyst surface has a decisive impact on the catalytic reaction process. This review initially introduces the definition of electron spin and methods for spin manipulation. Furthermore, we summarize the advanced characterization methods of electron spin. Then, we review the latest research advancements on the spin effect in the oxygen reduction reaction, oxygen evolution reaction, carbon dioxide reduction reaction, and nitrogen reduction reaction. The

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catalytic mechanisms of spin manipulation in these four reactions are thoroughly discussed. Finally, we propose key directions for the future development of spin effects in the field of electrocatalysis. This review contributes to a deeper understanding of the micromechanisms in electrocatalytic reactions.

1. Introduction

Developing new clean energy sources is an acknowledged global research direction within the context of the energy crisis and carbon-neutral economy [1–5]. Fuel cells, metal–air batteries, and water electrolyzers are important devices for new energy conversion and storage technologies [6–13]. They involve a series of catalytic conversion processes of small molecules, such as H_2 , O_2 , CO_2 , and N_2 , and include various reactions, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), CO_2 reduction reaction (CO_2RR), and nitrogen reduction reaction (NRR) [14–22]. However, energetic small-molecule-related reactions require multiple steps of electron transfer, which can lead to high activation barriers and slow kinetics [23–25]. Therefore, optimizing the efficiency and selectivity of electrocatalytic reactions is essential for achieving sustainable energy conversion and environmental protection. Electrocatalytic reactions occur at the catalyst interface, where the physicochemical properties of the material surface are crucial. Specifically, the electron spin behavior of the material surface can have a decisive impact on the catalytic reaction process [26]. Understanding how electron spin states affect the rate and selectivity of the reaction can provide us with in-depth insights into the reaction mechanism. By regulating the electron spin states, we can design catalysts that are more active and stable, optimize the performance of catalysts, and thus achieve higher reaction efficiency and selectivity. However the current research on electron spin states is still in the initial stage, and it is urgent to increase the research investment to promote the rapid development of this field.

Electron spin is an intrinsic property of electrons and is described by a quantum number representing the angular momentum of the electron spin [27,28]. In 1925, German physicist Wolfgang Pauli introduced the concept of electron spin to explain peculiar phenomena observed in atomic spectra. Subsequently, Swiss physicist Felix Bloch and Dutch physicists Samuel Goudsmit and George Uhlenbeck independently connected the concept of spin with experimental phenomena. They found that spin could explain the fine structure of atomic spectra and magnetic phenomena [29]. With the vigorous development of electron spin research, studies focusing on spin have expanded to cover multiple disciplines, such as physics, chemistry, and life sciences [30–33].

The application of electron spin in electrocatalytic reactions has gained significant interest over the past few years [34–38]. From the viewpoint of quantum mechanics, the orbital occupancy and electron spin orientation of individual atoms determine the characteristics of electron structures in the lattice. A change in orbital occupancy and spin orientation at the atomic level can cause electron density redistribution and modify interatomic exchange interactions throughout the bulk phase [27]. As we all know, the electron structure distribution of catalysts can affect the binding of catalysts and reaction intermediates [39]. For example, the regulation of the spin-state could modulate the occupation number of electrons on the e_g orbitals of transition metal oxides. The high-spin and low-spin structures of the same substance exhibit different binding strengths towards intermediates, so electron spin behavior directly affects the catalytic activity [40]. The spin configuration of the catalyst can also affect the charge transport in the electrochemical reaction and accelerate the reaction kinetics [41]. This emerging field of research focuses on manipulating the electron spin state to adjust the reactivity and selectivity of catalysts, leading to more efficient catalytic processes (Fig. 1) [42–44]. This opens up new avenues for the development of efficient electrochemical catalysts and the advancement of renewable energy technologies. The application of electron spin in electrocatalytic reactions involves multiple aspects. First, by controlling the spin state of electrons, the surface adsorption capacity and catalytic activity of catalysts can be altered [45–49]. Second, the modulation of the electron spin can also affect the electron transfer ability of the catalyst [50–53]. The spin coupling of electrons can regulate the electron transport behavior in catalysts, thereby influencing the rate and efficiency of electron transfer reactions. This is crucial for electron conduction in electrocatalytic reactions and the electron transfer process of the catalyst, leading to improved reaction efficiency and selectivity. Furthermore, the control of electron spin can also influence the formation of the catalytic active sites in the catalyst [54,55]. By adjusting the spin state of electrons, the atomic structure and electron density distribution on the catalyst surface can be changed, thereby modulating the formation of catalytic active sites and the structure of reaction centers. However, to date, there is still limited literature summarizing and reviewing the effects of spin control and spin effects on the performance of electrocatalysts.

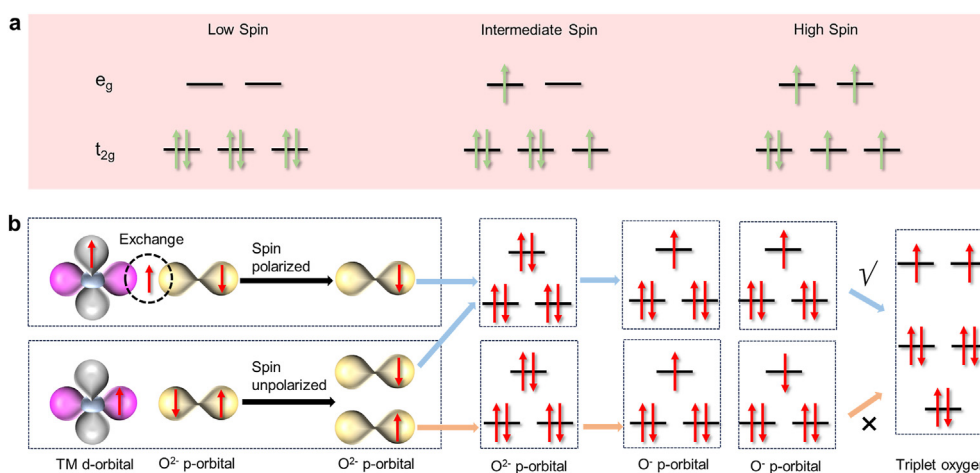


Fig. 1. (a) Schematic diagram for Co^{3+} in different spin states of low-spin, intermediate-spin, and high-spin state. (b) Schematic of spin-exchange mechanism for producing triplet oxygen by two oxygen radicals with parallel/opposite spin alignments. Reproduced with permission [55]. Copyright 2021, Springer Nature. Reproduced with permission [66]. Copyright 2021, Springer Nature.

In this review, we first outline the development history and applications of the electron spin effect in energy catalysis and then summarize five methods for controlling the electron spin state. Next, advanced characterization techniques for electron spin in electrocatalysis are introduced. We then review the latest research progress on spin control in four electrocatalytic reactions (ORR, OER, NRR, CO₂RR) and analyze the possible mechanisms of the spin effects in electrocatalytic processes. Finally, we present potential avenues for advancing spin effects in energy catalysis, providing theoretical guidance for the development of spin electrocatalysis.

2. Electron spin effect

2.1. Definition of the electron spin effect

In quantum mechanics, subatomic particles possess an inherent angular momentum known as spin, which results in the particles having a magnetic moment characterized by a specific magnitude and direction [56]. Electron spin can be described by a quantum number, typically represented as 1/2. According to the rules of quantum mechanics, the electron spin can only take two possible orientations, namely, spin-up (\uparrow) and spin-down (\downarrow). This spin property is of significant importance in explaining the properties of atoms, molecules, and solid materials. Electron spin is an intrinsic property of the elementary particles, and the spin state affects the electronic structure and chemical properties of matter [57, 58]. In atoms and molecules, the electron spin determines the arrangement and energy level structure of the electrons, along with the nature and rate of chemical reactions. In solid materials, the interaction between electron spin and other electrons affects the conduction properties, magnetic

properties, optical properties, etc. The spin states of electrons on an orbit are governed by the Pauli exclusion principle, which indicates that a specific spatial orbital can accommodate a maximum of two electrons with opposite spins [59]. The phenomenon in which the spin states of electrons in an atom or molecule align uniformly in a specific direction under certain conditions is called spin polarization [60]. In the field of chemistry, the control of chemical reactions is determined not only by free and activation energies but also by the primary factor of the electron spin. The conservation of the spin angular momentum, in addition to energy conservation, is widely recognized as a fundamental property of nature [61]. Notably, the foundation of the spin selection rule, also known as Wigner's spin conservation rule, is based on the principle that during any permissible electronic transition process that can occur between atoms or within an atom, the system's spin angular momentum remains constant [62]. Consequently, the transitions between the states of differing spin multiplicities are prohibited. The application of this principle dictates that a chemical reaction is permissible only when the combined spin angular momentum of the reactants matches the total spin angular momentum exhibited by the products. This leads to the emergence of electron and nuclear spin selectivity in reactions. Many electrocatalytic reactions, such as OER and ORR, involve oxygen-containing species with different spin states (triplet oxygen molecules and singlet OH⁻ and H₂O), causing these reactions to be spin-forbidden [63,64]. Many interaction effects, especially strong spin-orbit coupling, can supply sufficient energy to facilitate spin flips along the reaction path, a process known as intersystem crossing, enabling the occurrence of the reaction. Therefore, the choice of catalyst is very important, and the catalyst needs to be elements with spin-orbit coupling exchange interaction, usually Fe, Co, Ni, and other fourth and fifth-period transition elements [65–71]. The activity of the

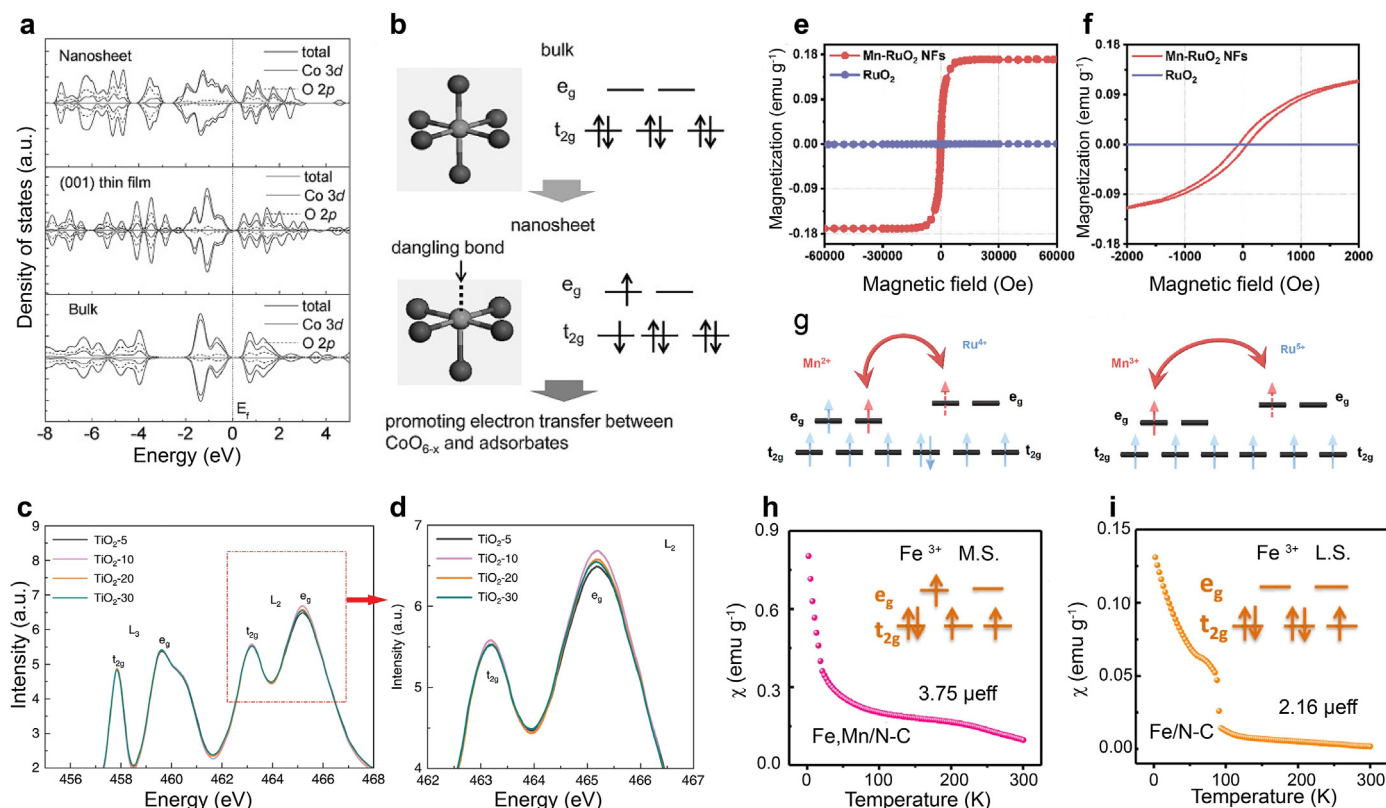


Fig. 2. Regulation of Electron Spin for defect and doping induction. (a) The calculated density of states (DOS) for γ -CoOOH nanosheet, γ -CoOOH (001) thin film and bulk γ -CoOOH. (b) Transformation of electronic structure in ultrathin γ -CoOOH nanosheets. Reproduced with permission [75]. Copyright 2015, Wiley-VCH. (c,d) Ti L-edge and high-resolution L₂ XAS spectra. Reproduced with permission [76]. Copyright 2020, Springer Nature. (e) Magnetization hysteresis M - H loops of Mn-RuO₂ NFs and RuO₂ at room temperature. (f) Close-up of the low-field region in M - H curves of Mn-RuO₂ NFs and RuO₂. (g) Schematic of the ferromagnetic exchange between Mn²⁺ and Ru⁴⁺ and the ferromagnetic exchange between Mn³⁺ and Ru⁵⁺. Reproduced with permission [77]. Copyright 2023, Wiley-VCH. Magnetic susceptibility of (h) Fe, Mn/N-C, and (i) Fe/N-C. Reproduced with permission [78]. Copyright 2021, Springer Nature.

electrocatalytic reaction can be influenced by regulating the spin state of the active center of the catalyst. The methods of regulating the electron spin state will be discussed in detail later.

2.2. Regulation of electron spin

To understand the impact of electron spin on electrocatalytic reactions, we first need to establish a series of model catalysts by reasonably controlling their electron spin states. At present, the spin control methods reported mainly include defect and doping induction, valence modulation, crystal structure regulation, strong metal-support interactions, magnetic field modulation, and chirality modulation [40, 72–74].

2.2.1. Defect and doping induction

The spin state is greatly influenced by the coordination structure of the active centers. Introducing defects or doping atoms modifies both the coordination environment and the local electronic structure of the active centers.

Defects in materials can cause spin state changes for various reasons. Firstly, the introduction of new local electronic states or the alteration of existing ones by defects can result in changes in spin-orbit coupling or local spin perturbations. Moreover, the interaction between the defect and surrounding electrons may lead to the localization of spin, or changes in spin coupling with other degrees of freedom, such as charge. Additionally, defects can induce local crystal structure changes or distortions, which in turn can influence the spin states of electrons. For example, decreasing the catalyst size generates a multitude of defects, thereby altering the spin state of the active center. Huang et al. achieved the synthesis of a γ -CoOOH nanosheet with a significant abundance of defects by reducing the thickness of the γ -CoOOH bulk to 1.4 nm [75]. The presence of these defects led

to a transition in the spin state of the Co ion, shifting it from a low-spin state to a high-spin state. This transition caused a rearrangement of the Co 3d electrons, resulting in the formation of a $t_{2g}^5 e_g^{1,2}$ configuration (Figs. 2a and b). The γ -CoOOH nanosheet exhibited excellent OER activity due to the theoretically optimal e_g orbital electron occupancy. At a current density of 10 mA cm^{-2} , the overpotential of the γ -CoOOH nanosheet was significantly reduced by 74 mV compared to the γ -CoOOH bulk, reaching a low of 0.30 V. In addition, anatase TiO_2 with different titanium defect concentrations was controllably prepared by Pan et al. [76]. The intrinsic correlation between electron spin polarization and photocatalytic performance was thoroughly explored. The Ti L-edge XAS (Figs. 2c and d) showed that the electron polarization states in the electron spin direction were the same in the TiO_2 -m samples. After the introduction of titanium defects, the spin-down polarization of TiO_2 -5 to TiO_2 -10 near the Fermi level increased. However, too many titanium defects (clusters) in TiO_2 -20 and TiO_2 -30 reduced the degree of spin polarization. Experimental results showed that the defect type $\text{Ti}_{0.936}\text{O}_2$ (TiO_2 -10) with the maximum spatial spin polarization could effectively enhance the charge separation efficiency and promote the surface reaction, showing the best photocatalytic performance. Additionally, the photocatalytic activity of spin-polarized $\text{Ti}_{0.936}\text{O}_2$ could be further promoted by an external magnetic field.

