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Microstructural engineering of two-dimensional clay-based materials for advanced electrochemical energy conversion

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ABSTRACT

Two-dimensional clay-based materials have shown significant potential in key electrochemical processes, including hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). Two-dimensional clay-based materials possess intrinsic properties such as porous structures, tunable specific surface areas, excellent thermal and mechanical stability, abundant reserves, and cost-effectiveness. However, limited electrocatalytic activity of two-dimensional clay-based materials remains a major challenge. The issue is closely tied to microscopic structures, including spin states, orbital hybridization, energy band alignment, and lattice stability of two-dimensional clay-based materials. The review delves into the relationship between modified two-dimensional clay-based materials and catalytic performance, summarizing strategies such as defect engineering and heteroatom doping to enhance orbital overlap, thereby improving HER, OER, and ORR activities. Finally, this review discusses the development prospects of clay-based materials, emphasizing the critical role of combining advanced computational and experimental techniques in driving innovations in energy conversion materials.

1. Introduction

Modern industrial development faces significant challenges from escalating energy consumption and environmental degradation. To counter these issues, advancing clean and sustainable energy technologies is paramount. Yet, uncontrollable factors such as solar intermittency, hydrological variability, and irregular wind patterns hinder the storage and efficient utilization of renewable energy [1–4]. Overcoming these constraints and converting natural energy variations into stable, scalable energy systems is vital for future progress. Among various renewable energy sources, hydrogen energy stands out due to its high energy density, sustainability, and zero-emission characteristics [5–8]. It finds broad applications in transportation, industrial processes, and power generation. In the energy transition era, hydrogen energy is poised to play a transformative role in achieving sustainable development [9,10].

The key to energy conversion technologies, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR), lies in electrocatalytic materials [9,11,12]. Noble metal catalysts (Pt, Ru, and Ir) have been widely applied in energy conversion due to their exceptional performance [13–16]. However, the high cost of noble metals poses a significant barrier to energy development [17,18].

Clay-based materials have emerged as highly promising candidates in energy conversion applications, owing to their exceptional physicochemical properties, cost efficiency, natural abundance, and robust thermomechanical stability [18–23]. Among them, two-dimensional clay-based materials such as montmorillonite (MMT), vermiculite (VMT), and layered double hydroxides (LDHs) are particularly distinguished by their high specific surface areas and intricate porous architectures [23–26]. The features of two-dimensional clay-based materials significantly enhance their electrolyte accessibility and promote rapid ion transport, rendering them ideal for a range of energy-related technologies. Nonetheless, the inherent low electronic conductivity and limited density of active sites in clay-based materials impose

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considerable constraints on their catalytic efficiency. Furthermore, their pronounced tendency to self-aggregate exacerbates these limitations, reducing the availability of catalytically active surfaces and impeding reaction kinetics [21,23,27]. Overcoming the barriers remains a critical focus for advancing the application of clay-based materials in next-generation energy systems. To overcome the challenges, researchers have devised a suite of innovative modification strategies: ion exchange, interlayer expansion, and surface functionalization to refine structural and chemical properties; integrating conductive materials such as graphene or carbon nanotubes and introducing heteroatom dopants to enhance electronic conductivity; employing templating or self-assembly methods to create hierarchical porous structures, thereby improving the dispersion of active species. Such approaches are designed to optimize the spin configurations, orbital hybridizations, and lattice stability of clay materials, unlocking their full potential in electrochemical energy conversion applications.

Two-dimensional clay-based materials demonstrate substantial potential as efficient catalysts, but further modification and research are required. By microstructural engineering, two-dimensional clay-based materials can significantly enhance their catalytic activity, positioning them as ideal alternatives to noble metal catalysts. This review discusses the structural characteristics and microstructural engineering of typical two-dimensional clay materials, such as MMT, VMT, and LDHs (Fig. 1). It systematically analyzes various microstructural engineering approaches for improving the catalytic performance of two-dimensional clay-based materials, including ion exchange to regulate electronic states, interlayer expansion to increase active site accessibility, defect engineering to introduce surface vacancies, and heteroatom doping to optimize electronic structures. Finally, recent advances in clay-based materials for electrochemical water splitting are reviewed, and the prospects of two-dimensional clay-based catalysts are proposed.

2. Structure of two-dimensional clays

Typical two-dimensional clays include MMT, VMT, and LDHs, which have garnered significant attention due to their unique microscopic structures and outstanding functional properties.

MMT features a characteristic chemical composition, $(M_y)[(Al_{2\text{-}y}Mg_y)(Si_4)O_{10}(OH)_2]\cdot nH_2O$, (where $M = Al^{3+}$, Mg^{2+}, Fe^{3+} or Fe^{2+}), and a 2:1 layered structure comprising one aluminum-oxygen octahedral sheet sandwiched between two silicon-oxygen tetrahedral sheets (Fig. 2a). This layered architecture contains adsorbed water molecules and exchangeable cations (e.g., Na^{+} or Ca^{2+}), endowing MMT with excellent adsorption capabilities and ion exchange properties [21–23,27,31]. The interlayer spacing of MMT can be modulated via ion exchange or intercalation techniques, offering remarkable structural tunability and functional versatility. Moreover, the layered framework of MMT plays a crucial role in the transport of electrons and ions, effectively regulating its electrochemical performance. Consequently, MMT has been widely employed in catalysis, adsorption, and ion transport, with its unique structural features demonstrating immense potential for optimizing electrochemical catalytic reactions such as hydrogen and oxygen evolution [23].

VMT, a hydrated silicate mineral, exhibits a characteristic two-dimensional layered structure, with its crystalline architecture comprising alternating silicon-oxygen tetrahedral layers and magnesium/aluminum octahedral layers (Fig. 2b). The chemical formula, $[Mg^{2+}, Fe^{2+}, Fe^{3+}]_3\ [(SiAl)_4\cdot O_{10}]\ OH_2\cdot 4H_2O$ [32] renowned for its superior ion exchange capacity, VMT features numerous active reaction sites exposed on its layered surfaces, substantially enhancing its surface

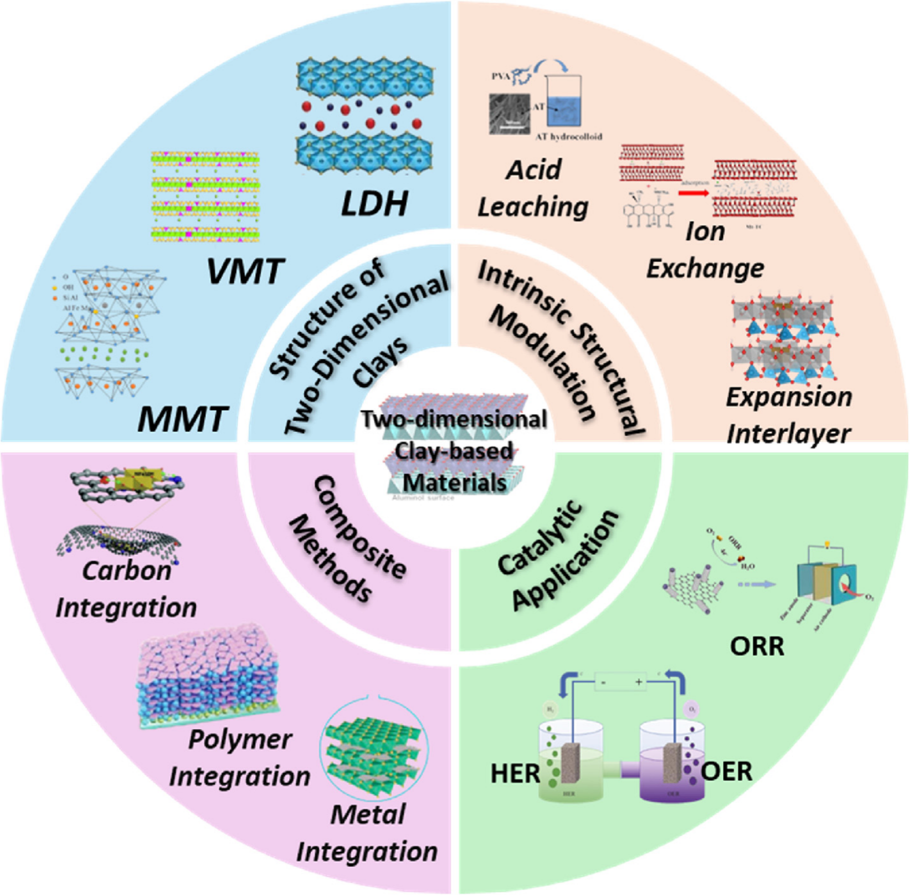

Fig. 1. Schematic diagram of design and synthesis of two-dimensional clay-based materials and their applications.

