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# Transition metal nanomaterial-based electrocatalysts for water and CO<sub>2</sub> electrolysis: preparation, catalytic activity, and prospects

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The production of hydrogen (H<sub>2</sub>) and multi-carbon fuels through water electrolysis (oxygen evolution reaction (OER)/hydrogen evolution reaction (HER)) and water–CO<sub>2</sub> co-electrolysis (OER/CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR)), respectively, is supposed to be the emergent energy carrier. These electrochemical processes are essential chemical conversion pathways that initiate the changes toward production of renewable energy. This review summarizes the systematic design of earth-abundant transition metal-based nanomaterials and their electrocatalytic activities toward electrochemical energy conversion reactions such as OER, HER, and CO<sub>2</sub>RR. The primary focus is on fabricating highly effective, low-cost, and advanced transition metal-based nanostructures for both the OER/HER and OER/CO<sub>2</sub>RR systems. Developing synthetic strategies for surface morphology-controlled nanostructured electrocatalysts, engineering the electrode surface, enhancing the electrocatalytic activity, understanding the relationship between intrinsic catalytic activity and preparation approaches or precursor choices, and exploring the reaction mechanism are focused on. Furthermore, the current challenges, figure-of-merit, and prospects of transition metal-based nanomaterials and their electrocatalytic activities toward water electrolysis and water–CO<sub>2</sub> co-electrolysis are described. This study may open new opportunities to develop shape-controlled and high-performance electrocatalysts for electrochemical energy conversion and storage reactions.

## KEYWORDS

transition metal-based nanomaterials, electrochemical methods, water electrolysis, CO<sub>2</sub> electrolysis, energy conversion process

## 1 Introduction

With the tremendous population explosion and globalization, as well as the corresponding rise in global energy supply and consumption, the discovery of methodologies for devising sustainable power conversion systems remains a major global concern (Chen C. et al., 2024; Maduraiveeran et al., 2019; Yuan et al., 2024; Zhang M. et al., 2024). The global energy crisis and the associated environmental pollution have prompted researchers to look for renewable sources of energy that can be used to replace fossil fuels (Arias-Hernandez et al., 2024; Bonod et al., 2023; Bordet and Leitner, 2023). Owing to the

energy scarcity, environmental concerns, and the excessive use of fossil fuels, fresh and renewable energy sources have emerged as a pressing need (Fang et al., 2024; Guo et al., 2024; Hatakeyama-Sato and Oyaizu, 2023). As a result, the search for sustainable alternatives such as energy conversion and energy storage technologies is vital. Electrochemical methods are deliberated as promising strategies for the generation of clean energy by using the conversion of small molecules, including water (H<sub>2</sub>O), hydrazine (N<sub>2</sub>H<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrogen (N<sub>2</sub>), into valued products hydrogen (H<sub>2</sub>), ammonia (NH<sub>3</sub>), hydrocarbons (CH), and fuels (Arivazhagan et al., 2020; Fan et al., 2024; Fang et al., 2024; Geng et al., 2024; Shankar et al., 2020).

The pursuit of sustainable energy sources drives the development of progressive nanostructured catalysts for a variety of electrocatalytic processes, such as oxygen evolution reaction (OER), hydrogen evolution reaction (HER), and CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) (Figure 1) (Wang J. et al., 2020). In particular, the slow kinetics and high energy barriers in the OER (anode side) and HER/CO<sub>2</sub>RR (cathode side) make it difficult to achieve better results and utilize the energy conversion process. When the CO<sub>2</sub>RR is combined with electrochemical water splitting, the energy conversion technologies do not necessitate an extra hydrogen feedstock. In its place, water could deliver the protons required for the reduction of CO<sub>2</sub>. The integration of the OER (anode process) and CO<sub>2</sub>RR (cathode process) is frequently stated as water–CO<sub>2</sub> co-electrolysis (Ebbesen et al., 2014; O'Brien et al., 2024; Zhang J. et al., 2023). The fundamental chemical conversion pathways that lead to transformations in renewable energy are these electrochemical processes. In these electrochemical reactions, the catalytic activity, mass activity, discrimination, and robustness of the catalysts play an active part in defining the energy efficacies and the performance of the device/system (Chatenet et al., 2022; Dondapati et al., 2022; Maduraiveeran, 2021; Shankar and Maduraiveeran, 2022; Shankar et al., 2023). Subsequently, the crucial goal of this electrochemical energy conversion technology is to find high-efficiency catalytic materials for several electrochemical reactions (Sun et al., 2020; Wang Y. et al., 2020; Yang et al., 2022).