Doping is also an effective way to regulate spintronic states. Doping can also affect spin-orbit coupling, altering the interaction between electron spin and orbit. Depending on the characteristics of the doping species, doping can enhance or inhibit the magnetic properties of the material, and even completely change the magnetic properties of the material. Li et al. reported the first spin-polarization-mediated strategy to enhance OER activity in acidic electrolytes by doping dilute manganese (Mn^{2+}) ($S = 5/2$) in antiferromagnetic RuO_2 to generate a net ferromagnetic moment (Figs. 2e–g) [77]. When Mn was introduced into the RuO_2 lattice, its magnetic structure changed. The doped Mn atom had a

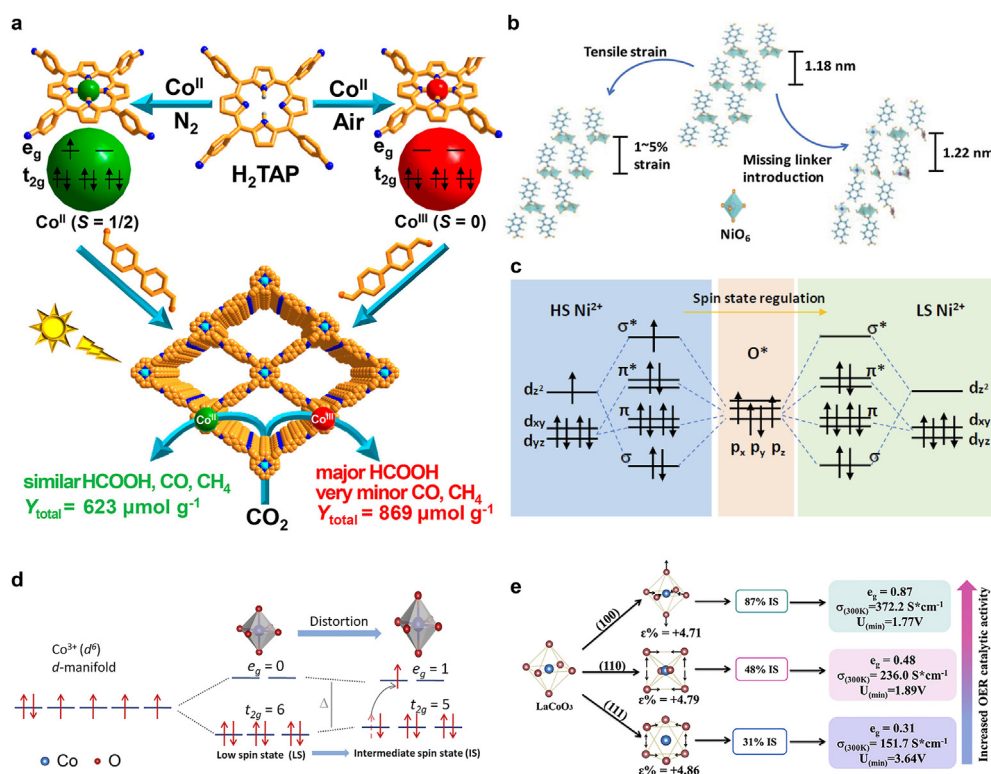


Fig. 3. Regulation of Electron Spin for Valence and crystal structure modulation. (a) Rational fabrication of COF-367-Co with various spin states of Co ions for efficient photocatalytic CO_2 reduction. Reproduced with permission [79]. Copyright 2020, American Chemical Society. (b) The crystal structures of the Ni-NDA model in its original state, as well as after their application of tensile strain or the addition of a missing linker. (c) Schematic depiction of orbital hybridization between Ni and O* intermediates under various spin states. Reproduced with permission [81]. Copyright 2023, Wiley-VCH. (d) Schematic depiction of the electron transition from t_{2g} to e_g orbital and the evolution of intermediate-spin state. (e) The correlation between OER activity and spin configuration of differently oriented LCO films. Reproduced with permission [82]. Copyright 2017, Elsevier.

large magnetic moment (~ 3.69) and induced a ferromagnetic arrangement of the magnetic moments of adjacent Ru atoms. Mn-RuO₂ nano-sheets showed OER activity enhanced by a strong magnetic field, showing a minimum overpotential of 143 mV and maintaining high activity for 480 h without any significant attenuation. Furthermore, the introduction of heteroatoms not only alters the magnetic properties of the catalyst but also directly influences the spintronic arrangement of the metal center. Yang et al. reasonably designed a bimetallic atom-dispersed catalyst (Fe, Mn/N-C) [78]. Mn-N dispersed by adjacent atoms could effectively activate the Fe^{III} site, enabling Fe^{III} to achieve a single e_g electron filling ($t_{2g}^4 e_g^1$) in the FeN₄ site, which was more conducive to electrons entering the anti-bonding orbital of O and achieving the activation of O₂. Based on the results obtained from magnetic susceptibility tests and theoretical calculations, it was found that Fe/N-C contained approximately 1.3 unpaired d electrons. This indicates that the Fe^{III} ions present in Fe/N-C exhibit a low-spin state without e_g filling (Figs. 2h and i). Conversely, the number of unpaired d electrons of Fe, Mn/N-C was approximately 3, demonstrating single e_g filling. Therefore, the neighboring Mn^{III} moieties in a low-spin state enable Fe^{III} in FeN₄ to achieve the desired e_g filling, resulting in an optimal electronic configuration.

This configuration leads to outstanding ORR activity and stability of Fe, Mn/N-C in both alkaline and acidic media.

2.2.2. Valence modulation

Controlling the electronic structure by regulating the oxidation state of the active site is an effective strategy. Valence regulation refers to the influence of electron spin states by adjusting the chemical valence state of a material. In different valence states, the filling state of electrons may also change. This change in the filling state will directly affect the electron configuration and spin state. In addition, different chemical valence states may lead to different spin-orbit coupling intensities and changes in crystal field effects, which in turn affect the spin orientation of electrons [50]. Gong et al. manipulated the spin state of Co in a covalent organic framework catalyst (COF-367-Co) by altering the gas environment during synthesis [79]. As shown in Fig. 3a, the catalyst synthesized under an N₂ atmosphere had a Co^{II} active center ($S = 1/2$), while the catalyst synthesized under an O₂ atmosphere had a Co^{III} center ($S = 0$). Electron paramagnetic resonance (EPR) spectra of COF-367-Co demonstrated the existence of unpaired electrons in COF-367-Co^{II}, and no unpaired electrons were observed in COF-367-Co^{III}, confirming the successful change

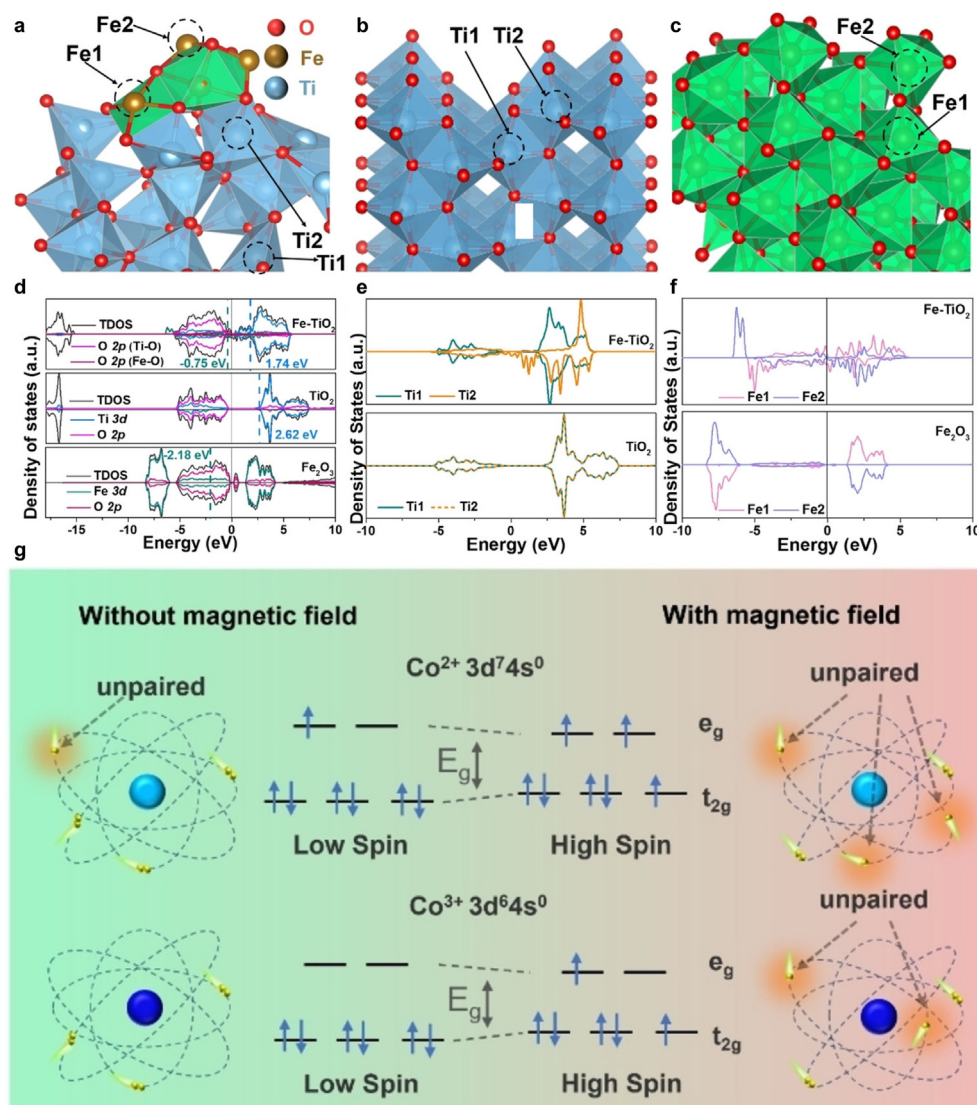


Fig. 4. Regulation of electron spin for strong metal-support interactions and magnetic field modulation. Side view model for DFT calculation of (a) Fe-TiO₂, (b) Fe₂O₃, and (c) TiO₂ models. (d) TDOS and projected DOS of Fe-TiO₂, Fe₂O₃, and TiO₂. Projected (e) Fe 3d and (f) Ti 3d DOS of selected atoms in the models. Reproduced with permission [74]. Copyright 2020, Wiley-VCH. (g) CNF/CoS_x electrode under magnetic field and no magnetic field for LiPS conversion. Reproduced with permission [85]. Copyright 2022, Wiley-VCH.

in the spin state of the Co center. The modulation of the oxidation state enabled control over the spin state. Valence regulation could enable precise control of spin states, providing valuable insights for studying the impact of spin electrocatalysis.

2.2.3. Crystal structure regulation

The alteration in lattice stress and orientation of the catalyst exerts a profound impact on the coordination structure of the metal center, ultimately disrupting the symmetry of the crystal lattice [80]. As the lattice changes, the coordination environment surrounding the metal site is also modified, leading to a transformation in its spin state. This transition can potentially impact the catalytic activity and selectivity of the catalyst, as the spin state of the active center is intricately linked to its catalytic performance. Consequently, comprehending the implications of catalyst crystallization stress and lattice orientation on the active center is of paramount importance for catalyst design and optimization. He et al. reported ultrathin nanosheets of a metal-organic framework (DD-Ni-NDA), which exhibited tensile strain and unsaturated coordination defects (Fig. 3b) [81]. The results of zero-field cooling (ZFC) temperature-dependent magnetic susceptibility indicated that more unpaired electrons occupied the e_g orbital in pristine Ni-NDA, while few unpaired electrons were present in the e_g orbital in DD-Ni-NDA nanosheets. Therefore, Ni^{2+} in pristine Ni-NDA is a high-spin state ($d_{z^2} = 1$) and Ni^{2+} in DD-Ni-NDA nanosheets is a low-spin state ($d_{z^2} = 0$). The change in the spin state of Ni^{2+} is due to the introduction of tensile strain and unsaturated coordination defect. The authors considered active sites usually adsorb oxygen intermediates through the hybridization of O 2p and Ni 3d orbitals. Therefore, they compared the orbital hybridization between Ni^{2+} with different spin states and O^* , as illustrated in Fig. 3c. In the high-spin state of Ni^{2+} ($d_{z^2} = 1$), an unpaired electron occupying the d_{z^2} orbitals were present compared to the low-spin state ($d_{z^2} = 0$). Consequently, due to spin-orbit interactions, the O^* intermediates displayed energy level densities of 1.5 and 2 in the high-spin and low-spin states of Ni^{2+} , respectively. Notably, higher bond order values and a lower spin state Ni^{2+} indicate the enhanced interaction between active sites and oxygen intermediates, which favors oxygen evolution reaction (OER) dynamics. As a result, DD-Ni-NDA delivered a better oxygen evolution activity.

Changes in the orientation of the lattice can indeed alter the local environment surrounding the active center, which includes the positions and interactions of the coordination atoms. These alterations can have an impact on the distribution of electron spins and the energy level structure. Consequently, the spin state of the electrons within the metal center can be modified. Tong et al. synthesized $LaCoO_3$ thin films with various lattice orientations [82]. The different crystallographic orientations of the catalyst resulted in varying degrees of distortion in the CoO_6 octahedra, resulting in a transition of the Co^{3+} spin state from a low-spin (LS) ($t_{2g}^6 e_g^0$) to an intermediate-spin (IS) state ($t_{2g}^5 e_g^1$, Fig. 3d). The $LaCoO_3$ thin film with the (100) crystallographic orientation exhibited the optimal Co^{3+} e_g orbital occupancy and the best OER performance (Fig. 3e).

2.2.4. Strong metal-support interactions

Strong metal-support interactions refer to the high interaction strength between the metal and the support in a catalyst system. The electronic structure of the active center can be optimized by utilizing the structural diversity of different materials. Strong metal-support interactions can adjust the electronic filling state of the active center, specifically adjusting the occupation of electrons in the d orbitals. The electrons in the metal are affected by the lattice structure of the carrier, resulting in the spin-orbit coupling, which affects the spin-flip and orientation of the electrons. This regulation can change the electronic spin state of the active center, thereby affecting the rate and selectivity of catalytic reactions. Single-atom catalysts provide an ideal model for studying the influence of strong metal-support interactions on the spin state transition of the active center in catalysts. By studying single-atom

catalysts, we can gain a deep understanding of the regulation mechanism of strong metal-support interactions on the catalyst activity and guide the design of more efficient catalysts. Deng et al. built a single Fe site loaded onto graphitic carbon nitride (Fe/g- C_3N_4) to investigate the impact of metal center spin polarization on the photocatalytic properties of g- C_3N_4 [83]. Based on the electronic structure analysis, the strong metal-support interaction leads to significant electronic energy changes in the Fe/g- C_3N_4 moiety due to the strong metal-intermediate coordination before and after intermediate adsorption. Shen et al. used a simple adsorption-oxidation strategy to immobilize Fe^{3+} atoms onto ultrathin TiO_2 nanobelts (Figs. 4a–c) [74]. Density functional theory (DFT) calculations showed that the strong metal-support interaction between Fe^{3+} and TiO_2 led to the center of the d-band for Fe 3d and Ti 3d shifted toward higher and lower energies, respectively (Figs. 4d and f). This strong metal-support interaction induced a transition of the Fe^{3+} spin state from a high-spin (HS) state to a low-spin (LS) state, leading to occupancy of the e_g orbitals of 1.08, close to the theoretically optimal value. This transition was beneficial for the adsorption of OER intermediates.

2.2.5. Magnetic field modulation

Magnetic field manipulation is also an important method for spin control [84]. By conducting a magnetic field, the distribution and orientation of spin states in a material can be adjusted, thereby achieving control over spin-related properties. For example, the energy level structure and spin flipping processes of spin states can be altered, thereby influencing the magnetic behavior of the material. This magnetic field manipulation method can be used to investigate and understand the fundamental mechanisms of spin-related phenomena. The magnetic field plays a crucial role in spin control, thus significantly advancing spintronics development. Zhang et al. synthesized a carbon nanofiber/cobalt sulfide (CNF/ CoS_x) composite through the electrospinning of polyacrylonitrile/cobalt (PAN/Co) fibers, followed by carbonization and low-temperature vulcanization [85]. The external magnetic field causes Co electrons to transition from low-spin to high-spin states, which leads to the presence of additional unpaired electrons in the Co 3d orbital. The spin polarization significantly impacts the chemical adsorption, band gap, and charge transport properties of catalysts. As depicted in Fig. 4g, the spin density of the Co atom in CoS_2 was uniformly distributed in the absence of an external magnetic field. However, the presence of an external magnetic field resulted in the alignment of electron spins. From the projected state density, after spin polarization, the overlap of Co 3d orbitals and S 2p orbitals increased, resulting in a stronger 3d–2p hybrid orbit. The enhancement of 3d–2p hybridization due to ligand holes facilitated the dynamics of charge transfer at the interface. Following the principle of spin angular momentum conservation, there is a possibility of electron–electron repulsion between the catalyst and the sulfur-adsorbing species. This interaction can enhance conductivity, lower the energy barrier of the electrochemical reaction, and enhance the kinetics of the Li–S reaction.

Ren et al. reported the use of ferromagnetic ordered catalysts for spin polarization with a magnetic field to promote the OER [55]. They initially investigated the magnetic properties of $CoFe_2O_4$, Co_3O_4 , and IrO_2 . The hysteresis loop results showed that $CoFe_2O_4$ exhibited ferromagnetic behavior at room temperature, while Co_3O_4 and IrO_2 exhibited antiferromagnetic or paramagnetic behavior at room temperature, respectively. The OER properties of catalysts with different magnetic properties were different with a constant magnetic field of 10,000 Oe and no magnetic field. The OER properties of ferromagnetic $CoFe_2O_4$ were significantly improved, while the changes in nonferromagnetic Co_3O_4 and IrO_2 were negligible. Ferromagnetic $CoFe_2O_4$ could promote the OER through spin polarization and rapid spin-electron exchange with adsorbed oxygen. The results showed that the Tafel slope of $CoFe_2O_4$ changed from ~ 120 mV dec^{-1} to ~ 90 mV dec^{-1} after the magnetic field was applied. This indicated that the rate-determining step (RDS) of the OER reaction under the external magnetic field had changed from the first electron transfer step to a mixed RDS involving the first electron transfer

step and second steps; specifically, the first electron transfer step was no longer the RDS. Based on the principle of spin angular momentum conservation, the exchange of spin-polarized electrons between CoFe_2O_4 and the adsorbed oxygen (reactant) resembled ferromagnetic exchange, leading to enhanced reaction kinetics for the first electron transfer. However, this phenomenon was not observed on nonferromagnetic catalysts.