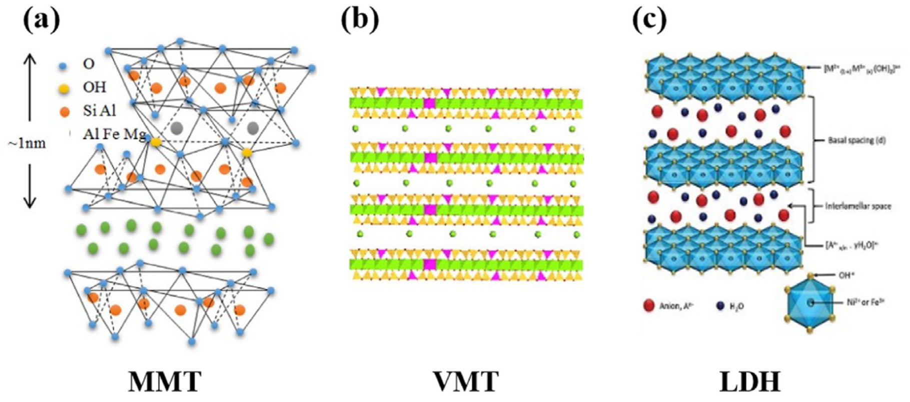

Fig. 2. The crystalline structure of 2D clay materials. (a) Schematic representation of the MMT structure. Reproduced with permission from Ref. [28]. Copyright ©2019, Elsevier. (b) Schematic representation of the VMT structure. Reproduced with permission from Ref. [29]. Copyright ©2016, Elsevier (c) Schematic representation of the LDH structure. Reproduced with permission from Ref. [30]. Copyright ©2021, Elsevier.

reactivity and specific surface area. These attributes endow VMT with significant potential for applications in catalysis, ion transport, and environmental remediation, making it a versatile candidate for advanced material design.

LDHs possess a unique lattice structure and abundant active sites, which enable them to exhibit exceptional capabilities in catalyzing electrochemical processes (Fig. 2c). The structure of LDHs comprises positively charged metal hydroxide layers intercalated with anions. The general chemical formula of LDHs is $[M^{2+}_{1\text{-}x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-}$, where M^{2+} represents divalent metal cations, M^{3+} represents trivalent metal cations, and A denotes the interlayer anions that balance the positive charges within the hydroxide layers [33]. LDHs demonstrate remarkable catalytic performance in applications such as organic transformations, pollutant degradation, and water splitting.

Two-dimensional clay materials, characterized by their expansive specific surface area and distinctive porous architecture, demonstrate remarkable potential for applications in energy conversion devices [23, 30]. Their layered configuration furnishes abundant active sites and significantly enhances electrolyte interaction efficiency, streamlining ion and electron transport pathways. Moreover, 2D clay structures are highly adaptable and can be engineered through intercalation, exfoliation, or surface modification to cater to specific electrochemical reactions. These exceptional structural and performance characteristics position 2D clays as key materials in energy conversion research, providing critical support for the development of efficient and cost-effective energy technologies.

3. Microstructural engineering in two-dimensional clay-based materials

Two-dimensional clay-based materials, characterized by their high specific surface area and porous architecture, are promising contenders for energy conversion applications. However, pristine 2D clay-based materials are constrained by intrinsic limitations, including low catalytic activity, limited electrochemical surface area, and insufficient multiphase transport pathways. Chemical modification is an effective strategy to enhance the catalytic performance of 2D clay-based materials. Modifications can adjust the intrinsic structural and electronic properties of clay-based materials or synergistically catalyze reactions by loading highly active substances.

3.1. Intrinsic structural modulation of two-dimensional clay-based materials

Acid Leaching. To mitigate the influence of impurities, natural clays typically undergo acid leaching. According to Kadu et al. [34], acid treatment significantly increases the density of acidic sites on the clay surface, facilitating subsequent modification and functional loading. Acid treatment confers the following primary benefits to clays [35–39]: (1) removal of impurities while preserving the fundamental clay structure [23]; (2) induction of chemical modifications on the clay surface, leading to an increase in active sites and enhanced catalytic performance; (3) alteration of surface charge properties, thereby improving the adsorption and ion exchange capabilities of the clay.

Ion Exchange. Due to the abundance of elements in clays, tailoring their elemental composition has become a key strategy for optimizing surface charge distribution and enhancing electrochemical performance. Young et al. [40], through cation exchange experiments, substituted interlayer cations in MMT with Na, Cs, and Sr. Combining experimental and molecular simulation approaches, they demonstrated that the introduction of different cations significantly altered the hydration mechanism of MMT, thereby modulating its ion transport properties. Similarly, Zampori et al. [41] replaced inorganic cations in MMT with organic ditallowylammonium ions (DMDTA), yielding a modified material with markedly increased specific surface area. The incorporation of bulky organic cations expanded the interlayer spacing, promoting reactant diffusion and improving compatibility between clay layers and organic or polymeric phases, thus enhancing mechanical and thermal stability. These enhancements stem from stronger interfacial interactions and reduced interlayer slippage [42,43]. These studies illustrate that cation exchange techniques not only improve the mechanical and thermal properties of natural clays but also expand interlayer spacing, increasing the adsorption and reaction activity of clays with electrolytes.

Expansion of interlayer spacing. Expanding the interlayer spacing of natural clays has been identified as a pivotal strategy to enhance ionic diffusion efficiency in energy storage systems. This expansion loosens the clay framework, facilitating more efficient ionic diffusion pathways, while markedly increasing material porosity to improve electrolyte adsorption capacity [23]. Hu et al. [44] achieved a significant interlayer expansion in NiCo LDH by intercalating a small amount of MoO_4^{2-}. Characterization revealed that this modification not only increased the density of active sites but also significantly accelerated the OER kinetics. The modulation of interlayer spacing highlights its immense potential in enhancing ion transport and electrochemical performance of clay-based materials, paving the way for innovative strategies in the design of high-efficiency energy storage and catalytic systems.

Electronic structure regulation. Regulating the electronic structure is a pivotal strategy for enhancing the electrochemical performance of two-dimensional clay-based materials. By fine-tuning their electronic configuration, significant improvements in charge transfer efficiency and intermediate adsorption can be achieved. Zhu et al. [45] synthesized cobalt silicate hydroxide nanosheets (CSHNs) via a one-step hydrothermal method and demonstrated enhanced OER activity through atomic-level iron doping. The optimized sample, FCSHNs-6 (6 at. % Fe), was confirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) to exhibit atomic-level dispersion of Fe. X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS) analyses revealed that Fe doping induced electron transfer from Fe to Co, optimizing the electronic configuration of Co *3d* and Fe *3d* orbitals and promoting the adsorption of oxygen intermediates. The incorporation of Co–O–Fe units suppressed the occupancy of antibonding orbitals, enhanced the covalency of Fe–O bonds, and stabilized the *OOH intermediates. Consequently, FCSHNs-6 exhibited a low overpotential of 293 mV and an ultralow Tafel slope of 47.2 mV dec^{-1} at 10 mA cm^{-2}, significantly outperforming undoped CSHNs. Density functional theory (DFT) calculations further supported these findings, demonstrating that Fe doping optimized the electronic interactions of active sites and achieved an ideal charge density distribution (Fig. 3). This study underscores the potential of atomic-level Fe doping to precisely tailor the spin states, orbital hybridizations, and electronic configurations of CSHNs, offering a blueprint for the rational design of high-performance non-noble metal OER electrocatalysts.

3.2. Composite methods of two-dimensional clay-based materials

Carbon integration for conductivity enhancement. Integrating Two-dimensional clay-based materials with carbon materials has been identified as an effective approach to overcome the intrinsic conductivity limitations of clay-based materials. The incorporation of carbon materials not only improves the electronic conductivity of the composites but also enhances the exposure of active sites. Malak-Polaczyk et al. [46] demonstrated that compounding LDH with activated carbon synergistically combines the redox activity of LDH with the excellent conductivity of carbon materials, leading to enhanced catalytic performance. Moreover, the function of carbon materials as dispersants has been well-established. For instance, Munonde et al. [47] achieved significant improvement in the electrochemical kinetics of the OER by loading carbon black onto NiFe LDH surfaces, demonstrating the superior catalytic efficiency of the modified material. Wang et al. [48] employed a NaCl template freeze-drying approach to prepare nitrogen-doped three-dimensional macroporous/mesoporous carbon (3D MPC) as a growth substrate for highly loaded (∼47 wt%) NiFe LDH nanodots (∼3 nm). Structural characterization revealed that the defect-rich mesoporous architecture promoted size-constrained growth of nanodots and enhanced interfacial interactions with the carbon substrate. This confined architecture improved electrical conductivity and active site exposure. The unique structural features induced significant modifications in the material's electronic structure, with XPS data revealing shifts in Ni and Fe binding energies, indicating strong electronic interactions between the nanodots and carbon matrix. This optimized electronic structure significantly boosted the material's bifunctional catalytic activity. In 0.1 M KOH, it achieved an OER overpotential of 340 mV at 10 mA cm^{-2}, an ORR half-wave potential of 0.862 V, and a record-low bifunctional catalytic potential gap of 0.71 V. Additionally, the material exhibited a high-power density of 97 mW cm^{-2} and excellent stability in Zn-air battery tests, underscoring its promise for energy storage applications.