Most of the electrocatalytic reactions extensively depend on the state-of-the-art catalysts of platinum (Pt)-, ruthenium (Ru)-, iridium (Ir)-, palladium (Pd)-, gold (Au)-, and rhodium (Rh)-based metal/metal oxides (Li et al., 2024a; Liu H. et al., 2024; Zhang X. et al., 2024). However, the scarcity and high expenses involved in producing these precious metal-based catalysts often limit the wide-ranging employment on scale-up progress and the commercial feasibility of the associated electrochemical energy technologies (Cai L. et al., 2024; Chang et al., 2024a; Chang et al., 2024b). Thus, the establishment of inexpensive, high earth-abundance, great catalytic activity, and durable electrocatalysts as substitutes for possible renewable technologies is both highly preferred and a grand challenge. Due to the extraordinary catalytic activity, high earth-abundance, great durability, facile fabrication, good conductivities, and ecological sociability, the first-row transition metals including copper (Cu)-, iron (Fe)-, nickel (Ni)-, and cobalt (Co)-based metal oxides and chalcogenide, sulfide, hydroxide, phosphide, and borate-derived electrocatalysts have emerged as substitutes (Figure 2) (Wang et al., 2021) that have raised interest in numerous electrocatalytic reactions, including water splitting, CO<sub>2</sub>RR, photo-electro catalytic reactions,

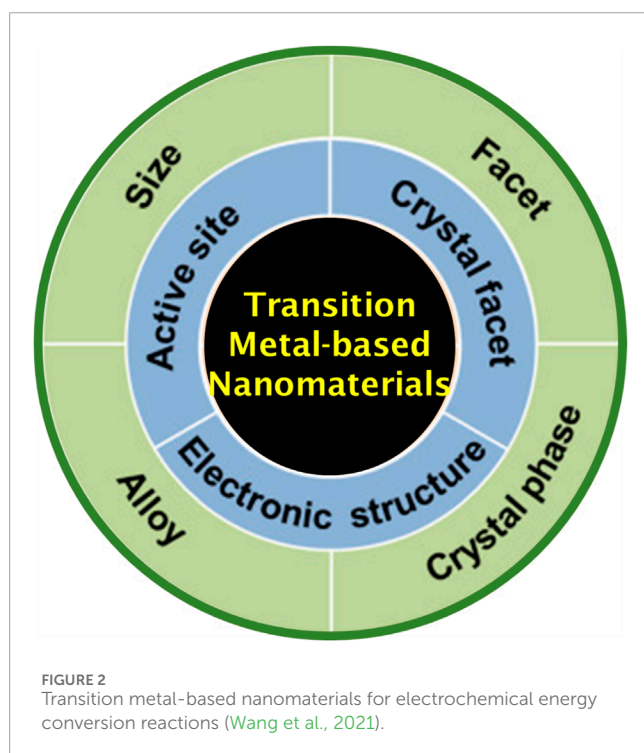
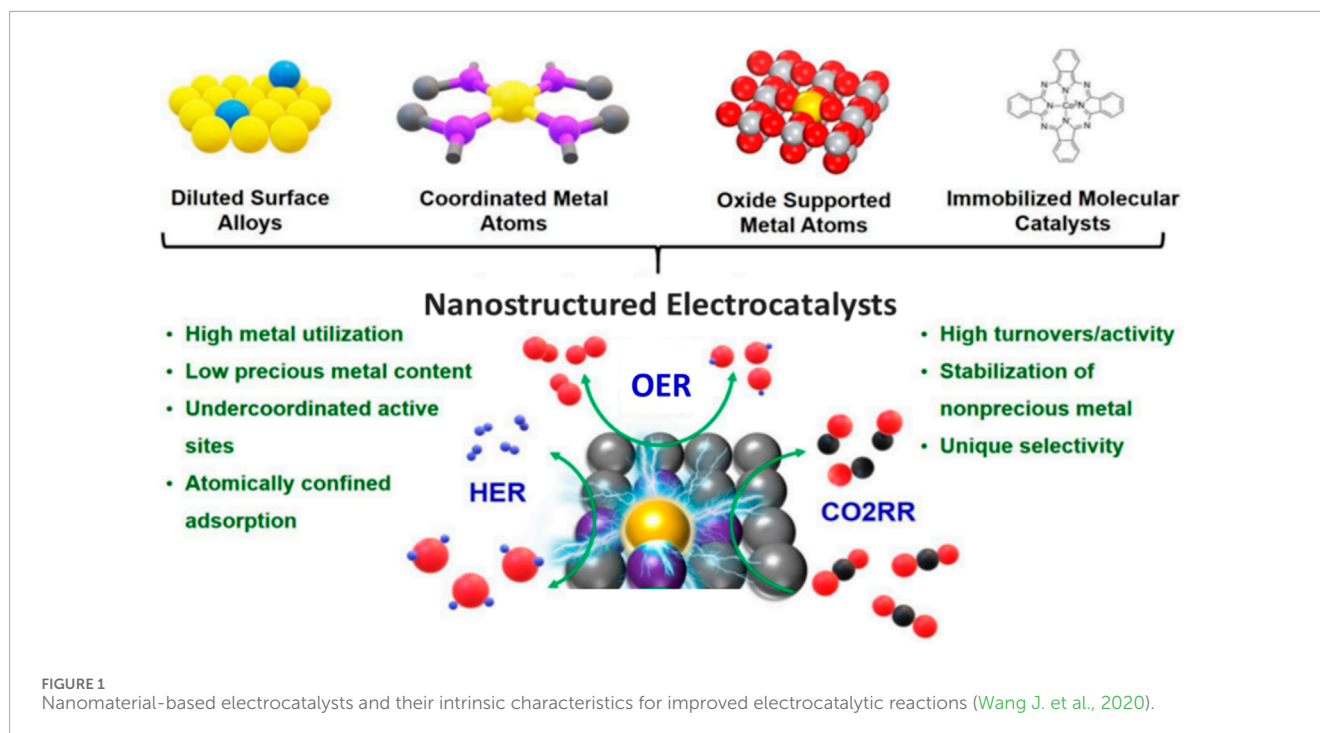
and metal–air batteries. (Cai M. et al., 2024; Cao et al., 2024; Chai et al., 2024; Marimuthu et al., 2023).