Under electrochemical conditions, surface reconfiguration of the catalyst often occurs to produce the true active substance [86]. Therefore, the control of the magnetic substrate and surface active layer by reconstruction is another important way to develop highly efficient spintronic catalysts. He et al. employed $\text{ZnFe}_{2-x}\text{Ni}_x\text{O}_4$ as a model, manipulating the number of Ni^{3+} ions to regulate the specific coordination environment, thereby enabling the in situ generation of highly active catalytic species through surface reconstruction and construction of a ferromagnetic core to facilitate spin-selective electron transfer [87]. Incorporating 20% Ni^{3+} results in the in situ formation of a paramagnetic $\text{FeNi}(\text{oxy})\text{hydroxide}$ catalytic layer on the ferromagnetic $\text{ZnFe}_{1.6}\text{Ni}_{0.4}\text{O}_4$ core during OER measurement. This catalytic layer accelerates the OER kinetics, exhibiting a low overpotential of 360 mV at a specific current density of 0.5 mA cm^{-2} , surpassing the benchmark IrO_2 (420 mV). The activity can be further enhanced by approximately 2.9 times under an external magnetic field, surpassing ZnFe_2O_4 by a factor of 39 at an overpotential of 350 mV. This enhancement is attributed to the promoted spin-selective electron transfer facilitated by the ferromagnetic exchange interaction, which penetrates through the paramagnetic reconstruction layers. This research offers a new approach to developing highly efficient catalysts through the coupling of ferromagnetic ordering channels and highly active catalytic species.

2.2.6. Chirality modulation

The asymmetry of chiral molecules or structures can lead to the non-uniform distribution of electron spins and induce spin-orbit coupling, an interaction between the electron spin and its orbital motion [88]. Therefore, by adjusting the chiral features of molecules or structures, it is possible to effectively influence the arrangement and distribution of spins. The impact of chiral modulation on spin structures involves multiple aspects, including the formation of spin states, spin polarization, and spin-orbit coupling. An in-depth exploration of the influence of chiral modulation on spin states is instructive for the development of efficient spin catalysts.

Vadakkayil et al. proposed a scalable method for preparing chiral cobalt oxide nanoparticle catalysts doped with iron ($\text{Co}_{(3-x)}\text{Fe}_x\text{O}_4$) [89]. The chiral-induced spin selectivity (CISS) effect is used to generate spin polarization reaction intermediates, thereby improving the efficiency of OER. Compared with similar achiral cobalt oxide nanoparticles, the chiral $\text{Co}_{(3-x)}\text{Fe}_x\text{O}_4$ catalyst improves Faraday efficiency, reduces overpotential, and changes the rate-determining step of OER. Besides, in the OER process, an external magnetic field with a ferromagnetic electrode can spin filter the electron current, increasing the current density by about 100 mA cm^{-2} .

ZnO crystals with hierarchical chirality were synthesized by using chiral methionine molecules as symmetry-breaking agents [90]. Magnetic circular dichroism spectroscopy and magnetic permeability atomic force probe microscopy confirm that the chiral structure plays a spin-filtering role in the photogenerated carrier migration and induces spin polarization of the carriers. Spin-polarized carrier not only has a long lifetime, but also can effectively increase the formation rate of triplet O_2 and inhibit the formation of singlet by-product H_2O_2 during the reaction.

3. Characterization of electron spin states

The analysis of electronic spin states can be viewed as a refined representation of the electronic structure, and obtaining precise information about the arrangement of extranuclear electrons is often challenging. Currently, methods for characterizing electronic spin states are being

gradually developed. Commonly used characterization techniques in the literature include temperature-dependent magnetization, Mössbauer spectroscopy, X-ray absorption spectroscopy, and electron paramagnetic resonance [91–97].

3.1. Temperature-dependent magnetization

Temperature-dependent magnetization is one of the methods applied to analyze the electronic spin structure of materials. When a catalyst is exposed to a magnetic field, its magnetization determines its response to the field. By measuring the magnetization of the material at different temperatures and plotting the magnetization–temperature curve, the electronic spin structure of the material can be inferred. Different electronic spin structures result in different magnetization behaviors. For example, the magnetization of paramagnetic materials decreases with increasing temperature, while the magnetization of ferromagnetic materials exhibits a distinct peak within a certain temperature range. By analyzing the shape and characteristics of the magnetization–temperature curve, the type of electronic spin structure present in the material, such as paramagnetic, ferromagnetic, and antiferromagnetic, can be inferred. The measurement of temperature-dependent magnetization requires the use of magnetization measurement instruments like a vibrating sample magnetometer (VSM) or superconducting quantum interference device (SQUID). Commonly, temperature-dependent measurements of magnetization are performed using field-cooling techniques at an applied magnetic field of 1000 Oe over a temperature range of 5–300 K. In the high-temperature regime (above 150 K), the susceptibilities obtained from the magnetizations ($\chi = M/H$) follow a paramagnetic Curie–Weiss law: $\chi = C/(T-\theta)$, where C represents the Curie constant and θ represents the Curie–Weiss temperature. The effective magnetic moment μ_{eff} can be calculated through the equation $\mu_{\text{eff}} = \sqrt{8} C \mu_B$, where μ_B is the Bohr magneton. Sun et al. obtained the μ_{eff} of ZnCo_2O_4 by temperature-dependent magnetization (Fig. 5a) [45]. The spin state of Co^{3+} was considered to be a combination of a high-spin state ($4.9 \mu_B$) and a low-spin state ($0 \mu_B$). By utilizing these values, the relative proportions of Co^{3+} in the high-spin and low-spin states could be determined using the following equation: $\mu_{\text{eff}} = g \mu_B \sqrt{S_{\text{LS}}(S_{\text{LS}} + 1)V_{\text{LS}} + S_{\text{HS}}(S_{\text{HS}} + 1)V_{\text{HS}}}$, where $S_{\text{LS}} (=0)$ and $S_{\text{HS}} (=2)$ are the number of unpaired spins in e_g orbitals for low-spin and high-spin state Co^{3+} , respectively; V_{LS} and $V_{\text{HS}} (=1 - V_{\text{LS}})$ are the volume fractions for Co^{3+} in low-spin and high-spin states, respectively; and g is the Landé g -factor and equals 2 for electrons.

Information regarding the electronic spin structure obtained through temperature-dependent magnetization measurements is typically an indirect method and requires combined analysis with other techniques. When only one type of metal site in the material contributes the effective magnetic moment, a more reliable number of unpaired electrons can be calculated, and in other cases only an approximate value can be obtained.

3.2. Mössbauer spectroscopy

Mössbauer spectroscopy is an experimental technique used to study the interaction between atomic nuclei and electrons. By measuring the energy level transitions of atomic nuclei, information regarding the electrons surrounding the atomic nuclei in the material can be obtained, including the electronic spin structure. Mössbauer spectroscopy can be used to determine many elements, such as Fe, Co, Mn, Sb, and Sn. However, the elements applied to Mössbauer spectroscopy are very limited, and the current Mössbauer spectroscopy research mainly focuses on ^{57}Fe nuclides. Mössbauer spectroscopy of Fe can yield valuable insights regarding the structure of iron compounds. In Mössbauer spectroscopy, there are three important parameters: isomer shift, quadrupole splitting, and magnetic interaction; these parameters are associated with different types of interactions. The isomer shift arises from the electric monopole interaction, which is connected to the $4s$ electron density surrounding the metal nucleus and indirectly linked to the $3d$ electron

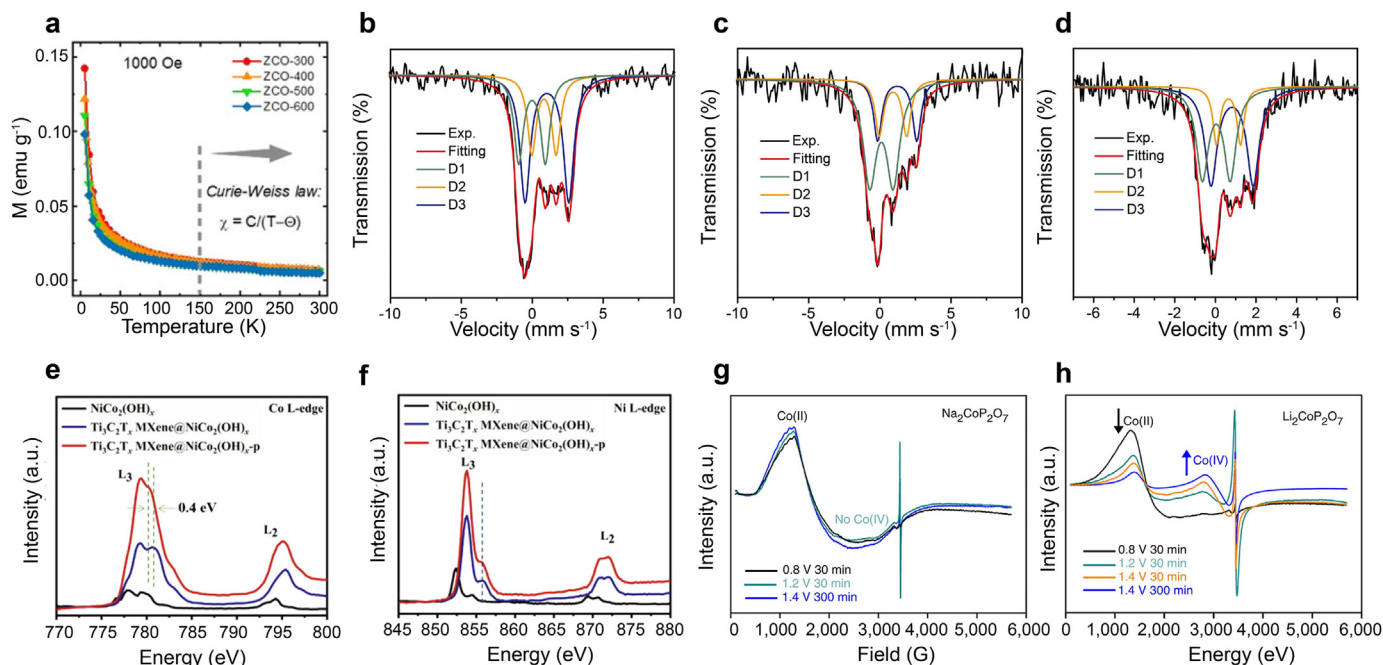


Fig. 5. The advanced characterization of spin state. (a) Temperature-dependent magnetization characterizations of the as-prepared samples at $H = 1000$ Oe. Reproduced with permission [45]. Copyright 2021, Wiley-VCH. (b–d) Room-temperature ^{57}Fe Mössbauer spectra of $\text{Fe}_1\text{-NC}$, $\text{Fe}_1\text{-NS}_{1.3}\text{C}$, $\text{Fe}_1\text{-NS}_{1.8}\text{C}$. Reproduced with permission [98]. Copyright 2021, Wiley-VCH. (e) Co L-edge XAS spectra and (f) Ni L-edge XAS spectra of $\text{NiCo}_2(\text{OH})_x$, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene@ $\text{NiCo}_2(\text{OH})_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene@ $\text{NiCo}_2(\text{OH})_x\text{-p}$. Reproduced with permission [100]. Copyright 2022, Elsevier. EPR spectra for (g) $\text{Na}_2\text{CoP}_2\text{O}_7$ and (h) $\text{Li}_2\text{CoP}_2\text{O}_7$ at 0.8 V for 30 min. Reproduced with permission [101]. Copyright 2015, Springer Nature.

density. The isomer shift describes the displacement of nuclear energy levels relative to a reference material. Quadrupole splitting is caused by the electric field gradient at the iron nucleus. It represents the deviation from cubic symmetry. The electric field gradient is caused by the charge distribution of the surrounding electrons; thus, quadrupole splitting provides information regarding the electron distribution. Magnetic interaction involves the interaction between nuclear magnetic moments and the surrounding magnetic field. Magnetic interaction can lead to more complex spectra, such as magnetic hyperfine structure and magnetic quadrupole splitting. Chen et al. conducted a study to investigate the effect of S doping on the spin polarization configuration of $\text{Fe}_1\text{-NC}$ material using ^{57}Fe Mössbauer spectroscopy (Figs. 5b–d) [98]. Based on the isomer shift and quadrupole splitting values, three distinct doublets (D1–D3) were identified in the three samples mentioned above, corresponding to low-spin Fe^{3+} , high-spin Fe^{2+} , and high-spin Fe^{2+} . S-doped $\text{Fe}_1\text{-NC}$ single-atom catalysts could generate more low-spin Fe^{3+} sites. Furthermore, in situ ^{57}Fe Mössbauer spectroscopy showed that the low-spin single Fe^{3+} atoms in the $\text{C-FeN}_4\text{-S}$ moiety served as active sites for the oxygen reduction reaction.

Notably, there are certain limitations in the application of Mössbauer spectroscopy. First, there are very few elements that can be fully tested using Mössbauer spectroscopy. Currently, the majority of Mössbauer spectroscopy research focuses on ^{57}Fe . Second, the long-range structure and electronic properties in transition metal compounds may differ from the active sites of catalysts, making it difficult to draw comprehensive conclusions. The measurement time of Mössbauer spectroscopy is relatively long, which may cause significant changes in the sample during the testing process. In addition, the temporal resolution of Mössbauer spectroscopy is relatively low, limiting the study of fast reactions or kinetic processes. Despite the demanding testing conditions, Mössbauer spectroscopy still holds high value in spin characterization due to its high resolution and strong resistance to interference. It can also be combined with other techniques to obtain more comprehensive information.

3.3. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is an effective technique to analyze the spin polarization and spin configuration of transition metals [76,99]. XAS spectra of the $\text{L}_{2,3}$ -edges of transition metals are highly sensitive to the oxidation state, spin state, and bonding of the transition metal ions. L_2 and L_3 -edge absorptions correspond to the transitions from $2p_{1/2}$ to $3d_{3/2}$ and $2p_{3/2}$ to $3d_{5/2}$, respectively, which are electric dipole-allowed transitions, and thus, the X-ray intensities absorbed at the L-edges are directly proportional to the density of electron holes in the 3d orbitals, making L-edge XAS a precise probe for the covalency of transition metal cations [27]. The L-edge signals obtained from the soft XAS can be used to semiquantitatively estimate the occupancy of electrons in the t_{2g} and e_g orbitals with consideration of the multiplet effect caused by the interaction between 2p core hole and 3d electrons and ligand field strength and spin configuration. By analyzing the characteristics of XAS spectra, valuable information regarding the spin configuration of transition metal ions can be obtained. For 3d transition metals, the measurement of XAS spectra at the metal L-edge enables the sensitive measurement of the unoccupied 3d states of the transition metal, and lower electron density transition metal ions can exhibit higher white line intensities. By analyzing the characteristics of XAS spectra, valuable information regarding the spin configuration of transition metal ions can be obtained. As presented in Figs. 5e and f, the spectral characteristics observed at the $\text{L}_{2,3}$ edges of Co (Ni) were attributed to the Co (Ni) $2p \rightarrow 3d$ transition, which was allowed by electric dipole selection rules [100]. These spectral features consisted of two main components corresponding to the $\text{Co}^{3+}/\text{Co}^{2+}$ ($\text{Ni}^{3+}/\text{Ni}^{2+}$) transitions at both the L_3 and L_2 edges, representing the Co (Ni) $2p_{3/2} \rightarrow 3d$ and Co (Ni) $2p_{1/2} \rightarrow 3d$ transitions, respectively. When $\text{NiCo}_2(\text{OH})_x$ was grown in situ on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, the binding energy of the peak shifted to 779.2 and 780.6 eV compared to 777.8 and 779.3 eV for $\text{NiCo}_2(\text{OH})_x$ alone. This shift indicated that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene@ $\text{NiCo}_2(\text{OH})_x$ had a greater concentration of occupied e_g

states. This implies that Co ions underwent a change from a low-spin state to a high-spin state, specifically a transition of the Co 3d electron configuration from $t_{2g}^6 e_g^0$ to $t_{2g}^4 e_g^2$.

The determination of electron spin states by XAS has the advantage of high sensitivity and element selectivity detection. However, due to the microscale resolution provided by XAS technology, high precision, and quality are also required for sample preparation and processing to obtain clear and accurate data.

3.4. Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) is used to analyze unpaired electrons. EPR is based on the principle of magnetic resonance and utilizes a magnetic field to excite and detect the spin of unpaired electrons. In the presence of an external magnetic field, the spin of unpaired electrons can undergo energy-level transitions. By measuring the microwave radiation absorbed or emitted during electron transitions between different energy levels, information regarding the electron spin state can be obtained. The most important parameters in an EPR spectrum are the *g*-factor and the hyperfine interaction. The *g*-factor is a dimensionless constant that describes the interaction between the magnetic moment of unpaired electrons and the external magnetic field. The hyperfine interaction arises from the interaction between unpaired electrons and the nuclear spins in their vicinity, providing information on the distance and relative orientation between the electron and the nucleus. By analyzing the shape, peak position, and line width of an EPR spectrum, the spin state of unpaired electrons, the nature of electron-nuclear interactions, and the environment surrounding the electrons can be determined. For example, EPR can be used to determine whether the electron is in a singlet or triplet state and study the effects of spin–lattice relaxation, spin–spin coupling, and spin–orbit coupling in paramagnetic materials. By comparing the EPR spectra of the original MOF (Ni-NDA) with that of the stressed MOF (DD-Ni-NDA), no evident signal was observed when the *g* value was 2800 at 120 K [81]. In contrast, the original Ni-NDA exhibited a robust signal, suggesting the lack of unpaired electrons in the DD-Ni-NDA nanosheets. Kim et al. observed the Co(II) and Co(IV) species in $\text{Na}_2\text{CoP}_2\text{O}_7$ and $\text{Li}_2\text{CoP}_2\text{O}_7$ directly using EPR analysis to analyze their structural stability [101]. The EPR spectrum of $\text{Na}_2\text{CoP}_2\text{O}_7$ showed only the characteristic Co(II) signal with $S = 3/2$ and $g_{\text{eff}} \approx 5$ after electrolysis at different potentials and for different durations (Fig. 5g). The stability of the EPR signal during the electrolysis process supported the high structural stability of $\text{Na}_2\text{CoP}_2\text{O}_7$. In contrast, under NHE conditions above 1.2 V, significant EPR signals appeared around $g_{\text{eff}} \approx 2.3$ during the electrolysis of $\text{Li}_2\text{CoP}_2\text{O}_7$, which were attributed to the low-spin Co(IV) species with a total spin of $S = 1/2$. As the Co(II) signal decreased, the Co(IV) signal increased with increasing applied potential or electrolysis time, indicating the oxidation of Co(II) to Co(IV) in $\text{Li}_2\text{CoP}_2\text{O}_7$ during the OER process (Fig. 5h).