Polymer integration to mitigate stacking. The inherent stacking of Two-dimensional clay-based materials limits the availability of active sites, posing a significant challenge for their use in high-efficiency electrolyzes. Polymers offer an effective strategy to mitigate this stacking issue. Ma et al. [49] utilized modified vermiculite as a ingredients to prepare polyacrylamide copolymer (PAMVT) microspheres via inverse emulsion polymerization. The experimental findings showed that the water adsorption capacity was up to 80.2 %, resulting in an increase in water flooding recovery from 69.33 % to 77.56 %. Wang et al. [50] proposed an electrostatic self-assembly technique to construct two-dimensional NiFe-LDH nanosheets into organized structures through layer-by-layer (LbL) assembly using hydrophilic polyelectrolytes or nanoparticles. Experimental results indicated that this method effectively mitigated the partial blocking of active sites caused by stacking 2D catalysts and the use of hydrophobic polymer binders. Characterization via XPS revealed that

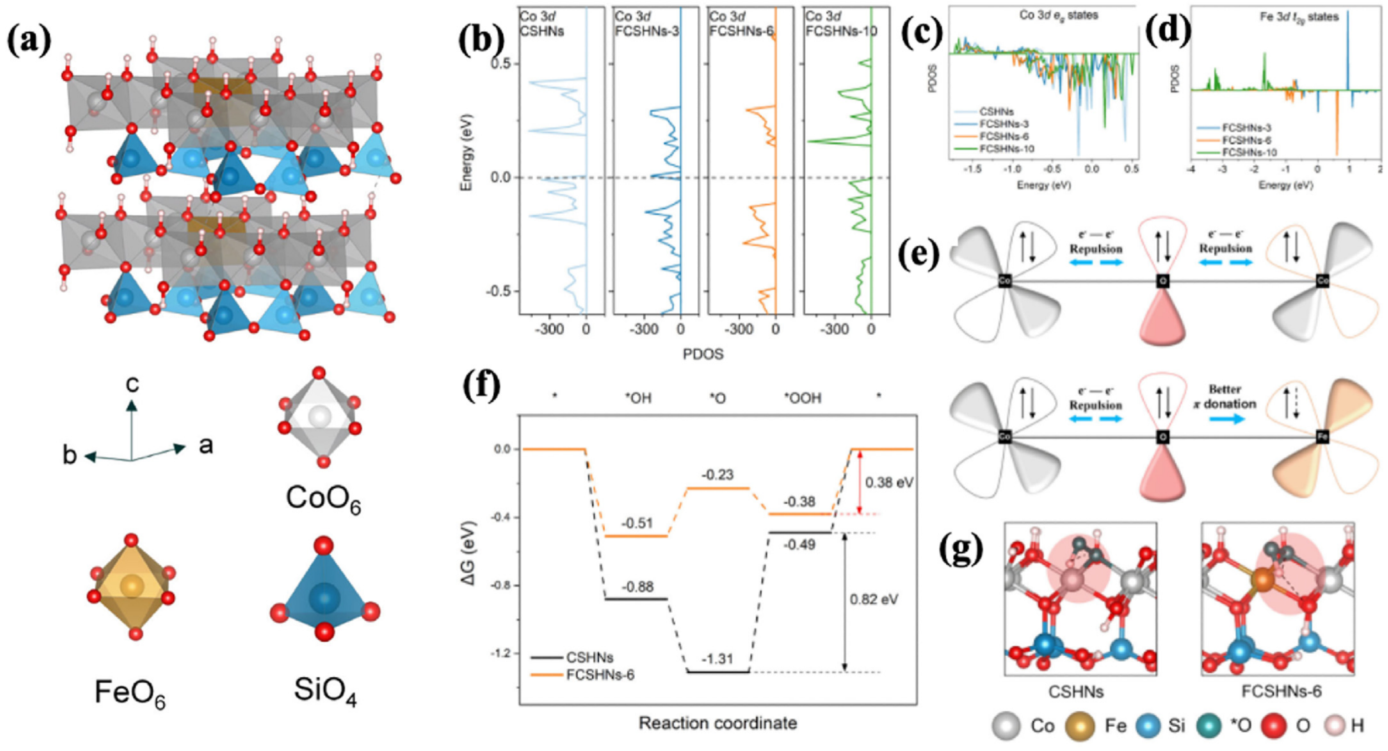

Fig. 3. Electronic state architecture of Fe-doped cobalt silicate hydroxide nanosheets. (a) Crystal structure of FCSHNs-6. (b) Partial density of states of Co *3d*-band. (c) Co *3d* e_g-band, and (d) Fe *3d* t_{2g}-band. (e) Schematic diagram of electronic coupling between Fe and Co. (f) The OER free energy diagrams of CSHNs and FCSHNs-6. (g) Structures for oxygen intermediates *OOH formation step of CSHNs and FCSHNs-6. Reproduced from Ref. [45] with permission. Copyright ©2022, Wiley.

the organized assembly structure enhanced interfacial electron transfer and the utilization efficiency of active sites. The NiFe-LDH nanosheet films fabricated via LbL assembly exhibited a mass activity of 2.267 mA μg^{-1} on planar electrodes and a deposition on 3D carbon cloth substrates achieved an overpotential of only 328 mV at 100 mA cm^{-2}, maintaining stability for 40 h. Furthermore, alternating LbL assembly of Pt nanoparticles and NiFe-LDH significantly improved oxygen and hydrogen evolution performance, enabling efficient overall water splitting under a 1.5 V battery drive. This study demonstrates an efficient strategy to optimize the catalytic performance of 2D materials through precise nanoscale spatial control.

Metal integration for catalytic synergy. Two-dimensional clay-based materials possess a high surface area and adjustable layered structures, serve as exceptional platforms for dispersing and stabilizing metal nanoparticles. Furthermore, metal active species effectively modulate the interlayer arrangements and surface properties of clays, unlocking their inherent catalytic capabilities and facilitating multiphase catalytic processes. Taherinia et al. [51] designed an advanced OER electrocatalyst by integrating $FeSe_2$ with natural halloysite clay minerals through composite formation. The confined effect of halloysite enabled the creation of a uniform nanostructure, significantly enhancing the material's conductivity and stability. XRD and XPS analyses highlighted alterations in surface chemistry and electronic structure of $FeSe_2$, demonstrating halloysite's synergistic role in tuning the electronic configuration and boosting catalytic performance. In 1 M KOH, the composite achieved a low overpotential of 280 mV at 10 mA cm^{-2} and demonstrated remarkable long-term stability. Electrochemical evaluations showed that the material outperformed pure $FeSe_2$ and other common OER catalysts in both mass activity and catalytic efficiency. This work provides a new pathway for improving electrocatalytic performance by integrating natural minerals with transition metal sulfides. Chen et al. [52] developed a composite electrocatalyst comprising ternary NiFeCr-LDH and MoS_2 and explored its catalytic performance in OER. XRD and XPS analyses revealed a synergistic interaction between NiFeCr-LDH and MoS_2, which markedly enhanced the material's conductivity and electrochemical activity. NiFeCr-LDH contributed abundant active sites, while MoS_2 improved electron transfer efficiency, showcasing a well-coordinated enhancement of catalytic performance.

4. Microstructural engineering in two-dimensional clay-based materials for advanced catalysis

4.1. Engineered microstructures for enhanced HER performance

Hydrogen energy conversion technologies are poised to play a pivotal role in future clean energy systems, yet their efficiency hinges on the selection of appropriate catalysts. While noble metal catalysts demonstrate exceptional performance, their prohibitive cost has driven the quest for more accessible alternatives. Clay materials, characterized by their abundant availability, cost-effectiveness, and tunable structural properties, present a promising pathway. By refining the elemental composition and layered structure of clays, it is possible to markedly enhance their catalytic performance, offering an effective and economical approach to advancing hydrogen energy conversion [53–57].

Peng et al. [58] developed a two-dimensional composite, MoWS/MMT, using a hydrothermal method (Fig. 4a), showcasing its synergistic electrocatalytic properties. The incorporation of MMT increased the density of active sites and improved the interfacial reaction environment of MoS through enhanced hydrophilicity, leading to a remarkable improvement in catalytic efficiency. The ion-exchange properties and surface polarity of MMT modulated the electronic orbital occupancy and distribution of MoS_2, optimizing the adsorption and desorption of critical reaction intermediates. As illustrated in Fig. 4b, this composite achieved an overpotential of approximately 300 mV at 10 mA cm^{-2}. In further studies, Peng et al. [59] employed interfacial engineering to construct hierarchical nanocomposites (MoS_2@RGO/MMT) by integrating MMT, graphene, and MoS_2 (Fig. 4c). The high conductivity of graphene and the exceptional hydrophilicity of MMT collectively enhanced the electron transport pathways and interfacial kinetics. The π-electron network of graphene strongly coupled with the *d* orbitals of MoS_2, accelerating charge transfer at the interface, while MMT further tuned the surface energy states of MoS, boosting HER catalytic activity. As depicted in Fig. 4d, MoS_2@RGO/MMT exhibited a significantly reduced overpotential of 230 mV at 10 mA cm^{-2}, highlighting its superior electrocatalytic performance.