3.5. Density functional theory calculations

DFT calculation is a quantum mechanical method to study the electronic structure of multi-electron systems, which is used to calculate the electronic structure and material properties [102]. DFT can provide critical insight when studying electron spin states and spin polarization [50]. DFT can give information such as electronic band structure and state density of materials, which helps understand the origin and influence of spin polarization. Through DFT calculations, the optimal position of the magnetic atoms and the strength of the exchange coupling between them can be determined [103]. This is essential for understanding and predicting the distribution and dynamical behavior of spin polarization in materials. It is important to note that although the DFT is a powerful tool, there may be certain challenges when describing spin polarization and strongly correlated electronic systems. For these cases, researchers may need to consider using more advanced methods such as Hubbard-U correction, spin–orbit coupling effects, or more advanced density

functionals to more accurately describe the nature of the electron structure and spin polarization.

Li et al. effectively controlled the spin polarization of Co_3O_4 catalysts by adjusting the concentration of cobalt defects and Co_3O_4 -50 with 14.5% cobalt defects demonstrating the highest spin polarization and displaying superior normalized oxygen evolution reaction activity [104]. DFT calculations were conducted to elucidate the electronic structure of both pristine Co_3O_4 and defective Co_3O_4 -50. The band gap of pristine Co_3O_4 measures 1.2 eV, a value significantly reduced to nearly 0 eV in the case of Co_3O_4 -50. The electron wave function of Co and O atoms exhibits larger overlap areas in Co_3O_4 -50 compared to pristine Co_3O_4 , indicating enhanced Co–O bond hybridization in the defective catalyst, which proves advantageous for charge transfer. Additionally, the projected density of states for the spin-down state near the Fermi level in Co_3O_4 -50 surpasses that of the spin-up state. This outcome suggests that Co defects induce electron spin polarization. Due to the Co defects result in conspicuous electron spin polarization in Co-defected Co_3O_4 , allowing for the regulation of spin polarization in surface-adsorbed oxygen species. The spin-polarized Co^{3+} active sites in Co-defected Co_3O_4 govern the spin polarization of oxygen species through a spin electron exchange process, such as $\text{M}-\text{O}(\downarrow)$ and $\text{M}-\text{O}(\downarrow)-\text{O}(\downarrow)-\text{H}$, facilitating the generation of triplet-state O_2 and significantly enhancing OER performance.

4. Electrocatalysis applications

As research on the spin effect in electrocatalysis continues to deepen, the thermodynamic and kinetic mechanisms of the spin effect in different electrocatalytic reactions become important [41,105]. By separately elucidating the mechanisms of action in different reactions, we can better understand and design efficient electrocatalytic systems. Future research will further show the role of the spin effect in electrocatalysis, offering novel perspectives and approaches for advancing renewable energy conversion. This section briefly summarizes and discusses the recent application of spin effects to electrocatalysis in the ORR, OER, HER, CO_2RR , NRR , and other reactions.

4.1. Spin regulation in ORR catalysts

The electrocatalytic ORR is essential for new-generation clean energy technologies, such as fuel cells and metal–air batteries, serving as the foundation for energy conversion and storage [106]. The ORR involves triplet oxygen molecules as reactants and singlet OH^- and H_2O as reaction products. Oxygen molecules have unpaired electrons in their orbitals and exhibit paramagnetic properties; additionally, OH^- and H_2O orbitals do not have unpaired electrons and show diamagnetic properties [107]. According to the principle of spin conservation, spin-conserving elementary reactions more easily occur, while spin-forbidden elementary reactions, which require additional energy to achieve spin coupling to facilitate the excitation and conversion of triplet-singlet states, result in higher reaction overpotentials. For ORR, there is a highly correlated scale relationship between the adsorption energies of oxygen-containing intermediates ($^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$) [108]. Therefore, the energy pathway of ORR is influenced by these scaling relationships, specifically those between the binding energies of oxygen-containing intermediates such as $^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$. Consequently, the properties of d-electrons (spin and energy) in the active transition metal centers play a crucial role in determining the materials' activities [27]. For example, the unity occupancy of the e_g orbital optimizes the ORR reaction in alkaline conditions for perovskites [109]. This observation was attributed to the presence of singly occupied e_g , which enhances dioxygen adsorption on the surface by weakening the binding of the hydroxide ion. Larger e_g fillings, on the other hand, lead to excessively destabilized O_2 binding, thereby impeding the reaction. Additionally, given that the paramagnetic triplet dioxygen constitutes the majority of natural oxygen, the spin properties of electrocatalytic materials become crucial in influencing the adsorption of O_2 on the catalytic surface [110,111]. Therefore, a

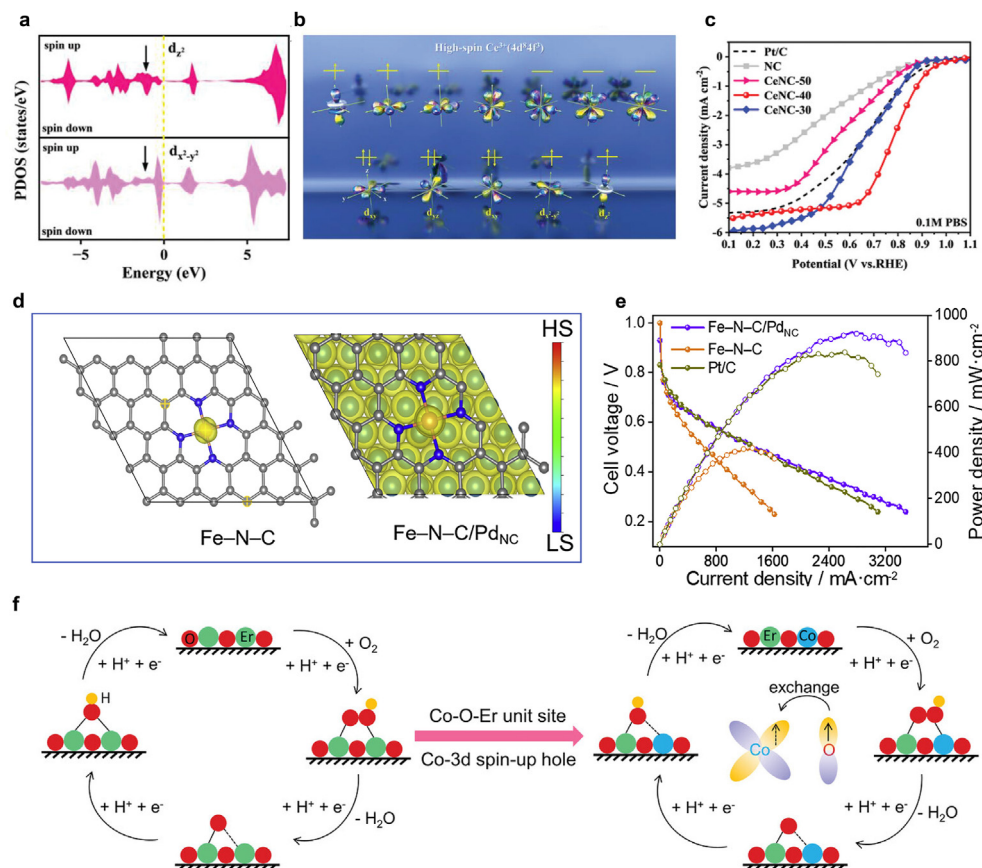


Fig. 6. ORR performance based on spin effect. (a) PDOS of d_{z^2} and $d_{x^2-y^2}$ orbitals of the edge model. (b) Schematic representation of the electronic configuration of the Ce atom in the high-spin state. (c) LSV polarization of CeNCs, NC, and Pt/C in 0.1 m PBS. Reproduced with permission [113]. Copyright 2023, Wiley-VCH. (d) Spin density diagrams of Fe-N-C and Fe-N-C/PdNC. (e) Performances of Fe-N-C/PdNC, Fe-N-C, and Pt/C catalyst for H_2 - O_2 fuel cell at 80 °C. Reproduced with permission [114]. Copyright 2023, Elsevier. (f) Proposed spin-up hole exchange for enhancing ORR at Er_2O_3 -Co with localized Er-O-Co unit site. Reproduced with permission [115]. Copyright 2023, Wiley-VCH.

thorough understanding of the electronic spin behavior in electrocatalytic reactions is crucial for determining the microscopic reaction principles of the ORR and is also a necessary path for designing high-performance nonprecious metal catalysts. At present, many reported works have paid attention to the mechanism between electron spin states and ORR performance [112].

Zhao et al. obtained excellent catalytic performance for the ORR under neutral conditions by regulating the electron spin states of a Ce single-atom catalyst (CeNC-40) [113]. A zero-field cooling test showed that CeNC-40 had a high-spin phenomenon, and its effective magnetic moment was calculated to be 5.7 μ_B . DFT calculations showed that the edge sites of CeNC-40 had higher magnetic moments and that the free energy was more favorable to the ORR process. Furthermore, the asymmetry between d_{z^2} and $d_{x^2-y^2}$ was revealed through PDOS (Fig. 6a). This result demonstrated that the electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals acted as electron donors, being excited to the 4f orbital, resulting in the transition from the $4d^{10}4f^1$ to the $4d^84f^3$ configuration (Fig. 6b). This transition led to the high-spin state of the Ce electron. The high-spin Ce site played a decisive role in the ORR process by efficiently activating oxygen molecules through the strong coupling of d-p-f orbitals and generating appropriate interaction forces with oxygen intermediates. At very low H^+ and OH^- concentrations, CeNC-40 showed a higher initial potential (1.03 V) and half-wave potential (0.78 V) under neutral conditions than commercial platinum-carbon catalysts (1.00 V and 0.68 V), as shown in Fig. 6c.

Wei et al. synthesized a Fe single-atom catalyst with an adjustable spin state by introducing Pd nanoclusters (Fe-N-C/PdNC) [114].

Theoretical and experimental results showed that the strong interaction between PdNC and Fe atoms triggered the transition of the Fe site from LS to medium spin (MS), as shown in Fig. 6d; this was beneficial to the side-on adsorption mode of O_2 , $4e^-$ dissociation path and rapid desorption of OH^* . Fe-N-C/PdNC showed better catalytic activity ($E_{1/2} = 0.87$ V (vs. RHE)) and stability than commercial Pt/C in acidic media. Assembled in MEA for proton membrane fuel cell testing, Fe-N-C/PdNC demonstrated superior performance to commercial Pt/C catalysts with a maximum power density of 920 $mW\ cm^{-2}$ at 2.79 $A\ cm^{-2}$ (Fig. 6e).

By uniformly injecting Er_2O_3 -Co particles into carbon nanofibers (Er_2O_3 -Co/CNF), Wang et al. successfully prepared a Mott-Schottky catalyst that enhanced ORR performance through spin-selective coupling [115]. By constructing localized Er-O-Co sites, the induced Co sites provided additional spin-up holes, reduced the band gap of Er_2O_3 , and regulated the covalency of Co(3d)-O(2p). The presence of spin-up holes in the Co 3d state in the z direction may facilitate ferromagnetic exchange between Co sites and O atoms in the adsorbate, thereby influencing the interaction between the Er-O-Co site and the oxygen intermediate (Fig. 6f).

Liu et al. proposed that magnetic moment as an ideal activity descriptor to predict the ORR performance instead of the active sites with the e_g^1 electron configuration [116]. The reduction of O_2 on the Fe-N₄ catalyst primarily takes place at the Fe(III) site with a medium spin state, where the presence of a single e_g electron ($t_{2g}^4e_g^1$) enables it to easily penetrate the antibonding π -orbital of oxygen, resulting in relatively weak adsorption of oxygen-containing intermediates. However, it has been observed that the catalytic activity of medium spin (e_g^1) catalysts

varies, indicating that the e_g theory is insufficient to explain ORR activity when multiple putative active sites with e_g^1 are present. Liu et al. developed a method to modify the spin state of Fe–N–C from low-spin to medium-spin ($\text{Fe}_{\text{SAC}}\text{-NC}$, e_g^1) by leveraging the secondary coordination sphere effect of adjacent N=C–N moieties. They constructed seventeen possible structures labeled as $\text{Fe}_{\text{SAC}}\text{-N}_x\text{C}$ ($x = 1\text{--}17$) to evaluate their ORR activity, with x representing different configurations of the N=C–N. DFT calculations revealed that the activities of the active sites with the e_g^1 electron configuration in these seventeen possible structures are not identical. Notably, a nearly linear relationship between the magnetic moment of $3d_{xz} + 3d_{yz}$ orbitals, ΔG^*_{OH} , and overpotential was identified, demonstrating that the magnetic moment of $3d_{xz} + 3d_{yz}$ orbitals can elucidate the origin of ORR activity. This finding of the relationship between magnetic moment and ORR activity provides new insight into the origin of M–N–C ORR activity.

The spin state also can regulate the stability of the active site of the ORR catalyst [117,118]. Li et al. synthesized a Fe–N–C catalyst with high-spin Fe(III)N_x site and intermediate- or low-spin Fe(II)N_x as demonstrated by D1 and D2 signal in ^{57}Fe Mössbauer spectroscopy, respectively [119]. Then the electrochemical test was conducted on the Fe–N–C catalyst to estimate the stability of active sites. After operating at a voltage of 0.5 V for 5 h, the activity declined sharply, and then slowly

but steadily for 50 h. The spin state of the Fe–N–C catalyst after the durability test was characterized with ^{57}Fe Mössbauer spectroscopy at 5 K. The fittings show consistent spectral parameters and absolute intensity for D2, with operation time. The signal intensity for D1 decreases continuously, while the signal intensity for the two sextets assigned to superparamagnetic ferric oxide increases continuously. The above results indicate that the high-spin Fe(III)N_x site (D1) is not durable in long-term operation and can be quickly converted to iron oxide, while the intermediate- or low-spin Fe(II)N_x site (D2) shows better durability. Hence, the active site of the catalyst may exhibit varying stability due to differences in spin states.

4.2. Spin regulation in OER catalysts

The oxygen evolution reaction is the reverse reaction of the oxygen reduction reaction and involves the conversion between the triplet and singlet states of the reactants. According to the spin conservation principle, the OER is also a spin-forbidden reaction [27]. Therefore, the spin effect may have a significant role in the OER reaction.

Recently, OER under magnetic field conditions has attracted increasing research attention. The presence of a magnetic field can lead to changes in the rate, selectivity, and yield of OER, providing a new field

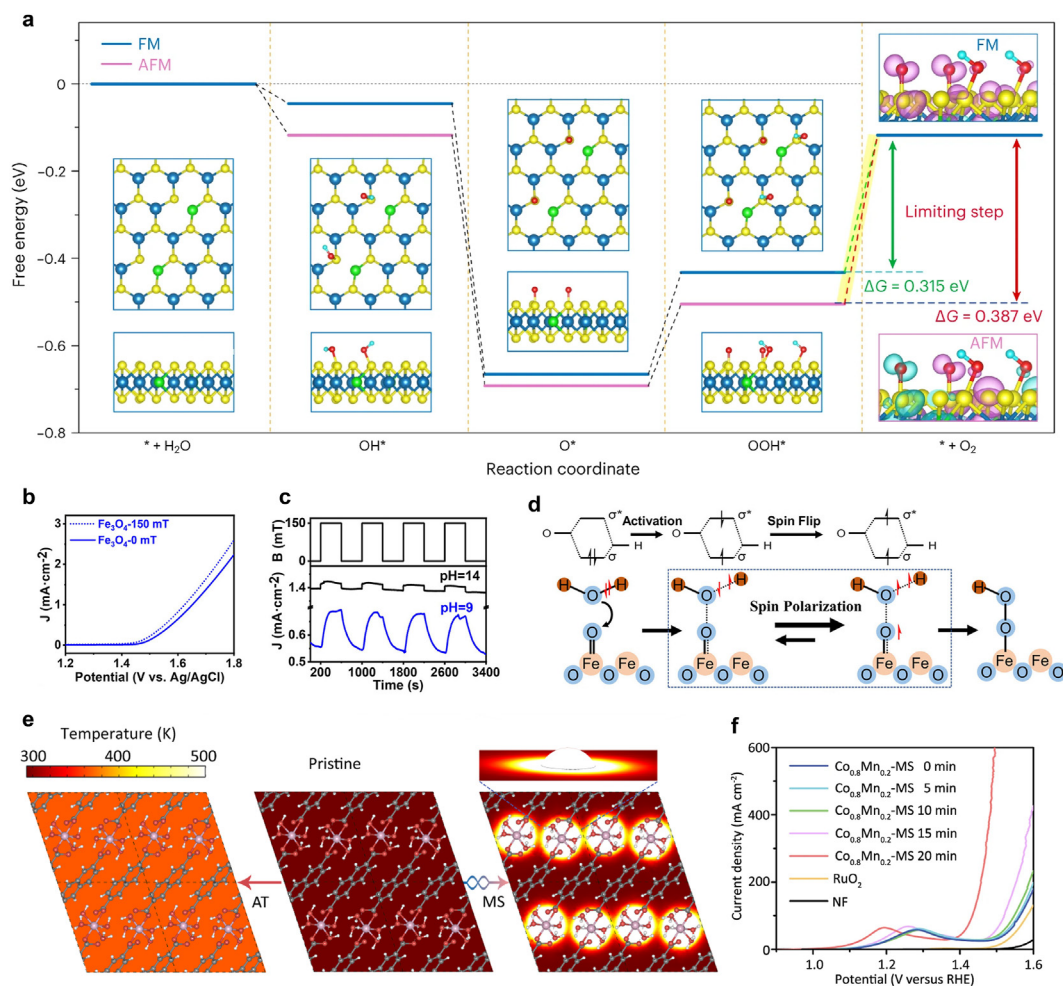


Fig. 7. OER performance based on spin effect. (a) Free energy profile of the OER over ferromagnetic (dark blue) and antiferromagnetic (pink) Ni_1/MoS_2 . Reproduced with permission [121]. Copyright 2023, Springer Nature. (b) LSV of Fe_3O_4 at pH 9 in the presence or absence of 150 mT magnetic fields. (c) Current–time (I–t) curve of Fe_3O_4 under the influence of a periodically alternating magnetic field (150 mT) at pH 9 or 14. (d) Spin polarization mechanisms for coupled O–O bonding and O–H breakage during the OER. Reproduced with permission [122]. Copyright 2023, Wiley-VCH. (e) Theoretical simulations compare the heating process of conventional annealing treatment and magnetic stimulation. (f) Polarization curves of the $\text{Co}_{0.8}\text{Mn}_{0.2}\text{-MOF}$ with different times of MS. Reproduced with permission [123]. Copyright 2021, Springer Nature.

of study. The influence of a magnetic field on OER can be achieved through various methods. One common approach is to utilize the magnetic effect of the field to control the movement and arrangement of the reactant molecules. Additionally, the magnetic field can also alter the spin state of the reactant molecules, affecting their interactions with other molecules and thereby regulating the reaction rate and selectivity [120]. Sun et al. developed a widely applicable method for synthesizing a range of single-atom spin catalysts in which magnetic atoms are incorporated into the MoS₂ structure [121]. Among them, Ni₁/MoS₂ adopted a distorted tetragonal crystal structure, which promoted ferromagnetic coupling with nearby S atoms and adjacent Ni₁ sites, resulting in global room-temperature ferromagnetism. The ferromagnetic coupling inside the Ni₁/MoS₂ catalyst facilitated spin-selective charge transfer and the formation of trilinear molecular oxygen ($\uparrow\text{O}=\text{O}\uparrow$) in the OER (Fig. 7a). Therefore, Ni₁/MoS₂ could achieve an ultrahigh current density at a magnetic field of 502 mT and had excellent catalytic performance in the range of 1.5–1.8 V; its performance was approximately an order of magnitude higher than that without an applied magnetic field, which was better than that of commercial IrO₂ catalysts.

When using ferromagnetic Fe₃O₄ to electrocatalytic water oxidation, Huang et al. found that an external magnetic field (150 mT) could effectively promote water oxidation (Fig. 7b) [122]. Unlike previous studies, the spin-enhancing effect of the external magnetic field on water oxidation showed a pH dependence (Fig. 7c); the increase in water oxidation current at pH 9 (approximately 20%) was 20 times greater than that at pH 14. Through hydrogen/deuterium kinetic isotope effect experiments, the main participant in water oxidation under neutral/weak

alkaline conditions was H₂O, while under strong alkaline conditions, it was OH[−]. Nucleophilic attack on the surface Fe^{IV}=O species to oxidize H₂O involved not only the formation of spin-parallel O–O bonds but also a coordinated spin-antiparallel O–H bond-breaking process (Fig. 7d). This showed that the parallel spin arrangement of electrons in the bonding and antibonding orbitals of excited O–H could promote the O–H bond-breaking process. Therefore, in the process of oxidizing H₂O, the external magnetic field copromoted O–O bonding and O–H bond breaking, which could produce a more significant spin enhancement effect than the oxidizing OH[−] process involving only O–O bonding. This work demonstrated for the first time that an external magnetic field promoted the bond-breaking process of a more common ground state singlet molecule and expanded the application of spin catalysis mechanisms.

Zhou et al. reported a magnetic field stimulation strategy to rearrange the spintronic-occupied states in metal–organic frameworks (MOFs) with thermally differentiated superlattices, where local magnetic field heating within a periodic spatial distribution could cause spin flip at specific active sites, showing a spin-dependent reaction pathway [123]. The organic molecules with low thermal conductivity constructed a thermal insulation layer, and at the same time, the coordination of the magnetic ions was injected between the layers as a thermal conductivity zone. When an alternating magnetic field (magnetic stimulation) was applied directionally, magnetic heating was strictly confined to the magnetic ions due to molecular thermal insulation (Fig. 7e). After magnetic heat treatment, the active center Co³⁺ changed from a high-spin state to a low-spin state. Therefore, a magnetic exchange interaction could be

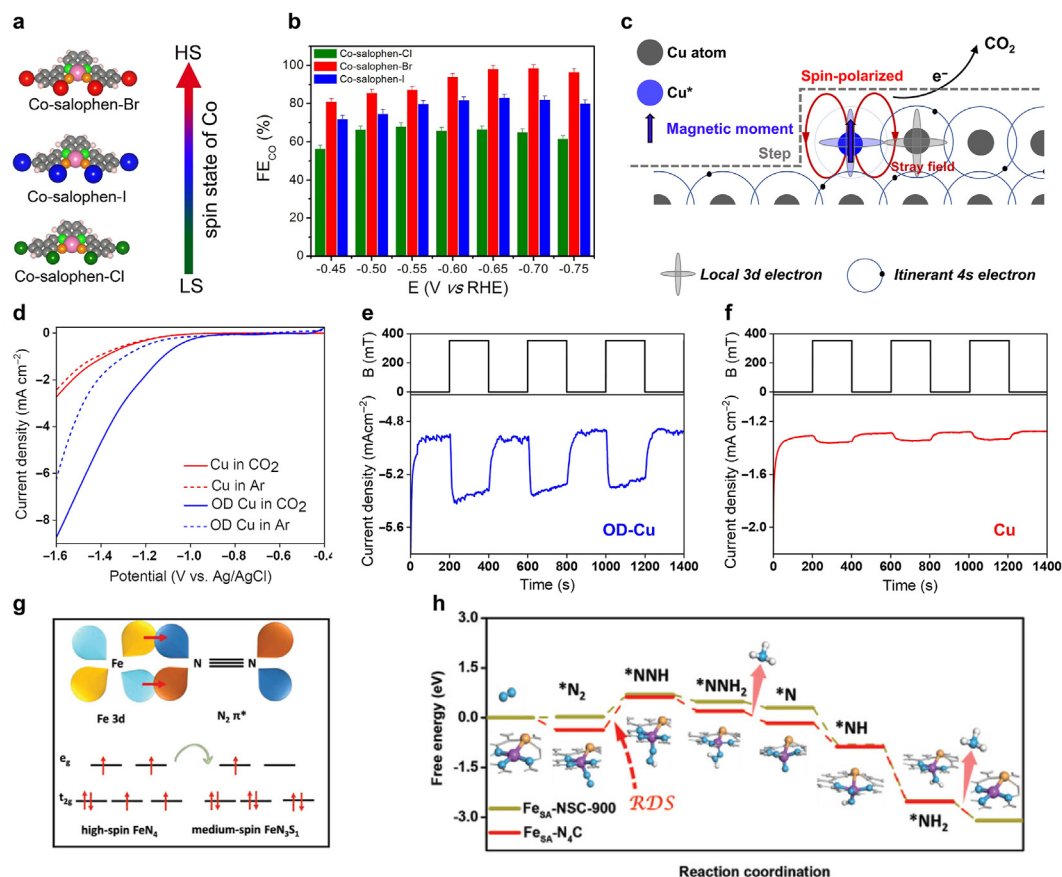


Fig. 8. CO₂RR and NRR performance based on spin effect. (a) Schematic diagram of three Co-based molecules with different spin states. (b) FE_{CO} at selected potentials over the three Co-based molecules. Reproduced with permission [125]. Copyright 2021, Elsevier. (c) Spin-related catalysis for CO₂RR in OD-Cu catalyst containing Cu⁺ species. (d) LSV curves of Cu and OD-Cu electrodes. The i–t curves under magnetic fields (350 mT) of (e) OD-Cu and (f) Cu catalysts. Reproduced with permission [126]. Copyright 2023, Chinese Chemical Society. (g) Molecular orbital diagram of N₂ and possible Fe spin configurations in FeN₄ and FeN₃S₁. (h) The free energy profiles of FeN₃S₁ and FeN₄ models at −0.4 V. Reproduced with permission [129]. Copyright 2022, Wiley-VCH.

forced to cause spin-flip and reconfiguration. The spin state changed the charge density of the active center, optimized the free energy in the reaction process, and then regulated the OER reactivity (Fig. 7f).

4.3. Spin regulation in CO₂RR catalysts

Electrocatalytic CO₂ reduction has multiple possible reduction pathways, and the selectivity of the products is a significant challenge [124]. Ideally, CO₂ should be selectively reduced to useful hydrocarbon compounds. Controlling the selectivity of the reaction is a complex problem that requires designing and optimizing the structure and active sites of the catalyst. In addition, the competing hydrogen evolution reaction also significantly affects the Faradaic efficiency of electrocatalytic CO₂ reduction. By controlling the spin state of the catalyst's active sites, the energy level distribution and reaction pathways can be adjusted, leading to higher selectivity and reaction activity. Kong et al. used peripheral ligand-substituted Co-based molecular catalysts (Co-salophen-X, X representing Cl, Br, and I) to study the mechanism of the electronic effects caused by the structural modification of ligands on the catalytic performance of CO₂RR (Fig. 8a) [125]. Through X-ray absorption spectroscopy and temperature-dependent magnetization, the Co centers of the three cobalt-based molecules were found to have different numbers of spin single electrons. The proportion of high-spin Co sites in Co-Salophen-Br was the highest among the three, reaching 65.6%. Co-Salophen-Br showed the highest CO₂RR activity compared to Co-Salophen-Cl and Co-Salophen-I (Fig. 8b). The calculation results of density functional theory showed that when the Co site had a high-spin, the energy barrier of electron transfer and proton coupling to produce *COOH in CO₂ was significantly lower than that when the Co site had a low-spin; this result indicated that the Co site with a high-spin had a higher activation ability for CO₂. They further proposed that the production of *COOH and *CO by the same Co-based molecule with different spin states did not follow a linear relationship between adsorbed species. Therefore, the electrocatalytic process of CO₂ could not only be studied from the perspective of reaction thermodynamics. To further obtain the reaction energy barrier, they conducted a transition state search for the reaction kinetic process of CO₂ formation *COOH. According to the calculated results, the high-spin state reaction energy barrier of the three Co-based molecular catalysts was lower than that of the low-spin state reaction energy barrier, which further confirmed the promotion effect of high-spin electrons on CO₂ activation.

Currently, copper is the only metal catalyst capable of catalyzing the reduction of CO₂ to produce multicarbon products (C₂₊). Among them, the intrinsic copper catalyst exhibits relatively low selectivity toward C₂₊ products; however, the copper catalysts obtained through oxide reduction (OD-Cu) can significantly reduce the overpotential for C₂₊ product generation and improve its selectivity. Existing research generally presumes that the preparation process of OD-Cu generates unsaturated coordinated Cu* sites. However, there is still considerable controversy regarding the exact role of these Cu* sites in promoting C₂₊ product generation. Hao et al. used a vibrating sample magnetometer (VSM) to characterize the magnetic properties of Cu-based catalysts and found that the magnetization curve (*M*-*H* loop) of OD-Cu had the same electron magnetic moment signal as Cu₂O at low fields; this result confirmed that a magnetic Cu* site that was not completely occupied by 3d orbitals was generated during the preparation of the OD-Cu catalyst (Fig. 8c) [126]. The CO₂RR current density of OD-Cu was significantly higher than that of Cu (Fig. 8d). When an external magnetic field (350 mT) was applied, the current of the OD-Cu catalyst was significantly increased (nearly 10%), while the current of the diamagnetic intrinsic Cu catalyst was almost unchanged (Figs. 8e and f). The catalytic performance of OD-Cu under a magnetic field was directly related to the magnetic properties of the Cu* site. The results of the magnetic field effect measurements at different potentials indicated that this spin catalysis mechanism could effectively inhibit the HER on the OD-Cu catalyst and improve its CO₂ reduction performance. Interestingly, the electron spin arrangement of the

asymmetric Cu*-Cu binary sites in OD-Cu could reduce the reaction energy barrier of the C-C bonding process, which was essential for the formation of C₂₊ products. Therefore, the spin-enhanced catalytic mechanism could significantly improve the Faraday efficiency and selectivity of C₂₊ products of OD-Cu catalysts at low overpotential.

4.4. Spin regulation in NRR catalysts

Electrochemical nitrogen reduction is a process that utilizes electrochemical methods to convert nitrogen gas into ammonia or other useful compounds [127]. Although this method has the potential to be environmentally friendly and efficient, there are still some challenges and difficulties. Nitrogen gas molecules have a highly stable triple bond structure, which requires overcoming a high energy barrier to reduce them into ammonia or other useful compounds. In addition, the insufficient electron density causes difficulty for nitrogen gas molecules to adsorb and dissociate on the electrode surface, thereby reducing the reactivity of the reaction. Effective catalysts are crucial for enhancing the reaction activity of nitrogen reduction. By finely controlling the electronic spin structure, the intermediate state energy barriers and stability in the nitrogen reduction reaction catalyst can be adjusted, thus constructing nitrogen reduction catalysts with high reaction activity.

Fang et al. conducted a systematic study on the NRR with a series of transition metals (M) from group IIIB-VB, which were embedded in defect sites of two-dimensional boron nitride (BN) nano monolayers, utilizing the density functional theory (DFT) calculation method [128]. Magnetic fluctuation of the active site existed in the sequential hydrogenation step of electrocatalytic nitrogen reduction, which showed that the electron spin state of the single atom active site played an important role in regulating the potential determination step of the NRR. If the active site of MN₂B₂ had a high-spin magnetic moment (μ), it was conducive to reducing the limit potential of the NRR. Increasing the electron spin state of the M center of the active site of MN₂B₂ helped to break the linear proportional relationship between the adsorption energies of the key nitrogen-containing reaction intermediates of NRR (*N₂H/*N₂ and *NH₂/*N₂), and the moderate nitrogen affinity of the active site was crucial to the efficient NRR.

Li et al. found that the incorporation of S into the coordination of Fe_{SA}-NSC could induce a transformation of the spin polarization configuration to form a medium spin state of Fe(t_{2g}⁶e_g¹), as presented in Fig. 8g, which was conducive to e_g electron penetration of the antibonding π orbital of nitrogen [129]. The medium spin structure of the Fe site facilitated accelerated N₂ activation and protonation in the rate-determining step from *N₂ to *NNH, as demonstrated by the free energy profiles (Fig. 8h).

4.5. Spin regulation in HER catalysts

HER refers to the process of inducing the generation of hydrogen gas under the influence of an external electric potential, utilizing catalysts [130]. This is a significant method for hydrogen production, characterized by its efficiency, controllability, and environmental advantages. Hydrogen evolution reaction finds widespread applications in fields such as fuel cells, water electrolysis, and other energy conversion domains. The involvement of catalysts is typically required to enhance the reaction rates and efficiency of HER. Spin control can influence the formation and stability of active centers on the catalyst's surface, thereby modulating the catalytic activity of the hydrogen evolution reaction. By adjusting the electron spin state, the adsorption and dissociation capabilities of the catalyst for hydrogen molecules can be increased or decreased, thereby impacting the reaction rate [63,131].

Li et al. developed Ce-CoP nanoarrays on carbon cloth (Ce-CoP@CC) as a representative catalyst to explore the impact of Ce-induced on Co sites in the hydrogen evolution reaction [132]. The Ce and Co elements are connected by the *p*-block P element, ensuring a strong coupling between Ce and Co through the Ce-P-Co unit. The introduction of Ce

induces modifications in the electronic state of Co sites, leading to exceptional HER performance in Ce–CoP@CC, characterized by low overpotentials, small Tafel slopes, and remarkable stability. These properties surpass those of individual CoP@CC and most reported Co-based catalysts. DFT calculations revealed that the Ce-4f state plays important regulatory roles for the spin state of Co sites during HER through f–p–d gradient orbital coupling. The preserved Ce-4f electron induces redistributed spin-parallel coupling at surface Co sites, enhancing the adsorption of *H intermediates and consequently optimizing the HER activity.