Furthermore, the surface-loaded active substances can be affected by pre-adjusting the crystalline structure of the clay. As shown in Fig. 5, Wang et al. [60] utilized a spatial confinement induction method,

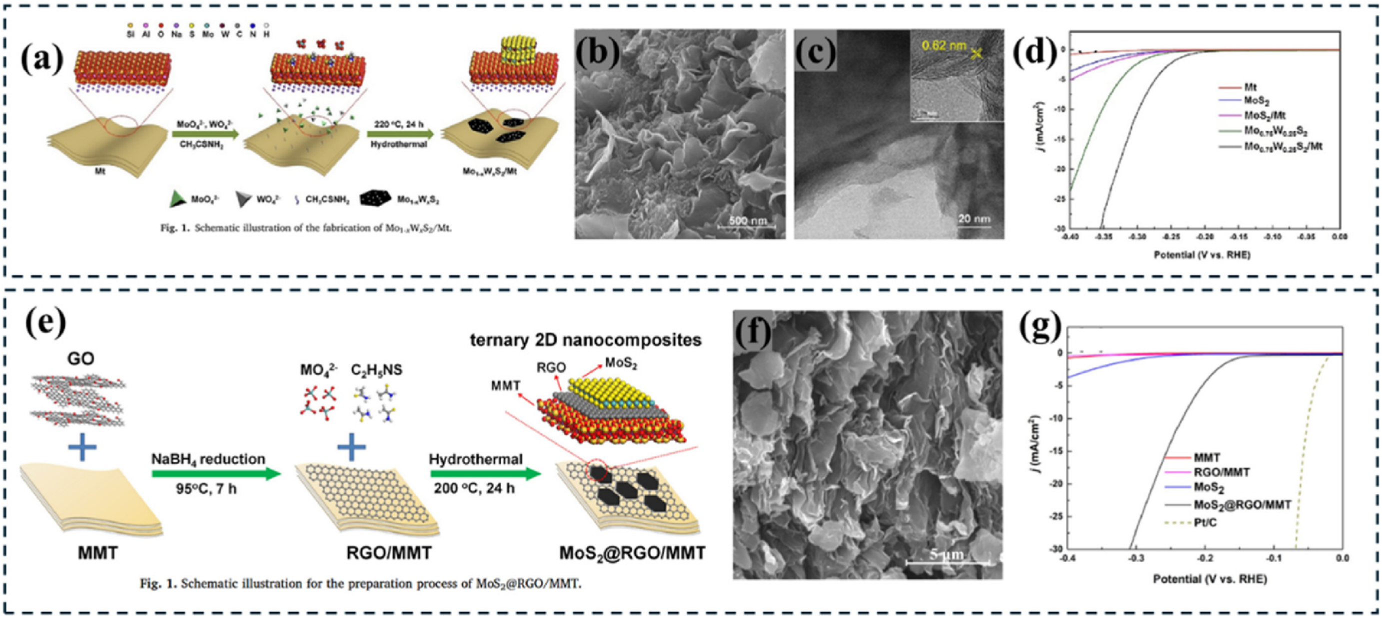

Fig. 4. The role of MMT in enhancing HER efficiency. (a) Schematic illustration of the fabrication of $Mo_{1\text{-}x}W_xS_2$/Mt. (b) Electrochemical properties of $Mo_{1\text{-}x}W_xS_2$/Mt. Reproduced from Ref. [58] with permission. Copyright ©2023, Elsevier. (c) Schematic illustration for the preparation process of MoS_2@RGO/MMT. (d) Electrochemical properties of MoS_2@RGO/MMT. Reproduced from Ref. [59] with permission. Copyright ©2020, Elsevier.

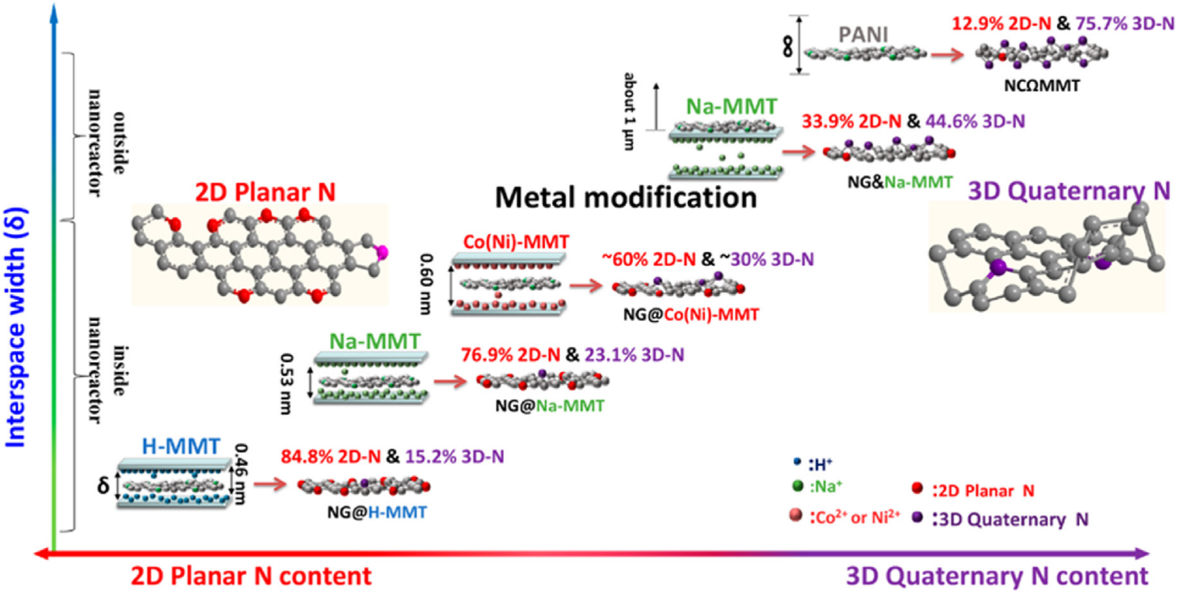

Fig. 5. Schematic representation of the synthesis of NG catalyst with different quaternary N content by using the nanoreactor MMT with different interspace widths. Reproduced from Ref. [60] with permission. Copyright ©2018, American Chemical Society.

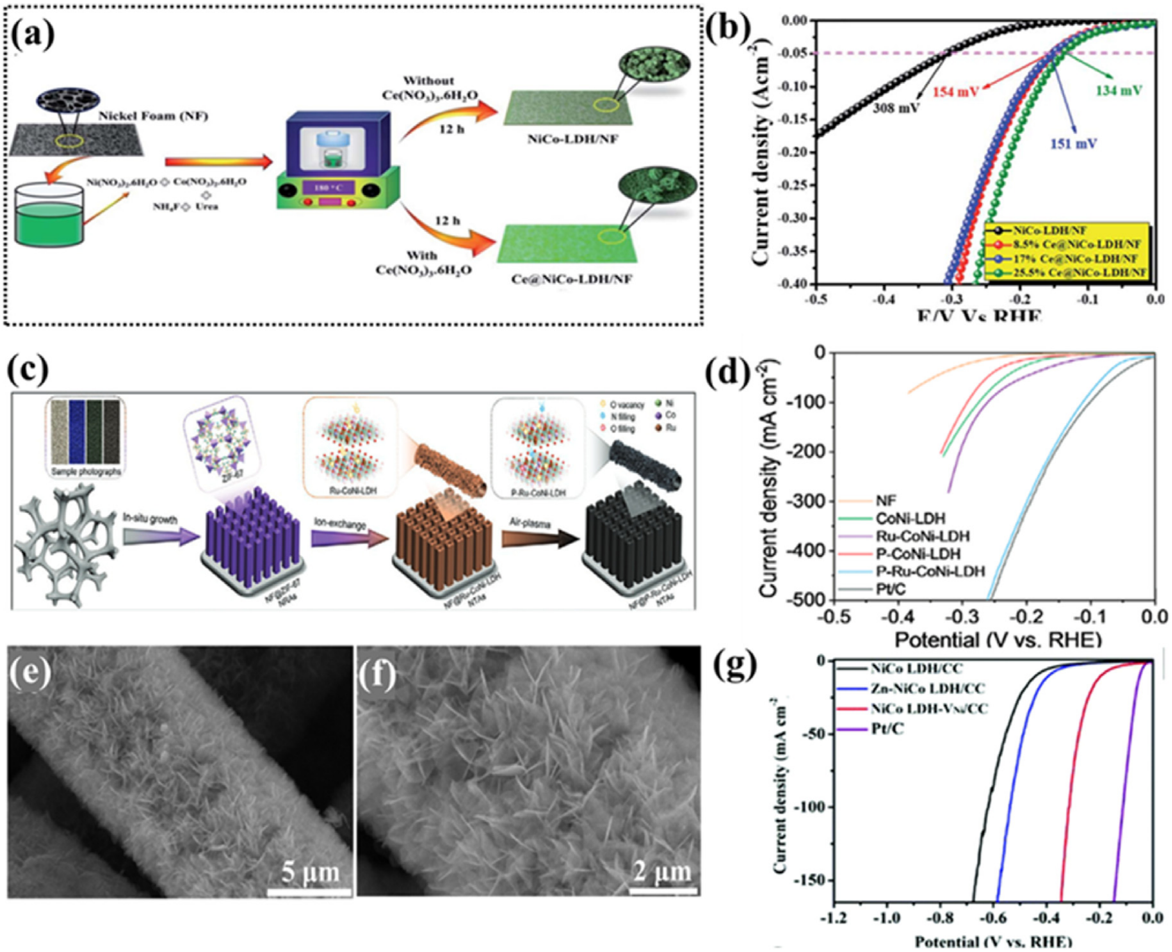

Fig. 6. The role of LDH in enhancing HER efficiency. (a) Schematic illustration of NiCo–LDH/NF and Ce@NiCo–LDH/NF. (b) Electrochemical properties of NiCo–LDH/NF and Ce@NiCo–LDH/NF [65]. Copyright ©2022, Elsevier. (c) Schematic illustration of NF@P-Ru-CoNi-LDH NTAs. (d) Electrochemical properties of NF@P-Ru-CoNi-LDH NTAs. Reproduced from Ref. [66] with permission. Copyright ©2020, Willey. (e) and (f) SEM images of NiCo LDH-VNi/CC. (g) Electrochemical properties of NiCo LDH-VNi/CC. Reproduced from Ref. [67] with permission. Copyright ©2020, Elsevier.

employing layered MMT as a quasi-closed planar nanoreactor to synthesize nitrogen-doped graphene (NG) catalysts with varied nitrogen configurations. This pioneering work established the correlation between nitrogen configurations and HER activity. In metal-free NG catalysts, HER activity was found to increase with the quaternary nitrogen content. However, the introduction of trace cobalt atoms dramatically enhanced the HER activity of planar nitrogen-doped NG compared to quaternary nitrogen-doped NG. XPS and electrochemical analyses revealed that quaternary nitrogen activates adjacent carbon atoms, while planar nitrogen-doped NG forms active cobalt sites that further activate surrounding carbon and nitrogen atoms, reducing the HER free energy barrier and achieving outstanding catalytic performance. In 0.5 M H_2SO_4, the NG@Co-MMT catalyst demonstrated an HER overpotential of -210 mV at 10 mA cm^{-2}, rivaling the best carbon-based HER catalysts. Furthermore, density functional theory (DFT) calculations highlighted the strong electronic interactions between cobalt and nitrogen atoms, significantly boosting electron transfer capabilities, whereas nickel incorporation suppressed HER activity. This research offers innovative theoretical foundations and design approaches for developing cost-effective and high-performance HER catalysts.