Zeng et al. utilized a high-frequency alternating magnetic field to influence the spin polarization direction of individual Gd atoms, triggering localized magnetic heating characteristics [133]. By heating the active single atoms without the need to increase the loading amount, they further enhanced the hydrogen evolution activity of single-atom catalysts. Building on the synthesis of large-area air-stable monolayer molybdenum disulfide, they anchored Gd single atoms into the monolayer molybdenum disulfide using laser molecular beam epitaxy technology, successfully creating Gd@MoS₂ single-atom catalysts. Due to strong hybridization between Gd (4f), Mo (4d), and S (3p), the Gd single-atom catalyst exhibits in-plane room-temperature ferromagnetism, with spin density primarily concentrated on the anchored Gd single atom. Spin-correlated electrochemical experiments indicate that the spin polarization direction of Gd single-atom catalysts changes with the direction of the magnetic field. Therefore, when applying a high-frequency alternating magnetic field, the Gd single-atom catalyst undergoes spin flipping (or canting) with the changing magnetic field, generating magnetic heating effects associated with Néel relaxation. This localized magnetic heating effect near the active site (Gd) significantly enhances the hydrogen evolution activity of this single-atom catalyst.

4.6. Spin regulation in other reactions

In addition to the types of reactions mentioned above, spin regulation can also be used to enhance the reactivity of other reactions, such as water purification, oxidation reaction of small organic molecules, lithium–sulfur batteries, and so on.

The adsorption capacity of Hematite for oxygen-containing pollutants can be improved by adjusting the electron spin state. Shen et al. reported a method of synthesizing a new type of highly efficient adsorbent by adjusting the spin state of Fe₂O₃ with crystal size restriction [134]. Using MCM-41 mesoporous silica as the skeleton, TiO₂@MCM-41(TM) is formed by TiO₂ deposition and etching, and then FeSO₄ is introduced and evenly distributed on the skeleton, and Fe₂O₃&TiO₂@MCM-41(FTM) is obtained after calcination in air. Finally, FTM is expanded and ruptured by rapid gas and air calcination to form the final product FTMC. This method enables the formation of Fe–O–Si bonds between Fe₂O₃ and SiO₂, transferring Fe electrons to Si through oxygen bridges, and forming Fe₂O₃ electron defects. This results in a decrease in the spin state of Fe and a decrease in the occupancy of e_g orbitals, resulting in a large amount of positive charge on the surface of FTMC, which greatly enhances its adsorption effect on anionic pollutants. The experimental results of the adsorption of dyes, antibiotics, and arsenic salt showed that the adsorption effect of FTMC was much higher than that of commercial activated carbon. The adsorption equilibrium time of FTMC for Rose Bengal dye was within 5 min, and the maximum adsorption capacity and adsorption rate were 8 times and 300 times that of commercial activated carbon, respectively.

Spin regulation provides an effective strategy for the oxidation of small organic molecules, which can optimize the reaction conditions by adjusting the spin state of the catalyst, and improve the catalytic activity and selectivity, to achieve a more efficient and environmentally friendly oxidation process. Especially, the application of spin control to the degradation of organic pollutants in the environment has been widely reported. Chai et al. regulated the electronic structure of Fe single-atom catalyst (Fe–NC) by introducing P in the second shell to improve the

activation capacity of peroxonosulfate (PMS) as widely applied in degrading contaminants [135]. Compared with Fe–NC (Fe–N₄, low-spin state), Fe–PNC has a unique coordination environment (Fe–N₄P₂) and a high-spin state. Due to the doping of P, the energy enhancement of the Fe 3d orbital electrons induces the production of more unpaired electrons, thus transforming the catalyst from the original low-spin state to a high-spin state. This allows the Fe 3d orbitals to better bind to the O 2p orbitals of the PMS, thus allowing more electrons to be transferred from the Fe site to the PMS, accelerating the decomposition of the PMS and leading to the degradation of bisphenol A. In addition, the doping of P reduces the splitting field energy and energy gap of the catalyst, and promotes the rapid and efficient transfer of electrons from bisphenol A to the Fe site, so that Fe is in a higher spin state, thus achieving continuous degradation of bisphenol A.

The current research on the catalysis of sulfur oxidation–reduction mainly focuses on the adsorption and catalytic conversion of lithium polysulfides, while neglecting the regulation of the catalyst's electronic structure, which involves charge transfer and orbital interactions related to spin. Li et al. used bimetallic phosphorus trisulfide embedded in nitrogen-doped hollow carbon nanotubes derived from Prussian blue analogs (FeCoPS₃/NCs) as hosts to investigate the relationship between the catalytic activity of Li–S batteries and the spin configuration [136]. The orbital spin splitting in FeCoPS₃ drives the electronic structure from a low-spin state to a high-spin state, resulting in more unpaired electrons in the 3d orbitals. Specifically, the non-derivatized orbitals involved in the high-spin configuration of FeCoPS₃ lead to an upward shift in energy levels, generating more active electronic states. This tailored electronic structure enhances charge transfer, affects the d-band center, and further alters the adsorption energy of lithium polysulfides and potential reaction pathways. As a result, the FeCoPS₃/NC primary battery exhibits extremely low capacity decay over 1000 cycles, with a decay rate of only 0.037% per cycle.

At present, an increasing number of studies have confirmed the important role of the spin effect in electrocatalysis. Further investigation is required to explore and understand the regulation and mechanism of electron spin as a novel research direction for electrocatalysts.

5. Conclusions and perspectives

In summary, the utilization of spin effects provides a new design strategy for the development of efficient electrocatalysts. By incorporating spin properties into the design and synthesis of electrocatalysts, researchers can manipulate the spin to regulate the activity and selectivity of the catalysts. By precisely controlling the spin state of electrocatalysts, researchers can achieve control over the stability of reaction intermediates, reaction rates, and selectivity of catalytic reactions. This spin manipulation strategy provides new insights and approaches for the design and development of efficient electrocatalysts. We surveyed the recent advances in the electron spin effect toward electrocatalytic applications, including the mechanism and regulation methods of the electron spin effect, characterization techniques, and their applications in electrochemical catalysis (ORR, OER, NRR, and CO₂RR). However, research on the electron spin effect is still in its infancy, and the practical application of the spin effect in the design of electrocatalysts inevitably has many challenges. Based on the reported results, prospects for the future development of spintronics in electrocatalysis center on the following aspects (Fig. 9).

First, there is a lack of precise control methods for electronic spin structures. Currently, the means of controlling the spin states also lead to other structural changes, such as changes in conductivity, valence states, and composition. This presents a problem where multiple structural changes coexist with spin state modulation, causing difficulty in determining which factor has a decisive impact on catalytic performance. Furthermore, the current methods for controlling the spin state are still not controllable, hindering the study of the effects of different spin states (low-spin, medium-spin, and high-spin) on activity by adjusting the spin

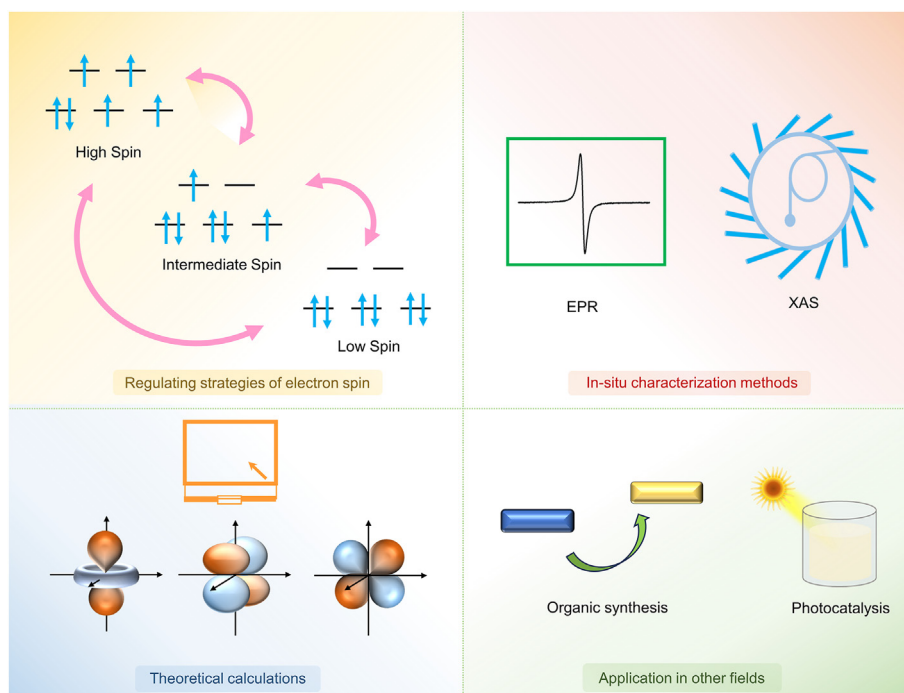


Fig. 9. Summary of challenges and perspectives of spin effect for application in electrocatalysis.

state in the same catalyst. Hence, a critical need arises for designing a spin state optimization system that minimizes unintended alterations during mechanistic studies.

Second, establishing advanced in situ characterization methods to directly observe the correlation between spin state and catalytic activity changes is crucial for understanding the mechanism of spin effects. Through this method, we can monitor the changes in the spin state in real-time and compare them with the changes in catalytic activity. Since electrocatalytic reactions are dynamic processes, the catalyst in solution may undergo spin state changes during the electrocatalytic process. Therefore, in situ characterization can show the actual state of active sites in chemical reactions. For example, in situ XAS can analyze the spin state of metal atoms by measuring the absorption spectra of X-rays interacting with the catalyst under catalytic reaction conditions. This direct observation method can clarify how spin states influence catalytic reactions and offer valuable guidance for designing new spin catalysts.

Third, due to the current challenges in the controllable modulation and in situ characterization of spin states, theoretical calculations have a unique advantage in studying spin processes in catalysis and are of great significance in exploring mechanisms. However, theoretical calculations of spin processes in electrocatalysis are complex and challenging, and there are few detailed reports on the computational aspects of spin processes in electrocatalysis. Therefore, developing suitable theoretical methods to observe the processes of spin transfer or flip occurring in electrocatalytic reactions could be a breakthrough in mechanistic studies. In addition, the development of suitable spin catalysis descriptors and the use of first-principles calculations combined with high-throughput screening methods based on machine learning frameworks can enable the rational prediction of catalytic activity, accelerate the design of novel spin electrocatalytic materials, and elucidate the relationship between reaction mechanisms and the spin properties of active centers.

Fourth, the spin effect has been applied to promote electrocatalytic reactions in research on the ORR, OER, NRR, and CO₂RR, opening up a new avenue for studying efficient electrocatalysts. However, the spin effect of metal site electrons is not only widely applied in electrocatalytic reactions but also shows potential applications in organic synthesis,

photocatalysis, electron transfer and transport, and biomedical fields. For example, the spin behavior of active site electrons can influence the rate and selectivity of organic synthesis reactions. The spin behavior of the metal center electrons is also crucial for the efficiency and selectivity of photocatalytic reactions. By controlling the spin state of the metal complexes, the charge transfer and energy transfer during light absorption and excitation processes can be adjusted, thereby achieving efficient photocatalytic reactions. Therefore, in-depth research on the application of the spin effects in other types of reactions is equally significant.

It is important to study and understand the electron spin effect for designing and optimizing electrocatalytic reactions. Although the future in-depth study of the electron spin effect is still challenging, we firmly believe that through persistent research efforts, the electron spin effect will aid in the preparation of high-performance electrocatalysts to solve the current energy problems.

Author contributions

Liu Lin: Conceptualization, Writing – original draft, Writing – review & editing. **Peiyuan Su:** Writing – review & editing. **Yiting Han:** Writing – review & editing. **Yunming Xu:** Writing – review & editing. **Qiao Ni:** Writing – review & editing. **Xinyue Zhang:** Writing – review & editing. **Peixun Xiong:** Writing – review & editing. **Zemin Sun:** Writing – original draft, Writing – review & editing. **Genban Sun:** Writing – review & editing. **Xuebo Chen:** Writing – review & editing.

Declaration of competing interest

The authors declare no competing financial interests.

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References

- [1] A. Goldthau, S. Tagliapietra, Energy crisis: five questions that must be answered in 2023, *Nature* 612 (2022) 627–630.
- [2] P. Zhu, Z.Y. Wu, A. Elgazzar, C. Dong, T.U. Wi, F.Y. Chen, Y. Xia, Y. Feng, M. Shakouri, J.Y.T. Kim, Z. Fang, T.A. Hatton, H. Wang, Continuous carbon capture in an electrochemical solid-electrolyte reactor, *Nature* 618 (2023) 959–966.
- [3] B. Wu, H. Meng, D.M. Morales, F. Zeng, J. Zhu, B. Wang, M. Risch, Z.J. Xu, T. Petit, Nitrogen-rich carbonaceous materials for advanced oxygen electrocatalysis: synthesis, characterization, and activity of nitrogen sites, *Adv. Funct. Mater.* 32 (2022) 2204137.
- [4] Y. Zhao, B.P. Setzler, J. Wang, J. Nash, T. Wang, B. Xu, Y. Yan, An efficient direct ammonia fuel cell for affordable carbon-neutral transportation, *Joule* 3 (2019) 2472–2484.
- [5] Y. Huang, L.W. Jiang, B.Y. ShiS, K.M. Ryan, J.J. Wang, Highly efficient oxygen evolution reaction enabled by phosphorus doping of the Fe electronic structure in iron-nickel selenide nanosheets, *Adv. Sci.* 8 (2021) e2101775.
- [6] G.A. Kamat, J.A. Zamora Zeledón, G. Gunasooriya, S.M. Dull, J.T. Perryman, J.K. Norskov, M.B. Stevens, T.F. Jaramillo, Acid anion electrolyte effects on platinum for oxygen and hydrogen electrocatalysis, *Commun. Chem.* 5 (2022) 20.
- [7] X. Li, H. Lei, L. Xie, N. Wang, W. Zhang, R. Cao, Metalloporphyrins as catalytic models for studying hydrogen and oxygen evolution and oxygen reduction reactions, *Acc. Chem. Res.* 55 (2022) 878–892.
- [8] J. Quílez-Bermejo, S. García-Dalí, A. Daouli, A. Zitolo, R.L.S. Canevesi, M. Emo, M.T. Izquierdo, M. Badawi, A. Celzard, V. Fierro, Advanced design of metal nanoclusters and single atoms embedded in C₁N₁-derived carbon materials for ORR, HER, and OER, *Adv. Funct. Mater.* 33 (2023) 2300405.
- [9] X. Lei, Q. Tang, Y. Zheng, P. Kidkhunthod, X. Zhou, B. Ji, Y. Tang, High-entropy single-atom activated carbon catalysts for sustainable oxygen electrocatalysis, *Nat. Sustain.* 6 (2023) 816–826.
- [10] Y. Ni, L. Lin, Y. Shang, L. Luo, L. Wang, Y. Lu, Y. Li, Z. Yan, K. Zhang, F. Cheng, J. Chen, Regulating electrocatalytic oxygen reduction activity of a metal coordination polymer via d- π conjugation, *Angew. Chem. Int. Ed.* 60 (2021) 16937–16941.
- [11] X. Wang, M. Yu, X. Feng, Electronic structure regulation of noble metal-free materials toward alkaline oxygen electrocatalysis, *eScience* 3 (2023) 100141.
- [12] Y. Huang, L.-W. Jiang, H. Liu, J.-J. Wang, Electronic structure regulation and polysulfide bonding of Co-doped (Ni, Fe)_{1-x}S enable highly efficient and stable electrocatalytic overall water splitting, *Chem. Eng. J.* 441 (2022) 136121.
- [13] L.W. Jiang, Y. Huang, Y. Zou, C. Meng, Y. Xiao, H. Liu, J.J. Wang, Boosting the stability of oxygen vacancies in α -Co(OH)₂ nanosheets with coordination polyhedrons as rivets for high-performance alkaline hydrogen evolution electrocatalyst, *Adv. Energy Mater.* 12 (2022) 2202351.
- [14] S. Chandrasekaran, R. Hu, L. Yao, L. Sui, Y. Liu, A. Abdelkader, Y. Li, X. Ren, L. Deng, Mutual self-regulation of d-electrons of single atoms and adjacent nanoparticles for bifunctional oxygen electrocatalysis and rechargeable zinc-air batteries, *Nano-Micro Lett.* 15 (2023) 48.
- [15] T. Wu, M.M. Melander, K. Honkala, Coadsorption of NRR and HER intermediates determines the performance of Ru–N₄ toward electrocatalytic N₂ reduction, *ACS Catal.* 12 (2022) 2505–2512.
- [16] C. Kim, F. Dionigi, V. Beermann, X. Wang, T. Moller, P. Strasser, Alloy nanocatalysts for the electrochemical oxygen reduction (ORR) and the direct electrochemical carbon dioxide reduction reaction (CO₂RR), *Adv. Mater.* 31 (2019) e1805617.
- [17] K. Zhu, X. Zhu, W. Yang, Application of in situ techniques for the characterization of NiFe-based oxygen evolution reaction (OER) electrocatalysts, *Angew. Chem. Int. Ed.* 58 (2019) 1252–1265.
- [18] Z. Li, X. Wu, X. Jiang, B. Shen, Z. Teng, D. Sun, G. Fu, Y. Tang, Surface carbon layer controllable Ni₃Fe particles confined in hierarchical N-doped carbon framework boosting oxygen evolution reaction, *Adv. Powder Mater.* 1 (2022) 100020.
- [19] Z. Huan, H. Fu, X. Zheng, H. Ji, Disordered rocksalts with lattice oxygen activation as efficient oxygen evolution electrocatalysts, *Trans. Tianjin Univ.* 29 (2023) 304–312.
- [20] Y. Huang, L.-W. Jiang, X.-L. Liu, T. Tan, H. Liu, J.-J. Wang, Precisely engineering the electronic structure of active sites boosts the activity of iron-nickel selenide on nickel foam for highly efficient and stable overall water splitting, *Appl. Catal. B Environ.* 299 (2021) 120678.
- [21] Y. Huang, L. Zhang, L.W. Jiang, X.L. Liu, T. Tan, H. Liu, J.J. Wang, Electronic structure regulation and surface reconstruction of iron diselenide for enhanced oxygen evolution activity, *Small* 19 (2023) e2302970.
- [22] Z.-H. Yin, Y. Huang, L.-W. Jiang, C. Meng, Y.-Z. Wu, H. Liu, J.-J. Wang, Revealing the in situ evolution of tetrahedral NiMoO₄ micropillar array for energy-efficient alkaline hydrogen production assisted by urea electrolysis, *Small Struct.* 4 (2023) 2300028.
- [23] D. Mei, Z.D. He, Y.L. Zheng, D.C. Jiang, Y.X. Chen, Mechanistic and kinetic implications on the ORR on a Au(100) electrode: pH, temperature and H-D kinetic isotope effects, *Phys. Chem. Chem. Phys.* 16 (2014) 13762–13773.
- [24] J. Masa, I. Sinev, H. Mistry, E. Ventosa, M. de la Mata, J. Arbiol, M. Muhler, B. Roldan Cuenya, W. Schuhmann, Ultrathin high surface area nickel boride (Ni₃B) nanosheets as highly efficient electrocatalyst for oxygen evolution, *Adv. Energy Mater.* 7 (2017) 1700381.
- [25] C. Bie, L. Wang, J. Yu, Challenges for photocatalytic overall water splitting, *Chem* 8 (2022) 1567–1574.
- [26] Z. Sun, L. Lin, J. He, D. Ding, T. Wang, J. Li, M. Li, Y. Liu, Y. Li, M. Yuan, B. Huang, H. Li, G. Sun, Regulating the spin state of Fe(III) enhances the magnetic effect of the molecular catalysis mechanism, *J. Am. Chem. Soc.* 144 (2022) 8204–8213.
- [27] V.H. Do, J.M. Lee, Orbital occupancy and spin polarization: from mechanistic study to rational design of transition metal-based electrocatalysts toward energy applications, *ACS Nano* 16 (2022) 17847–17890.
- [28] O.V. Khavryuchenko, V.D. Khavryuchenko, D. Su, Spin catalysts: a quantum trigger for chemical reactions, *Chin. J. Catal.* 36 (2015) 1656–1661.
- [29] H. Lustig, The life and times of Werner Heisenberg, *Phys. Perspect.* 12 (2010) 470–496.
- [30] V.K. Sreenivasan, A.V. Zvyagin, E.M. Goldys, Luminescent nanoparticles and their applications in the life sciences, *J. Phys. Condens. Matter* 25 (2013) 194101.
- [31] A.K. Mondal, N. Brown, S. Mishra, P. Makam, D. Wing, S. Gilead, Y. Wiesenfeld, G. Leitun, L.J.W. Shimon, R. Carmieli, D. Ehre, G. Kamieniarz, J. Fransson, O. Hod, L. Kronik, E. Gazit, R. Naaman, Long-range spin-selective transport in chiral metal-organic crystals with temperature-activated magnetization, *ACS Nano* 14 (2020) 16624–16633.
- [32] B. Lampe, E. Reya, Spin physics and polarized structure functions, *Phys. Rep.* 332 (2000) 1–163.
- [33] M.B. Franzoni, L. Buljubasic, H.W. Spiess, K. Munneemann, Long-lived 1H singlet spin states originating from para-hydrogen in Cs-symmetric molecules stored for minutes in high magnetic fields, *J. Am. Chem. Soc.* 134 (2012) 10393–10396.
- [34] J. Ge, R.R. Chen, X. Ren, J. Liu, S.J.H. Ong, Z.J. Xu, Ferromagnetic-antiferromagnetic coupling core-shell nanoparticles with spin conservation for water oxidation, *Adv. Mater.* 33 (2021) e2101091.
- [35] R. Wang, L. Zhang, J. Shan, Y. Yang, J.F. Lee, T.Y. Chen, J. Mao, Y. Zhao, L. Yang, Z. Hu, T. Ling, Tuning Fe spin moment in Fe–N–C catalysts to climb the activity volcano via a local geometric distortion strategy, *Adv. Sci.* 9 (2022) e2203917.
- [36] Y. Liu, X. Liu, Z. Lv, R. Liu, L. Li, J. Wang, W. Yang, X. Jiang, X. Feng, B. Wang, Tuning the spin state of the iron center by bridge-bonded Fe–O–Ti ligands for enhanced oxygen reduction, *Angew. Chem. Int. Ed.* 61 (2022) e202117617.
- [37] Y. Liu, C. Xiao, P. Huang, M. Cheng, Y. Xie, Regulating the charge and spin ordering of two-dimensional ultrathin solids for electrocatalytic water splitting, *Chem* 4 (2018) 1263–1283.
- [38] W. Zhang, W. Gao, X. Zhang, Z. Li, G. Lu, Surface spintronics enhanced photocatalytic hydrogen evolution: mechanisms, strategies, challenges and future, *Appl. Surf. Sci.* 434 (2018) 643–668.
- [39] J. Zhou, Z. Han, X. Wang, H. Gai, Z. Chen, T. Guo, X. Hou, L. Xu, X. Hu, M. Huang, S.V. Levchenko, H. Jiang, Discovery of quantitative electronic structure-OER activity relationship in metal-organic framework electrocatalysts using an integrated theoretical-experimental approach, *Adv. Funct. Mater.* 31 (2021) 2102066.
- [40] Z. Zhang, P. Ma, L. Luo, X. Ding, S. Zhou, J. Zeng, Regulating spin states in oxygen electrocatalysis, *Angew. Chem. Int. Ed.* 62 (2023) e202216837.
- [41] J. Li, Y. Yu, S. Xu, W. Yan, S. Mu, J.-N. Zhang, Function of electron spin effect in electrocatalysts, *Acta Phys. Chim. Sin.* 39 (2023) 2302049.
- [42] Y. Wang, W. Cheng, P. Yuan, G. Yang, S. Mu, J. Liang, H. Xia, K. Guo, M. Liu, S. Zhao, G. Qu, B.A. Lu, Y. Hu, J. Hu, J.N. Zhang, Boosting nitrogen reduction to ammonia on FeN₄ sites by atomic spin regulation, *Adv. Sci.* 8 (2021) e2102915.
- [43] Y. Liu, X. Hua, C. Xiao, T. Zhou, P. Huang, Z. Guo, B. Pan, Y. Xie, Heterogeneous spin states in ultrathin nanosheets induce subtle lattice distortion to trigger efficient hydrogen evolution, *J. Am. Chem. Soc.* 138 (2016) 5087–5092.
- [44] C.C. Lin, T.R. Liu, S.R. Lin, K.M. Boopathi, C.H. Chiang, W.Y. Tzeng, W.C. Chien, H.S. Hsu, C.W. Luo, H.Y. Tsai, H.A. Chen, P.C. Kuo, J. Shiue, J.W. Chiou, W.F. Pong, C.C. Chen, C.W. Chen, Spin-polarized photocatalytic CO₂ reduction of Mn-doped perovskite nanoplates, *J. Am. Chem. Soc.* 144 (2022) 15718–15726.
- [45] Y. Sun, X. Ren, S. Sun, Z. Liu, S. Xi, Z.J. Xu, Engineering high-spin state cobalt cations in spinel zinc cobalt oxide for spin channel propagation and active site enhancement in water oxidation, *Angew. Chem. Int. Ed.* 60 (2021) 14536–14544.
- [46] Y. Zhang, Q. Zhang, D.-X. Liu, Z. Wen, J.-X. Yao, M.-M. Shi, Y.-F. Zhu, J.-M. Yan, Q. Jiang, High spin polarization ultrafine Rh nanoparticles on CNT for efficient electrochemical N₂ fixation to ammonia, *Appl. Catal. B Environ.* 298 (2021) 120592.
- [47] L. Lin, R. Xin, M. Yuan, T. Wang, J. Li, Y. Xu, X. Xu, M. Li, Y. Du, J. Wang, S. Wang, F. Jiang, W. Wu, C. Lu, B. Huang, Z. Sun, J. Liu, J. He, G. Sun, Revealing spin magnetic effect of iron-group layered double hydroxides with enhanced oxygen catalysis, *ACS Catal.* 13 (2023) 1431–1440.
- [48] Z. Li, Z. Wang, S. Xi, X. Zhao, T. Sun, J. Li, W. Yu, H. Xu, T.S. Herng, X. Hai, P. Lyu, M. Zhao, S.J. Pennycook, J. Ding, H. Xiao, J. Lu, Tuning the spin density of cobalt single-atom catalysts for efficient oxygen evolution, *ACS Nano* 15 (2021) 7105–7113.
- [49] H. Li, S. Di, P. Niu, S. Wang, J. Wang, L. Li, A durable half-metallic diatomic catalyst for efficient oxygen reduction, *Energy Environ. Sci.* 15 (2022) 1601–1610.
- [50] Y. Sun, S. Sun, H. Yang, S. Xi, J. Gracia, Z.J. Xu, Spin-related electron transfer and orbital interactions in oxygen electrocatalysis, *Adv. Mater.* 32 (2020) e2003297.
- [51] H. Li, J. Wang, R. Qi, Y. Hu, J. Zhang, H. Zhao, J. Zhang, Y. Zhao, Enhanced Fe 3d delocalization and moderate spin polarization in Fe Ni atomic pairs for bifunctional ORR and OER electrocatalysis, *Appl. Catal. B Environ.* 285 (2021) 119778.
- [52] I. Carmeli, K.S. Kumar, O. Heifler, C. Carmeli, R. Naaman, Spin selectivity in electron transfer in photosystem I, *Angew. Chem. Int. Ed.* 53 (2014) 8953–8958.
- [53] W. Zhang, K.J. Gaffney, Mechanistic studies of photoinduced spin crossover and electron transfer in inorganic complexes, *Acc. Chem. Res.* 48 (2015) 1140–1148.
- [54] J. Hao, Z. Zhuang, K. Cao, G. Gao, C. Wang, F. Lai, S. Lu, P. Ma, W. Dong, T. Liu, M. Du, H. Zhu, Unraveling the electronegativity-dominated intermediate adsorption on high-entropy alloy electrocatalysts, *Nat. Commun.* 13 (2022) 2662.