LDHs have emerged as promising HER catalysts, offering exceptional tunability, stability, and cost-effectiveness, making them leading non-noble metal alternatives [61–64]. As shown in Fig. 6a, Dhandapani et al. [65] developed a Ce-doped NiCo-LDH catalyst using a hydrothermal approach and systematically examined its electrocatalytic properties for overall water splitting. Structural and electronic analyses via XRD and XPS revealed that Ce doping introduced significant modifications to the microstructure and electronic distribution of NiCo-LDH. The incorporation of Ce optimized the electronic configuration, enhancing catalytic performance, as corroborated by DFT calculations, which highlighted the critical role of Co 3*d* states in both OER and HER processes. In 1 M KOH, the Ce-doped catalyst exhibited remarkable electrocatalytic performance, achieving a current density of 50 mA cm^{-2} at an overpotential of 250 mV for OER and 134 mV for HER (Fig. 6b). Furthermore, with 25.5 % Ce doping, the NiCo-LDH catalyst demonstrated exceptional stability during overall water splitting at 1.68 V for 36 h. This work underscores the potential of electronic structure modulation and active site exposure in designing high-performance, low-cost water-splitting catalysts. As shown in Fig. 6c, Li et al. [66] leveraged ion exchange and air plasma treatment to synthesize Ru-doped hollow CoNi-LDH nanotube arrays (P-Ru-CoNi-LDH) and systematically explored the mechanisms behind their enhanced HER performance. Structural analyses using XRD and XPS revealed that the synergistic effects of Ru doping and plasma treatment effectively tuned the oxygen vacancy concentration and surface wettability, leading to optimized electronic structure, improved water adsorption, and accelerated HER kinetics. Electrochemical evaluation showed that P-Ru-CoNi-LDH achieved an exceptionally low HER overpotential of 29 mV at 10 mA cm^{-2}, demonstrating outstanding catalytic efficiency (Fig. 6d). Furthermore, in a two-electrode urea-assisted water-splitting system, P-Ru-CoNi-LDH, used as both cathode and anode, required only 1.36 V to deliver a current density of 10 mA cm^{-2}, maintaining remarkable stability over 100 h. Complementary Raman spectroscopy and DFT calculations confirmed that Ru doping and plasma treatment enhanced material conductivity and lowered the free energy barrier of critical HER intermediates, thereby substantially boosting catalytic performance. This research offers key theoretical insights and design principles for advancing highly efficient HER catalysts. He et al. [67] employed hydrothermal synthesis and chemical etching to fabricate NiCo LDH nanosheet arrays (Fig. 6e and f) with nickel vacancies (NiCo LDH-VNi/CC) and systematically evaluated their bifunctional catalytic performance for HER and OER. Structural analyses using XRD, XPS, and EPR revealed that nickel vacancies reduced electron density near active sites and optimized the electronic configuration, resulting in markedly enhanced intrinsic catalytic activity. Electrochemical tests showed that the catalyst achieved low HER overpotentials of 195 mV at a current density of 10 mA cm^{-2} (Fig. 6g), along with outstanding stability in 1 M KOH for 100 h with less than 2 % current decay.

Two-dimensional clay-based catalysts, celebrated for their affordability, structural flexibility, and remarkable environmental adaptability, are emerging as critical players in electrochemical energy conversion. Their distinctive layered lattice architecture provides an abundance of ion-exchange sites and a tunable electronic environment, positioning them as vital candidates for optimizing catalytic performance. By strategically modulating spin states, orbital interactions, and band structure, these catalysts can significantly lower activation energy barriers, improve electron transport pathways, and enhance the adsorption capabilities of reaction intermediates.

4.2. *Engineered microstructures for enhanced OER performance*

The OER, a pivotal efficiency-limiting step in water electrolysis, lags behind the HER due to its intricate multi-electron transfer mechanism and substantial energy barriers [68,69]. Clay-based materials, distinguished by their layered architectures, abundant active sites, and superior ion-exchange capacities, emerge as promising candidates for enhancing OER catalysis. Through the strategic modulation of interlayer spacing, elemental composition, and lattice strain distribution, it is possible to fine-tune the surface electronic structure and increase active site accessibility, thereby facilitating the adsorption and transformation of key reaction intermediates such as OH^-, O^-, and O_2 [70,71].

Boshnakova et al. [72] employed the sol-gel method to fabricate Ir/MMT catalysts with Ir loading levels of 10 %, 20 %, and 30 %. Comprehensive characterizations using XRD confirmed the successful incorporation of Ir nanoparticles into the layered architecture of MMT. XRD results revealed a shift in the (001) diffraction peak of MMT from 8.03° to 6.88° upon Ir loading, corresponding to an expansion in basal spacing from 1.1 nm to 1.28 nm. This indicates that Ir nanoparticles were effectively intercalated into the interlayer structure of MMT through cation exchange. Electrochemical tests revealed that the Ir30/MMT catalyst delivered superior OER activity in 0.5 M H_2SO_4, achieving a remarkable current density of 200 mA cm^{-2} at 1.6 V. Furthermore, the catalyst exhibited outstanding catalytic stability and long-term durability in a proton exchange membrane electrolyze cell (PEMEC). The unique layered structure and cation exchange capacity of MMT significantly increased the active surface area and enhanced the electrochemical properties of the catalyst. Attributes of MMT present a cost-effective and robust alternative to carbon-based support, enabling efficient and stable OER performance even under stringent acidic conditions. As shown in Fig. 7a, Wang et al. [73] leveraged montmorillonite (H-MMT) nanoreactors and a spatial confinement strategy to fabricate iron and nitrogen co-doped two-dimensional multilayer graphene (Fe/N-G) catalysts. The resulting Fe/N-G lacked crystalline phases of iron, iron carbides, or iron nitrides, instead featuring uniformly distributed planar Fe-N_x coordination structures. HRTEM confirmed the presence of a wrinkled and porous graphene morphology, which provides a high specific surface area and abundant electron transport channels. Raman spectroscopy revealed an I_D/I_G ratio of 1.01 for Fe/N-G, surpassing nitrogen-doped graphene (NG), indicating increased defect density due to iron doping, which contributes to the formation of active sites. Fe/N-G exhibited outstanding catalytic performance in both ORR and OER. In 0.1 M KOH, its ORR half-wave potential reached 0.877 V (vs. RHE), outperforming 20 wt% Pt/C (0.822 V). For OER, Fe/N-G displayed an overpotential of 400 mV at 10 mA cm^{-2}, superior to NG and NC (Fig. 7b). As shown in Fig. 7c, Zhang et al. [74] employed MMT to fabricate thin-layer metal-organic framework-derived Co/Co_9S_8 nanoparticles embedded in nitrogen and sulfur co-doped graphene-like carbon nanosheets (T-CCSNC). XRD and HRTEM analyses confirmed that T-CCSNC featured uniformly distributed, highly crystalline nanoparticles, with lattice spacings of 0.204 nm and 0.3 nm corresponding to metallic Co and Co_9S_8, respectively. These nanoparticles were encapsulated in amorphous carbon, significantly enhancing their resistance to acid corrosion. The OER overpotential of T-CCSNC was as low as 550 mV at 10 mA cm^{-2}, with a Tafel slope of 265

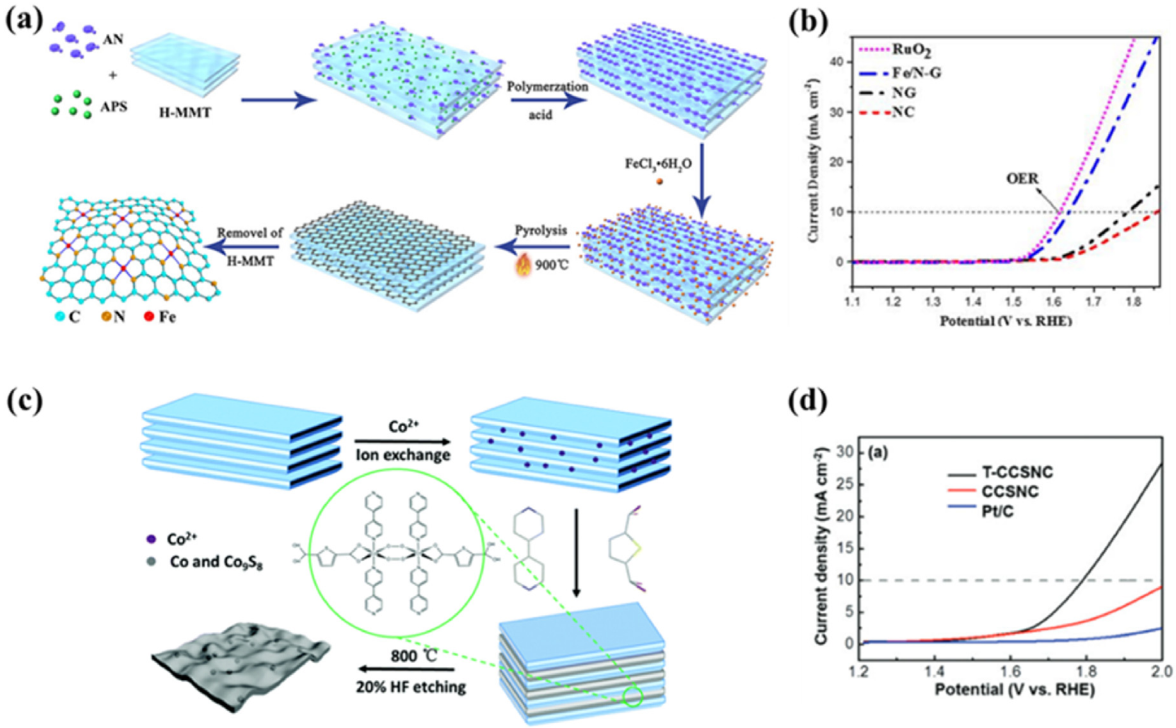

Fig. 7. The role of MMT in enhancing OER efficiency. (a) Schematic illustration of the fabrication of Fe/N-G catalyst. (b) Electrochemical properties of Fe/N-G catalyst [73]. Copyright ©2019, Willey. (c) Schematic illustration for the preparation process of Schematic illustration of the preparation of T-CCSNC. (d) Electrochemical properties of T-CCSNC [74]. Copyright ©2019, Royal Society of Chemistry.

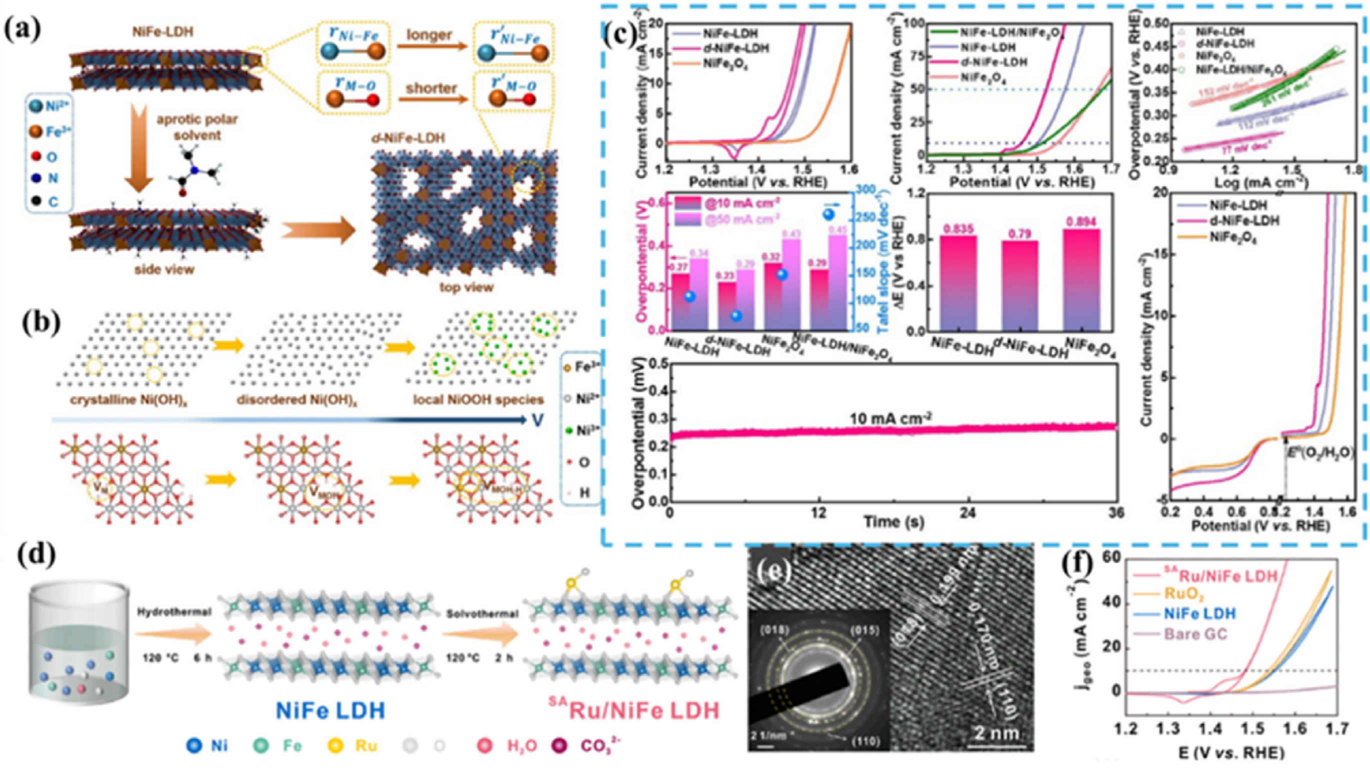

Fig. 8. The role of LDH in enhancing OER efficiency. (a) The coordination between the aprotic polar solvent DMF and cations in NiFe-LDH leading to the dissolution of the metal cations and formation of defective NiFe-LDH. (b) Local conversion of crystalline Ni(OH)$_x$ species to their disordered or defective status and eventually to NiOOH, and the evolution of cationic defects from V$_M$ to V$_{MOH}$ and then to V$_{MOH\text{-}H}$ along with increasing applied voltage. (c) Electrochemical properties of NiFe-LDH. Reproduced from Ref. [77] with permission. Copyright ©2021, Willey. (d) Schematic illustration of the fabrication of ^{SA}Ru/NiFe LDH. (e) TEM of ^{SA}Ru/NiFe LDH. (f) Electrochemical properties of ^{SA}Ru/NiFe LDH. Reproduced from Ref. [78] with permission. Copyright ©2023, American Chemical Society.

mV dec^{-1} (Fig. 7d).

LDHs catalysts, celebrated for their intrinsic activity and catalytic durability, are pivotal in energy storage and conversion [19,75,76]. Among them, NiFe LDH materials exhibit exceptional performance. Wu et al. [77] engineered cation vacancy defects in NiFe LDH nanosheets by dissolving metal cations in non-ionic solvents (Fig. 8a), disrupting local lattice symmetry and inducing a transition from ordered to disordered lattice states during OER (Fig. 8b). This localized lattice reconstruction adjusted the Fermi level and optimized intermediate adsorption by enhancing uneven electronic distribution around active sites. Defective NiFe LDH (d-NiFe LDH) displayed remarkable OER performance, requiring only 230 and 290 mV overpotentials to achieve current densities of 10 and 50 mA cm^{-2}, respectively, outperforming pristine NiFe LDH (270 and 320 mV, Fig. 8c). As shown in Fig. 8d, Yang et al. [78] advanced this by anchoring single Ru atoms onto NiFe LDH nanosheets using a solution reduction method, forming robust oxygen coordination bonds (^{SA}Ru/NiFe LDH). The inclusion of Ru single atoms shifted the Fermi level toward the conduction band, reducing the Gibbs free energy of intermediates and enhancing OER efficiency. ^{SA}Ru/NiFe LDH demonstrated a significantly lower overpotential of 251 mV (10 mA cm^{-2}) in alkaline media compared to 316 mV for pure NiFe LDH (Fig. 8f). The synergistic interaction between Ru single atoms and the LDH framework enhanced active site electronic density and formed stable centers with low charge transfer resistance. Combining cation vacancy and single-atom engineering offers precise control over lattice structures, orbital configurations, and band structures, paving the way for advanced OER catalyst designs.

Two-dimensional clay-based materials, celebrated for their high specific surface area and structural flexibility, have demonstrated immense potential in OER catalysis. Among then, LDHs distinguish themselves with exceptional catalytic activity, positioning them as viable alternatives to noble metal catalysts. However, the intrinsic poor electrical conductivity of clay materials presents a significant challenge. Employing advanced strategies, including electronic structure modulation, conductive phase integration, and defect engineering, holds great promise for realizing high-performance clay-based catalysts.

4.3. Engineered microstructures for enhanced ORR performance

The ORR is widely acknowledged as the rate-determining step in fuel cells and metal-air batteries, primarily due to its intrinsically slow kinetics associated with the four-electron transfer process. While decades of research have advanced the development of various catalysts, platinum-based catalysts continue to dominate as the preferred electrode materials, owing to their unparalleled performance and commercial practicality [69,79,80]. Two-dimensional clay-based materials, characterized by their low cost and structural tunability, emerge as promising candidates for efficient and cost-effective ORR catalysis. In evaluating the ORR, both activity indicators—such as onset potential and limiting current density—and reaction pathway selectivity must be considered. ORR may proceed via a preferred four-electron route that reduces O_2 directly to H_2O or OH^-, or via a less efficient two-electron pathway that generates H_2O_2 as an undesirable intermediate. The pathway selectivity is critical, as it directly affects energy conversion efficiency and the long-term stability of the electrode.