- [55] X. Ren, T. Wu, Y. Sun, Y. Li, G. Xian, X. Liu, C. Shen, J. Gracia, H.J. Gao, H. Yang, Z.J. Xu, Spin-polarized oxygen evolution reaction under magnetic field, *Nat. Commun.* 12 (2021) 2608.
- [56] R. Naaman, Y. Paltiel, D.H. Waldeck, Chiral molecules and the electron spin, *Nat. Rev. Chem.* 3 (2019) 250–260.
- [57] M.S. Zollner, A. Saghatchi, V. Mujica, C. Herrmann, Influence of electronic structure modeling and junction structure on first-principles chiral induced spin selectivity, *J. Chem. Theory Comput.* 16 (2020) 7357–7371.
- [58] M. Jain, L. Kronik, J. Chelikowsky, V. Godlevsky, Electronic structure and spin polarization of Mn-containing dilute magnetic III-V semiconductors, *Phys. Rev. B* 64 (2001) 245205.
- [59] X.D. Hu, S. Das Sarma, Hilbert-space structure of a solid-state quantum computer: two-electron states of a double-quantum-dot artificial molecule, *Phys. Rev. A* 61 (2000) 062301.
- [60] R.J. Soulen Jr., J.M. Byers, M.S. Osofsky, B. Nadgorny, T. Ambrose, S.F. Cheng, C.T.P.R. Broussard, J. Nowak, J.S. Moodera, A. Barry, J.M.D. Coey, Measuring the spin polarization of a metal with a superconducting point contact, *Science* 282 (1998) 85–88.
- [61] D. Guo, T.E. Knight, J.K. McCusker, Angular momentum conservation in dipolar energy transfer, *Science* 334 (2011) 1684–1687.
- [62] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, third ed., Springer, New York, 2006.
- [63] R.R. Chen, Y. Sun, S.J.H. Ong, S. Xi, Y. Du, C. Liu, O. Lev, Z.J. Xu, Antiferromagnetic inverse spinel oxide LiCoVO_4 with spin-polarized channels for water oxidation, *Adv. Mater.* 32 (2020) e1907976.
- [64] W. Orellana, Catalytic properties of transition metal– N_4 moieties in graphene for the oxygen reduction reaction: evidence of spin-dependent mechanisms, *J. Phys. Chem. C* 117 (2013) 9812–9818.
- [65] J. Li, J. Ma, Z. Ma, E. Zhao, K. Du, J. Guo, T. Ling, Spin effect on oxygen electrocatalysis, *Adv. Energy Sustain. Res.* 2 (2021) 2100034.
- [66] T. Wu, X. Ren, Y. Sun, S. Sun, G. Xian, G.G. Scherer, A.C. Fisher, D. Mandler, J.W. Ager, A. Grimaud, J. Wang, C. Shen, H. Yang, J. Gracia, H.J. Gao, Z.J. Xu, Spin pinning effect to reconstructed oxyhydroxide layer on ferromagnetic oxides for enhanced water oxidation, *Nat. Commun.* 12 (2021) 3634.
- [67] R.R. Chen, G. Chen, X. Ren, J. Ge, S.J.H. Ong, S. Xi, X. Wang, Z.J. Xu, SmCo_5 with a reconstructed oxyhydroxide surface for spin-selective water oxidation at elevated temperature, *Angew. Chem. Int. Ed.* 60 (2021) 25884–25890.
- [68] H. Cai, B. Chen, X. Zhang, Y. Deng, D. Xiao, D. Ma, C. Shi, Highly active sites of low spin $\text{Fe}^{\text{II}}\text{N}_4$ species: the identification and the ORR performance, *Nano Res.* 14 (2020) 122–130.
- [69] Y. Xie, Y. Yang, W. Yang, N. Liu, X. Chen, The relationship between the local environment, N-type, spin state and catalytic functionality of carbon-hosted $\text{Fe}^{\text{II}}/\text{III}-\text{N}_4$ for the conversion of CO_2 to CO, *Phys. Chem. Chem. Phys.* 25 (2023) 18889–18902.
- [70] Y. Wen, J. Liu, F. Zhang, Z. Li, P. Wang, Z. Fang, M. He, J. Chen, W. Song, R. Si, L. Wang, Mesoporous MnO_2 nanosheets for efficient electrocatalytic nitrogen reduction via high spin polarization induced by oxygen vacancy, *Nano Res.* 16 (2022) 4664–4670.
- [71] G. Song, R. Gao, Z. Zhao, Y. Zhang, H. Tan, H. Li, D. Wang, Z. Sun, M. Feng, High-spin state $\text{Fe}(\text{III})$ doped TiO_2 for electrocatalytic nitrogen fixation induced by surface F modification, *Appl. Catal. B Environ.* 301 (2022) 120809.
- [72] H. Bai, J. Feng, D. Liu, P. Zhou, R. Wu, C.T. Kwok, W.F. Ip, W. Feng, X. Sui, H. Liu, H. Pan, Advances in spin catalysts for oxygen evolution and reduction reactions, *Small* 19 (2023) e2205638.
- [73] W. Gao, Y. Zou, Y. Zang, X. Zhao, W. Zhou, Y. Dai, H. Liu, J.-J. Wang, Y. Ma, Y. Sang, Magnetic-field-regulated Ni–Fe–Mo ternary alloy electrocatalysts with enduring spin polarization enhanced oxygen evolution reaction, *Chem. Eng. J.* 455 (2023) 140821.
- [74] G. Shen, R. Zhang, L. Pan, F. Hou, Y. Zhao, Z. Shen, W. Mi, C. Shi, Q. Wang, X. Zhang, J.J. Zou, Regulating the spin state of $\text{Fe}(\text{III})$ by atomically anchoring on ultrathin titanium dioxide for efficient oxygen evolution electrocatalysis, *Angew. Chem. Int. Ed.* 59 (2020) 2313–2317.
- [75] J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. Cheng, F. Hu, Y. Jiang, Z. Pan, S. Wei, CoOOH nanosheets with high mass activity for water oxidation, *Angew. Chem. Int. Ed.* 54 (2015) 8722–8727.
- [76] L. Pan, M. Ai, C. Huang, L. Yin, X. Liu, R. Zhang, S. Wang, Z. Jiang, X. Zhang, J.J. Zou, W. Mi, Manipulating spin polarization of titanium dioxide for efficient photocatalysis, *Nat. Commun.* 11 (2020) 418.
- [77] L. Li, J. Zhou, X. Wang, J. Gracia, M. Valvidares, J. Ke, M. Fang, C. Shen, J.M. Chen, Y.C. Chang, C.W. Pao, S.Y. Hsu, J.F. Lee, A. Ruotolo, Y. Chin, Z. Hu, X. Huang, Q. Shao, Spin-polarization strategy for enhanced acidic oxygen evolution activity, *Adv. Mater.* 35 (2023) e2302966.
- [78] G. Yang, J. Zhu, P. Yuan, Y. Hu, G. Qu, B.A. Lu, X. Xue, H. Yin, W. Cheng, J. Cheng, W. Xu, J. Li, J. Hu, S. Mu, J.N. Zhang, Regulating Fe-spin state by atomically dispersed Mn–N in Fe–N–C catalysts with high oxygen reduction activity, *Nat. Commun.* 12 (2021) 1734.
- [79] Y.N. Gong, W. Zhong, Y. Li, Y. Qiu, L. Zheng, J. Jiang, H.L. Jiang, Regulating photocatalysis by spin-state manipulation of cobalt in covalent organic frameworks, *J. Am. Chem. Soc.* 142 (2020) 16723–16731.
- [80] D. Liu, D. Luo, A.N. Iqbal, K.W.P. Orr, T.A.S. Doherty, Z.H. Lu, S.D. Stranks, W. Zhang, Strain analysis and engineering in halide perovskite photovoltaics, *Nat. Mater.* 20 (2021) 1337–1346.
- [81] F. He, Q. Zheng, X. Yang, L. Wang, Z. Zhao, Y. Xu, L. Hu, Y. Kuang, B. Yang, Z. Li, L. Lei, M. Qiu, J. Lu, Y. Hou, Spin state modulation on metal-organic frameworks for electrocatalytic oxygen evolution, *Adv. Mater.* 35 (2023) e2304022.
- [82] Y. Tong, Y. Guo, P. Chen, H. Liu, M. Zhang, L. Zhang, W. Yan, W. Chu, C. Wu, Y. Xie, Spin-state regulation of perovskite cobaltite to realize enhanced oxygen evolution activity, *Chem* 3 (2017) 812–821.
- [83] C. Deng, S. Xie, Y. Li, Y. Zhao, P. Zhou, H. Sheng, H. Ji, C. Chen, J. Zhao, Strong spin polarization effect of atomically dispersed metal site boosts the selective photocatalytic nitrobenzene hydrogenation to aniline over graphitic carbon nitride, *J. Phys. Chem. A* 127 (2023) 2787–2794.
- [84] U.E. Steiner, T. Ulrich, Magnetic-field effects in chemical-kinetics and related phenomena, *Chem. Rev.* 89 (1989) 51–147.
- [85] C.Y. Zhang, C. Zhang, G.W. Sun, J.L. Pan, L. Gong, G.Z. Sun, J.J. Biendicho, L. Balcells, X.L. Fan, J.R. Morante, J.Y. Zhou, A. Cabot, Spin effect to promote reaction kinetics and overall performance of lithium-sulfur batteries under external magnetic field, *Angew. Chem. Int. Ed.* 61 (2022) e202211570.
- [86] S. Chen, S. Zhang, L. Guo, L. Pan, C. Shi, X. Zhang, Z.F. Huang, G. Yang, J.J. Zou, Reconstructed Ir–O–Mo species with strong Brønsted acidity for acidic water oxidation, *Nat. Commun.* 14 (2023) 4127.
- [87] Z. He, X. Liu, M. Zhang, L. Guo, M. Ajmal, L. Pan, C. Shi, X. Zhang, Z.-F. Huang, J.-J. Zou, Coupling ferromagnetic ordering electron transfer channels and surface reconstructed active species for spintronic electrocatalysis of water oxidation, *J. Energy Chem.* 85 (2023) 570–580.
- [88] A. Maity, H. Haick, Spin-induced nanomaterials for detection of chiral volatile organic compounds, *Appl. Phys. Rev.* 10 (2023) 031301.
- [89] A. Vadakkayil, C. Clever, K.N. Kunzler, S. Tan, B.P. Bloom, D.H. Waldeck, Chiral electrocatalysts eclipse water splitting metrics through spin control, *Nat. Commun.* 14 (2023) 1067.
- [90] M. Ai, L. Pan, C. Shi, Z.F. Huang, X. Zhang, W. Mi, J.J. Zou, Spin selection in atomic-level chiral metal oxide for photocatalysis, *Nat. Commun.* 14 (2023) 4562.
- [91] T. Xu, D. Jiao, M. Liu, L. Zhang, X. Fan, L. Zheng, W. Zheng, X. Cui, Ni center coordination reconstructed nanocorals for efficient water splitting, *Adv. Sci.* 10 (2023) e2205605.
- [92] D. Xue, P. Yuan, S. Jiang, Y. Wei, Y. Zhou, C.-L. Dong, W. Yan, S. Mu, J.-N. Zhang, Altering the spin state of Fe–N–C through ligand field modulation of single-atom sites boosts the oxygen reduction reaction, *Nano Energy* 105 (2023) 108020.
- [93] T. He, Y. Chen, Q. Liu, B. Lu, X. Song, H. Liu, M. Liu, Y.N. Liu, Y. Zhang, X. Ouyang, S. Chen, Theory-guided regulation of FeN_4 spin state by neighboring Cu atoms for enhanced oxygen reduction electrocatalysis in flexible metal-air batteries, *Angew. Chem. Int. Ed.* 61 (2022) e202201007.
- [94] C. Zhang, X. Wang, Z. Ma, H. Yao, H. Liu, C. Li, J. Zhou, R. Xu, X. Zheng, H. Wang, Q. Li, M. Gu, H. Jiang, M. Huang, Spin state modulation on dual Fe center by adjacent Ni sites enabling the boosted activities and ultra-long stability in Zn-air batteries, *Sci. Bull.* 68 (2023) 2042–2053.
- [95] Q. Xue, Y. Wang, M. Jiang, R. Cheng, K. Li, T. Zhao, C. Fu, Engineering electronic spin state of a CoNi alloy for an efficient oxygen reduction reaction, *ACS Appl. Energy Mater.* 6 (2023) 1888–1896.
- [96] C.Y. Huang, H.M. Lin, C.H. Chiang, H.A. Chen, T.R. Liu, D. Vishnu, S. K, J.W. Chiou, R. Sankar, H.M. Tsai, W.F. Pong, C.W. Chen, Manipulating spin exchange interactions and spin-selected electron transfers of 2D metal phosphorus trisulfide crystals for efficient oxygen evolution reaction, *Adv. Funct. Mater.* 33 (2023) 2305792.
- [97] H. Tang, D. Yang, M. Lu, S. Kong, Y. Hou, D. Liu, D. Liu, S. Yan, Z. Chen, T. Yu, Z. Zou, Spin unlocking oxygen evolution reaction on antiperovskite nitrides, *J. Mater. Chem. A* 9 (2021) 25435–25444.
- [98] Z. Chen, H. Niu, J. Ding, H. Liu, P.H. Chen, Y.H. Lu, Y.R. Lu, W. Zuo, L. Han, Y. Guo, S.F. Hung, Y. Zhai, Unraveling the origin of sulfur-doped Fe–N–C single-atom catalyst for enhanced oxygen reduction activity: effect of iron spin-state tuning, *Angew. Chem. Int. Ed.* 133 (2021) 25608–25614.
- [99] N. Huse, T.K. Kim, L. Jamula, J.K. McCusker, F.M. de Groot, R.W. Schoenlein, Photo-induced spin-state conversion in solvated transition metal complexes probed via time-resolved soft X-ray spectroscopy, *J. Am. Chem. Soc.* 132 (2010) 6809–6816.
- [100] J. Xu, X. Zhong, X. Wu, Y. Wang, S. Feng, Optimizing the electronic spin state and delocalized electron of $\text{NiCo}_2(\text{OH})/\text{MXene}$ composite by interface engineering and plasma boosting oxygen evolution reaction, *J. Energy Chem.* 71 (2022) 129–140.
- [101] H. Kim, J. Park, I. Park, K. Jin, S.E. Jeong, S.H. Kim, K.T. Nam, K. Kang, Coordination tuning of cobalt phosphates towards efficient water oxidation catalyst, *Nat. Commun.* 6 (2015) 8253.
- [102] M. Stohr, T. Van Voorhis, A. Tkatchenko, Theory and practice of modeling van der Waals interactions in electronic-structure calculations, *Chem. Soc. Rev.* 48 (2019) 4118–4154.
- [103] V. Borisov, Y.O. Kvashnin, N. Taltis, D. Thonig, P. Thunström, M. Pereiro, A. Bergman, E. Sjöqvist, A. Delin, L. Nordström, O. Eriksson, Heisenberg and anisotropic exchange interactions in magnetic materials with correlated electronic structure and significant spin-orbit coupling, *Phys. Rev. B* 103 (2021) 174422.
- [104] Y. Li, T.Z. Wang, M. Asim, L. Pan, R.R. Zhang, Z.F. Huang, Z.C. Chen, C.X. Shi, X.W. Zhang, J.J. Zou, Manipulating spin polarization of defected CoO for highly efficient electrocatalysis, *Trans. Tianjin Univ.* 28 (2022) 163–173.
- [105] X. Li, Z. Cheng, X. Wang, Understanding the mechanism of the oxygen evolution reaction with consideration of spin, *Electrochem. Energy Rev.* 4 (2020) 136–145.
- [106] C.Y. Lin, D. Zhang, Z. Zhao, Z. Xia, Covalent organic framework electrocatalysts for clean energy conversion, *Adv. Mater.* 30 (2018) 1703646.
- [107] J. Hassoun, F. Croce, M. Armand, B. Scrosati, Investigation of the O_2 electrochemistry in a polymer electrolyte solid-state cell, *Angew. Chem. Int. Ed.* 123 (2011) 3055–3058.
- [108] J. Liu, H. Liu, H. Chen, X. Du, B. Zhang, Z. Hong, S. Sun, W. Wang, Progress and challenges toward the rational design of oxygen electrocatalysts based on a descriptor approach, *Adv. Sci.* 7 (2020) 1901614.

- [109] J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J.B. Goodenough, Y. Shao-Horn, Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal-air batteries, *Nat. Chem.* 3 (2011) 546–550.
- [110] W.T. Borden, R. Hoffmann, T. Stuyver, B. Chen, Dioxygen: what makes this triplet diradical kinetically persistent? *J. Am. Chem. Soc.* 139 (2017) 9010–9018.
- [111] S. Chretien, H. Metiu, O₂ evolution on a clean partially reduced rutile TiO₂(110) surface and on the same surface precovered with Au1 and Au2: the importance of spin conservation, *J. Chem. Phys.* 129 (2008) 074705.
- [112] R. Gao, L. Pan, Z. Li, C. Shi, Y. Yao, X. Zhang, J.J. Zou, Engineering facets and oxygen vacancies over hematite single crystal for intensified electrocatalytic H₂O₂ production, *Adv. Funct. Mater.* 30 (2020) 1910539.
- [113] Y. Zhao, H. Wang, J. Li, Y. Fang, Y. Kang, T. Zhao, C. Zhao, Regulating the spin-state of rare-earth Ce single atom catalyst for boosted oxygen reduction in neutral medium, *Adv. Funct. Mater.* 33 (2023) 2305268.
- [114] X. Wei, S. Song, W. Cai, X. Luo, L. Jiao, Q. Fang, X. Wang, N. Wu, Z. Luo, H. Wang, Z. Zhu, J. Li, L. Zheng, W. Gu, W. Song, S. Guo, C. Zhu, Tuning the spin state of Fe single atoms by Pd nanoclusters enables robust oxygen reduction with dissociative pathway, *Chem* 9 (2023) 181–197.
- [115] X. Wang, M. Li, P. Wang, D. Sun, L. Ding, H. Li, Y. Tang, G. Fu, Spin-selective coupling in Mott-Schottky Er₂O₃-Co boosts electrocatalytic oxygen reduction, *Small Method.* 7 (2023) e2300100.
- [116] F. Liu, C. Shi, L. Pan, Z.-F. Huang, X. Zhang, J.-J. Zou, Manipulating the spin state to activate the atomically dispersed Fe–N–C catalyst for oxygen reduction, *EES Catal.* 1 (2023) 562–570.
- [117] S. Liu, C. Li, M.J. Zachman, Y. Zeng, H. Yu, B. Li, M. Wang, J. Braaten, J. Liu, H.M. Meyer, M. Lucero, A.J. Kropf, E.E. Alp, Q. Gong, Q. Shi, Z. Feng, H. Xu, G. Wang, D.J. Myers, J. Xie, D.A. Cullen, S. Litster, G. Wu, Atomically dispersed iron sites with a nitrogen-carbon coating as highly active and durable oxygen reduction catalysts for fuel cells, *Nat. Energy* 7 (2022) 652–663.
- [118] X. Xie, C. He, B. Li, Y. He, D.A. Cullen, E.C. Wegener, A.J. Kropf, U. Martinez, Y. Cheng, M.H. Engelhard, M.E. Bowden, M. Song, T. Lemmon, X.S. Li, Z. Nie, J. Liu, D.J. Myers, P. Zelenay, G. Wang, G. Wu, V. Ramani, Y. Shao, Performance enhancement and degradation mechanism identification of a single-atom Co–N–C catalyst for proton exchange membrane fuel cells, *Nat. Catal.* 3 (2020) 1044–1054.
- [119] J. Li, M.T. Sougrati, A. Zitolo, J.M. Ablett, I.C. Oğuz, T. Mineva, I. Matanovic, P. Atanassov, Y. Huang, I. Zenyuk, A. Di Cicco, K. Kumar, L. Dubau, F. Maillard, G. Dražić, F. Jaouen, Identification of durable and non-durable FeN_x sites in Fe–N–C materials for proton exchange membrane fuel cells, *Nat. Catal.* 4 (2020) 10–19.
- [120] M.J. Hulsey, C.W. Lim, N. Yan, Promoting heterogeneous catalysis beyond catalyst design, *Chem. Sci.* 11 (2020) 1456–1468.
- [121] T. Sun, Z. Tang, W. Zang, Z. Li, J. Li, Z. Li, L. Cao, J.S. Dominic Rodriguez, C.O.M. Mariano, H. Xu, P. Lyu, X. Hai, H. Lin, X. Sheng, J. Shi, Y. Zheng, Y.R. Lu, Q. He, J. Chen, K.S. Novoselov, C.H. Chuang, S. Xi, X. Luo, J. Lu, Ferromagnetic single-atom spin catalyst for boosting water splitting, *Nat. Nanotechnol.* 18 (2023) 763–771.
- [122] Q. Huang, S. Xie, J. Hao, Z. Ding, C. Zhang, H. Sheng, J. Zhao, Spin-enhanced O–H cleavage in electrochemical water oxidation, *Angew. Chem. Int. Ed.* 62 (2023) e202300469.
- [123] G. Zhou, P. Wang, H. Li, B. Hu, Y. Sun, R. Huang, L. Liu, Spin-state reconfiguration induced by alternating magnetic field for efficient oxygen evolution reaction, *Nat. Commun.* 12 (2021) 4827.
- [124] T.K. Todorova, M.W. Schreiber, M. Fontecave, Mechanistic understanding of CO₂ reduction reaction (CO₂RR) toward multicarbon products by heterogeneous copper-based catalysts, *ACS Catal.* 10 (2019) 1754–1768.
- [125] X. Kong, J. Ke, Z. Wang, Y. Liu, Y. Wang, W. Zhou, Z. Yang, W. Yan, Z. Geng, J. Zeng, Co-based molecular catalysts for efficient CO₂ reduction via regulating spin states, *Appl. Catal. B Environ.* 290 (2021) 120067.
- [126] J. Hao, S. Xie, Q. Huang, Z. Ding, H. Sheng, C. Zhang, J. Yao, Spin-enhanced C–C coupling in CO₂ electroreduction with oxide-derived copper, *CCS Chem.* 5 (2023) 2046–2058.
- [127] X. Cui, C. Tang, Q. Zhang, A review of electrocatalytic reduction of dinitrogen to ammonia under ambient conditions, *Adv. Energy Mater.* 8 (2018) 1800369.
- [128] C. Fang, W. An, Single-metal-atom site with high-spin state embedded in defective BN nanosheet promotes electrocatalytic nitrogen reduction, *Nano Res.* 14 (2021) 4211–4219.
- [129] Y. Li, Y. Ji, Y. Zhao, J. Chen, S. Zheng, X. Sang, B. Yang, Z. Li, L. Lei, Z. Wen, X. Feng, Y. Hou, Local spin-state tuning of iron single-atom electrocatalyst by S-coordinated doping for kinetics-boosted ammonia synthesis, *Adv. Mater.* 34 (2022) e2202240.
- [130] L. Lin, Z. Sun, H. Yao, M. Yuan, H. Yang, H. Li, Q. Zhang, D. Wang, L. Gu, G. Sun, J. Zhu, W. Fang, Z. Tang, Tuning surface lattice strain toward a Pt-skin CoPt_x truncated octahedron for hydrogen evolution reaction, *J. Phys. Chem. C* 123 (2019) 29722–29728.
- [131] S. Sun, G. Shen, J. Jiang, W. Mi, X. Liu, L. Pan, X. Zhang, J.J. Zou, Boosting oxygen evolution kinetics by Mn–N–C motifs with tunable spin state for highly efficient solar-driven water splitting, *Adv. Energy Mater.* 9 (2019) 1901505.
- [132] M. Li, X. Wang, K. Liu, Z. Zhu, H. Guo, M. Li, H. Du, D. Sun, H. Li, K. Huang, Y. Tang, G. Fu, Ce-induced differentiated regulation of Co sites via gradient orbital coupling for bifunctional water-splitting reactions, *Adv. Energy Mater.* 13 (2023) 2301162.
- [133] W. Zeng, Z. Jiang, X. Gong, C. Hu, X. Luo, W. Lei, C. Yuan, Atomic magnetic heating effect enhanced hydrogen evolution reaction of Gd@MoS₂ single-atom catalysts, *Small* 19 (2022) 2206155.
- [134] G. Shen, L. Pan, R. Zhang, S. Sun, F. Hou, X. Zhang, J.J. Zou, Low-spin-state hematite with superior adsorption of anionic contaminations for water purification, *Adv. Mater.* 32 (2020) e1905988.
- [135] Y. Chai, H. Dai, X. Duan, Z. Sun, F. Hu, J. Qian, X. Peng, Elucidation of the mechanistic origin of spin-state-dependent P-doped Fe single-atom catalysts for the oxidation of organic pollutants through peroxymonosulfate activation, *Appl. Catal. B Environ.* 341 (2024) 123289.
- [136] H. Li, M. Chuai, X. Xiao, Y. Jia, B. Chen, C. Li, Z. Piao, Z. Lao, M. Zhang, R. Gao, B. Zhang, Z. Han, J. Yang, G. Zhou, Regulating the spin state configuration in bimetallic phosphorus trisulfides for promoting sulfur redox kinetics, *J. Am. Chem. Soc.* 145 (2023) 22516–22526.