Yang et al. [81] employed clay minerals with diverse structures as templates to synthesize nitrogen-doped carbon materials (Fig. 9a), investigating the role of clay structures and clay-tetracycline (TC) interactions in shaping the materials' microstructure and electrocatalytic performance. TC-C has high catalytic activity for ORR in alkaline medium with excellent methanol tolerance. However, when compared to 20 wt% Pt/C, the ORR activity performance of TC-C (Fig. 9b), including the value of onset potential, the limiting diffusion current (2.4 mA cm^{-2}) and $E_{1/2}$, was still not as good as that of commercial Pt/C (4.2 mA cm^{-2}). Li et al. [82] prepared cationic-intercalated MMT via a simple cation exchange reaction between Na-MMT and cobalt cations, in which Co-MMT and multi-walled carbon nanotube nanocomposites (Co-MMT/MWCNT) exhibited better ORR catalytic activity than Na-MMT, Co-MMT, and MWCNT in an aqueous alkaline medium with a 4e-route mechanism, indicating a synergistic effect between Co-MMT and MWCNT. In addition, further studies showed that the Co-MMT/MWCNT mixture exhibited higher ORR positive onset potential and higher peak oxygen reduction current compared to the commercial 5 % Pt/C ORR electrocatalyst. Yang et al. [83] utilized various structured clay mineral templates to synthesize nitrogen-doped carbon materials. As shown in Fig. 9c

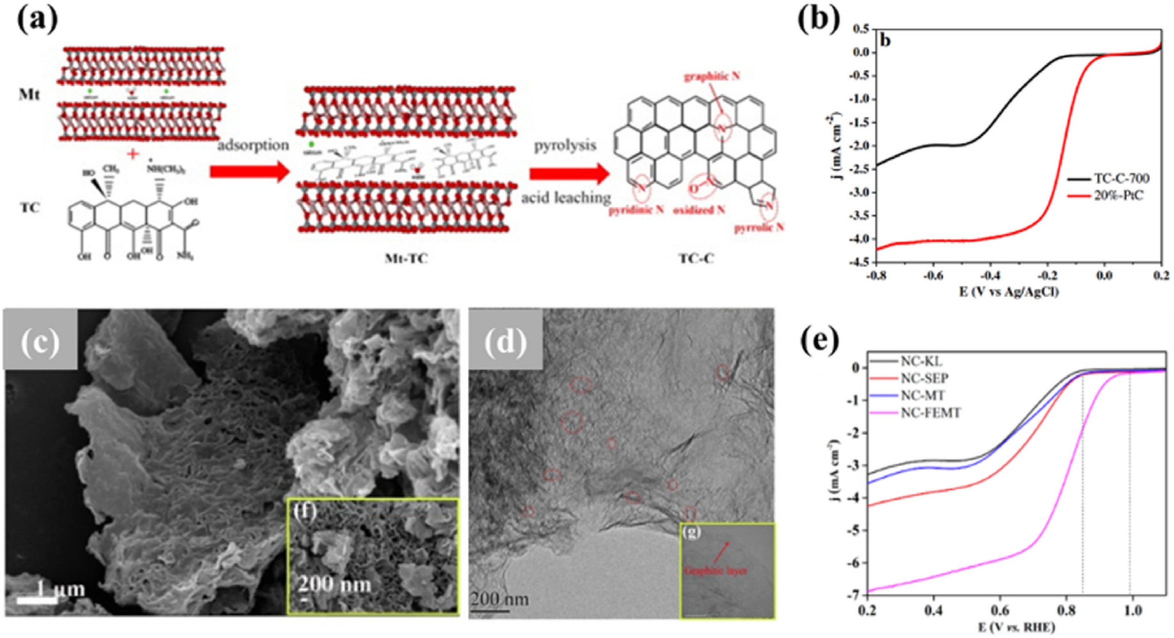

Fig. 9. The role of MMT in enhancing ORR efficiency. (a) Schematic diagram of the synthesis route of TC-C. (b) The LSV curves of TC-C and 20 % Pt/C. Reproduced from Ref. [81] with permission. Copyright ©2016, Elsevier. (c) SEM images of NC-FEMT. (d) TEM images of NC-FEMT. (e) The LSV curves of NC-FEMT other samples. Reproduced from Ref. [83] with permission. Copyright ©2022, Elsevier.

and d, materials derived from layered montmorillonite and kaolinite templates (NC-MT and NC-KL) displayed typical mesoporous structures, while the synergistic effect of iron-saturated montmorillonite (NC-FEMT) notably enhanced graphitization, yielding wrinkled and porous graphene-like carbon nanosheets. Electrochemical evaluations revealed that NC-FEMT exhibited an impressive ORR onset potential of 0.99 V (vs. RHE) in alkaline media, with a limiting diffusion current density of 6.98 mA cm^{-2}, following a near four-electron transfer pathway and surpassing the performance of commercial 20 % Pt/C catalysts. The layered structure of clay templates, coupled with the synergistic effect of iron, optimized the lattice configuration and orbital coupling properties of the materials, boosting conductivity and active site efficiency. This study highlights the potential of leveraging interactions between clay templates and carbon precursors to design high-performance non-noble metal electrocatalysts, providing theoretical insights and strategic frameworks for energy conversion technologies.

Tian et al. [84] utilized VMT as a template to fabricate vertically aligned carbon nanotube arrays (CNTAs) with tunable interlayer spacing. Nitrogen doping was employed to modulate the surface properties of CNTAs, transforming them from superhydrophobicity to superhydrophilicity (Fig. 10a). These superhydrophilic N-doped CNTAs (N-CNTAs) were uniformly loaded with cobalt oxide nanoparticles (Co_3O_4 NPs), yielding an efficient bifunctional electrocatalyst (Co_3O_4/N-CNTAs). Expanded vermiculite facilitated alignment and uniform nitrogen incorporation of CNTAs, boosting electronic density at active sites. As depicted in Fig. 10b and c, Co_3O_4/N-CNTAs demonstrate outstanding bifunctional catalytic performance, achieving a high onset potential of 0.91 V (vs. RHE) for the ORR and a remarkably low overpotential of 1.66 V at 10 mA cm^{-2} for the OER.

LDHs have emerged as highly promising materials for the ORR due to their tunable layered structure, extensive specific surface area, and abundance of metal sites. The metal cations in LDHs, such as Ni, Fe, and Co, play a pivotal role in modulating electronic structures, optimizing O_2 adsorption and activation, while interlayer defects and intercalated ions boost active site utilization. The unique two-dimensional structure of LDHs effectively exposes edge-active sites, enhancing selectivity and

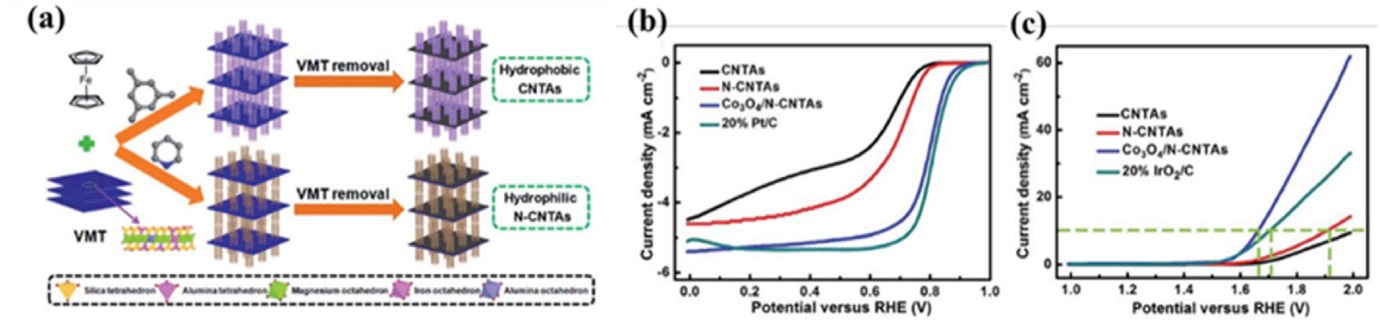

Fig. 10. Application of MMT to enhance ORR catalysis. (a) Schematic diagram showing the fabrication of sandwich-structured CNTAs [84]. (b) LSV curves and (c) OER LSV curves of Co_3O_4/N-CNTAs compared with CNTAs, N-CNTAs, and Pt/C or IrO_2/C. Reproduced from Ref. [84] with permission. Copyright ©2016, Elsevier.

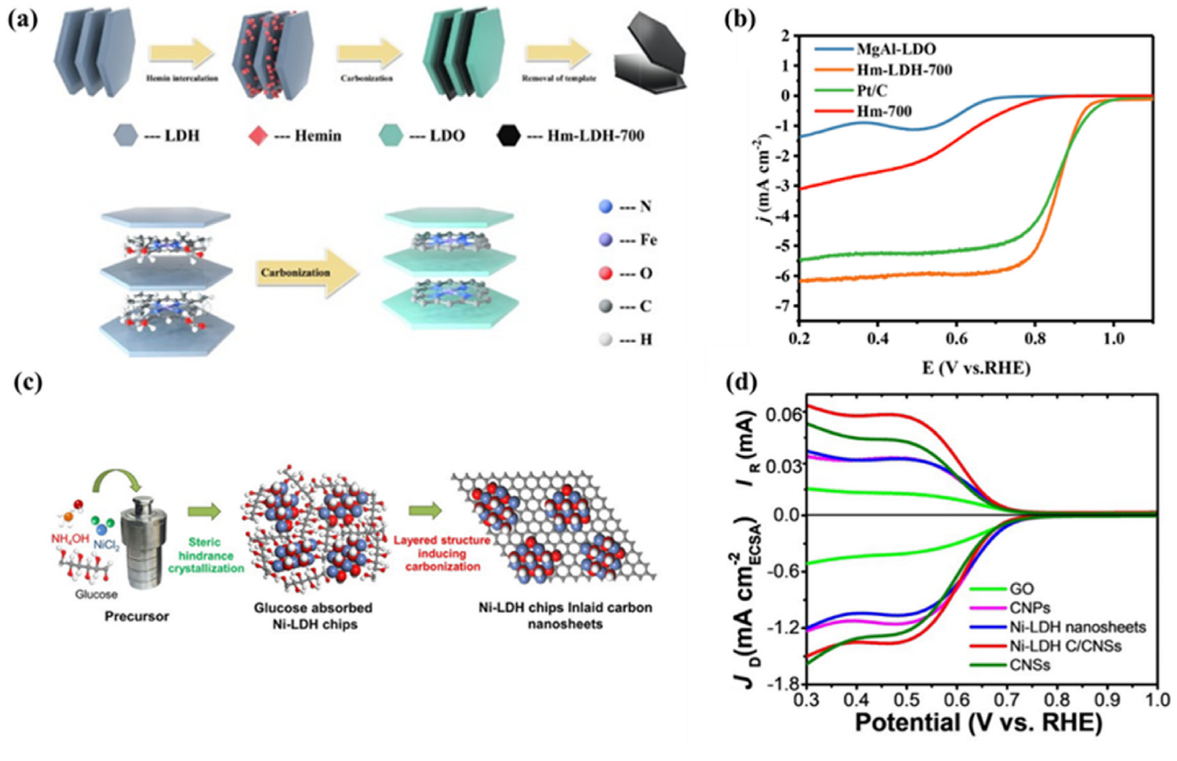

Fig. 11. Application of LDH to enhance ORR catalysis. (a) Schematic illustration of the preparation of Ni-LDH. (b) Electrochemical properties of Ni-LDH. (d) Electrochemical properties of Ni-LDH. Reproduced with permission from Ref. [88]. Copyright ©2020, Willey. (c) Schematic illustration of the fabrication of Hm-LDH-700. (d) Electrochemical properties of Hm-LDH-700. Reproduced from Ref. [89] with permission. Copyright ©2022, Elsevier.

catalytic efficiency by fine-tuning the binding energies of intermediates like OOH*. Despite their inherent low conductivity, which hinders electron transfer, coupling LDHs with carbon materials can overcome this limitation, ensuring efficient electron transport and structural integrity [69,79,85–87]. Huang et al. [88] developed ultrathin Ni-LDH nanosheets embedded into carbon nanosheets (Ni-LDH/CNS) using a one-pot hydrothermal method to catalyze oxygen reduction to H_2O_2 (Fig. 11a and 11b). XPS and EXAFS analyses confirmed the presence of defect oxygen and unsaturated Ni atoms at the edge sites, which optimized the adsorption energy of the OOH* intermediate during the ORR, thereby promoting the selectivity of the two-electron pathway. Electrochemical testing showed that Ni-LDH/CNS achieved remarkable H_2O_2 production in alkaline media, with a Faradaic efficiency of 95 % and a mass activity of 22.2 A g^{-1}, outperforming pure Ni-LDH and commercial GO catalysts by 1.8 and 4.5 times, respectively. LDHs have emerged as excellent platforms for hosting highly active species. Yang et al. [89] harnessed the interlayer confinement effect of MgAl-LDH to fabricate a single-atom Fe-N-C catalyst (Hm-LDH-700), employing natural heme as the precursor (Fig. 11c). The layered architecture of LDHs served as a confinement template, preventing the agglomeration of heme molecules and enabling the formation of two-dimensional porphyrin-derived carbon nanosheets. Hm-LDH-700 exhibited abundant mesoporous structures and an impressive specific surface area of 1065.79 m^2 g^{-1}, markedly enhancing the exposure of active sites and facilitating efficient oxygen mass transport and rapid electron transfer. Microscopic analysis revealed uniformly dispersed Fe atoms within Hm-LDH-700, with XPS confirming Fe-N coordination. Additionally, the significantly increased proportions of pyrrolic and graphitic nitrogen optimized the electronic structure, effectively lowering the adsorption energy of intermediates. Hm-LDH-700 demonstrated exceptional ORR activity in alkaline media, achieving a half-wave potential of 0.86 V (vs. RHE), a limiting diffusion current density of 6.21 mA cm^{-2}, and a Tafel slope of only 74 mV dec^{-1}, surpassing the performance of commercial Pt/C catalysts.

Clay-based materials have emerged as promising ORR catalysts, demonstrating remarkable potential. Strategies such as interlayer engineering, synergistic composite design, and computationally guided optimization of active site structures offer transformative opportunities to further elevate the catalytic performance of clay-based materials, thereby paving the way for the development of low-cost and sustainable energy catalysts.

5. Conclusions and outlook

Two-dimensional clay-based materials, such as montmorillonite, vermiculite, and layered double hydroxides, have emerged as highly promising candidates for electrochemical water splitting (HER, OER) and the oxygen reduction reaction (ORR), owing to their tunable layered structures, high specific surface areas, and abundant active sites. The 2D layered architecture offers abundant ion exchange sites, optimizes electronic states and intermediate binding energies, and serves as a robust substrate for the dispersion and stabilization of active species. However, the intrinsic poor conductivity and limited active site density remain key challenges. Innovative strategies such as doping, defect engineering, and interlayer modulation have shown great potential to manipulate spin states, orbital hybridization, and lattice parameters, thereby enhancing electron transfer efficiency, optimizing active site utilization, and fine-tuning intermediate adsorption energies. Integrating clays with carbon- or metal-based materials overcomes conductivity barriers, unlocks hierarchical synergies, and significantly improves catalytic performance, paving the way for low-cost, high-performance non-noble metal catalysts.

Achieving comprehensive performance improvements in clay-based materials necessitates a deeper understanding of the correlation between microstructural features and electrochemical properties of clay-based materials, with a focus on the following pivotal directions:

(1) *Tailoring spin states and orbital interactions.* Delving into the d-orbital and spin state dynamics in clay-based materials unveils new opportunities for optimizing catalytic pathways and electron distribution. Incorporation of heteroatoms like Fe and Ru enables precise tuning of e_g orbital filling and spin polarization, thereby refining the adsorption energies of intermediates such as OOH* or H*. Combining density functional theory (DFT) simulations with experimental validation deepens our understanding of the interplay between orbital hybridization and catalytic performance.

(2) *Engineering band structures and interfaces.* Optimizing the band structures of clay-based materials through interlayer expansion and heterointerface design holds the key to improving electronic conductivity. Synergistic effects of intercalated anions and oxygen vacancies enhance electron density and charge mobility, while introducing interfacial strain refines charge distribution and intermediate binding energy at active sites, unlocking higher catalytic performance.

(3) *Defect engineering and heteroatom doping.* A synergistic approach leveraging oxygen vacancies, cation vacancies, and heteroatom doping (Such as N, S, P) enables precise manipulation of material microstructure and electronic properties. Doping elements modulate local lattice symmetry and electron distribution, fostering the formation of hybridized orbitals. This tailored approach reduces free energy barriers along catalytic pathways, significantly enhancing HER and ORR performance.

(4) *Engineering hierarchical porous architectures.* Integrating conductive materials such as carbon nanotubes and graphene with clay-based composites offers a promising approach to construct hierarchical porous architectures. These structures enhance the exposure of active sites and accelerate mass transport of reactants. Strategies such as template-assisted synthesis and confined reactions enable the optimization of microstructural features, ensuring uniform distribution of active species and improving catalytic stability.

(5) *Data-driven high-throughput catalyst design.* Harness the power of machine learning and experimental datasets to establish quantitative relationships between microstructural features and electrochemical performance. This approach enables the rapid identification of optimal modification strategies for clay-based catalysts. High-throughput simulations provide valuable predictions of material performance potential, streamlining the transition from molecular-level design to real-world applications.

(6) *Expanding Applications and Integrative Technologies.* Explore the utilization of clay-based materials in complex energy systems, such as multifunctional electrolyzers, solid-state batteries, and catalytic membranes. Dynamic surface reconstruction and multiphase interface engineering enable the stability and adaptability of clay-based catalysts across varied reaction environments, paving the way for their broader deployment in energy applications.

CRediT authorship contribution statement

Ruiqian Zhang: Writing – review & editing, Writing – original draft, Conceptualization. **Binbin Qian:** Visualization, Supervision. **Ke Xu:** Formal analysis, Data curation. **Amir Said:** Software. **Kunfeng Chen:** Resources, Investigation. **Chunlei Yang:** Supervision, Resources, Project administration. **Sridhar Komarneni:** Software. **Dongfeng Xue:** Software, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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