Numerous studies have been conducted based on transition metal nitrides, phosphides, selenides, carbides, and sulfides catalysts for various electrochemical energy conversion reactions (Cai L. et al., 2024; Chang Y. et al., 2024; Chang et al., 2024a; Chen G. et al., 2023; Chen X. et al., 2023; Chen Y. et al., 2023; Chen X. et al., 2024). It has been demonstrated that the covalently synchronized transition metal centers may have good properties for adsorption and robustness in a range of electrocatalytic applications (Abdelghafar et al., 2024; Chen G. et al., 2023; Deng L. et al., 2023; Deng M. et al., 2023). Moreover, the improved turnover rates and mass activity (employment of metal efficacy) have been advantageous for engineering the catalytic performance through the captivating benefit of the atomic- and nano-scale confinement of adsorption intermediates, which increase the divergent electrocatalytic performances since their bulk equivalent stating repetitive active sites (Abdelghafar et al., 2022; Kong D. et al., 2024; Kong X. et al., 2024; Kothandam et al., 2023). Substantial research has been conducted on the progress of synthetic strategy, the size–shape-controlled fabrication of nanostructured transition metal-based electrocatalysts that demonstrate improved electrocatalytic activity owing to their fascinating physical–chemical and electrochemical properties (Lee et al., 2023; Li et al., 2024b; Li D. et al., 2024; Li Z. et al., 2024). The present review summarizes the systematic design of earth-abundant transition metal-based nanomaterials and their electrocatalytic activities toward the electrochemical energy conversion reactions such as the OER, HER, and CO<sub>2</sub>RR. Fabricating improved transition metal-based nanostructures for energy conversion reactions at low cost and high efficiency is the focus of this review. There is also significant focus on preparation techniques, monitoring of structure and composition, electrode fabrication, catalytic effect, connections between synthesis methods and precursors, intrinsic catalytic activity, and reaction mechanism comprehension and investigation.

## 2 Water electrolysis

Recently, there have been several studies that focused on the hydrogen energy economy (HEE), which is regarded as the ultimate replacement for fossil fuels, as a result of its high density and water being the sole byproduct (Figure 3) (Rebouillat et al., 2011; Niu and Yang, 2018). Hydrogen is an alternative fuel with a sustainable and environmentally friendly nature that has been presented as both the supreme and perfect fuel for such a futuristic world (Li et al., 2024a; Zhang W. et al., 2023; Zhu et al., 2024). Considering the dual heavy burdens of energy constraint and environmental contamination, establishing sustainable fuel sources has developed into one of the most relevant global issues (Wei et al., 2023; Yan et al., 2021). The production of green hydrogen mostly depends on electrochemical processes such as HER and OER (Figure 4A) (Xu et al., 2019). The hydrogen energy source may also provide emission-free, environmentally beneficial, and alternative/sustainable energy cycling (H<sub>2</sub>O) (You and Sun, 2018). The hydrogen system needs to perform better and be less expensive, but it is still in the pre-civilization stage. Two energy conversion methods, namely, water splitting and fuel cells, can achieve the environmentally friendly production and consumption of hydrogen (You and Sun, 2018).

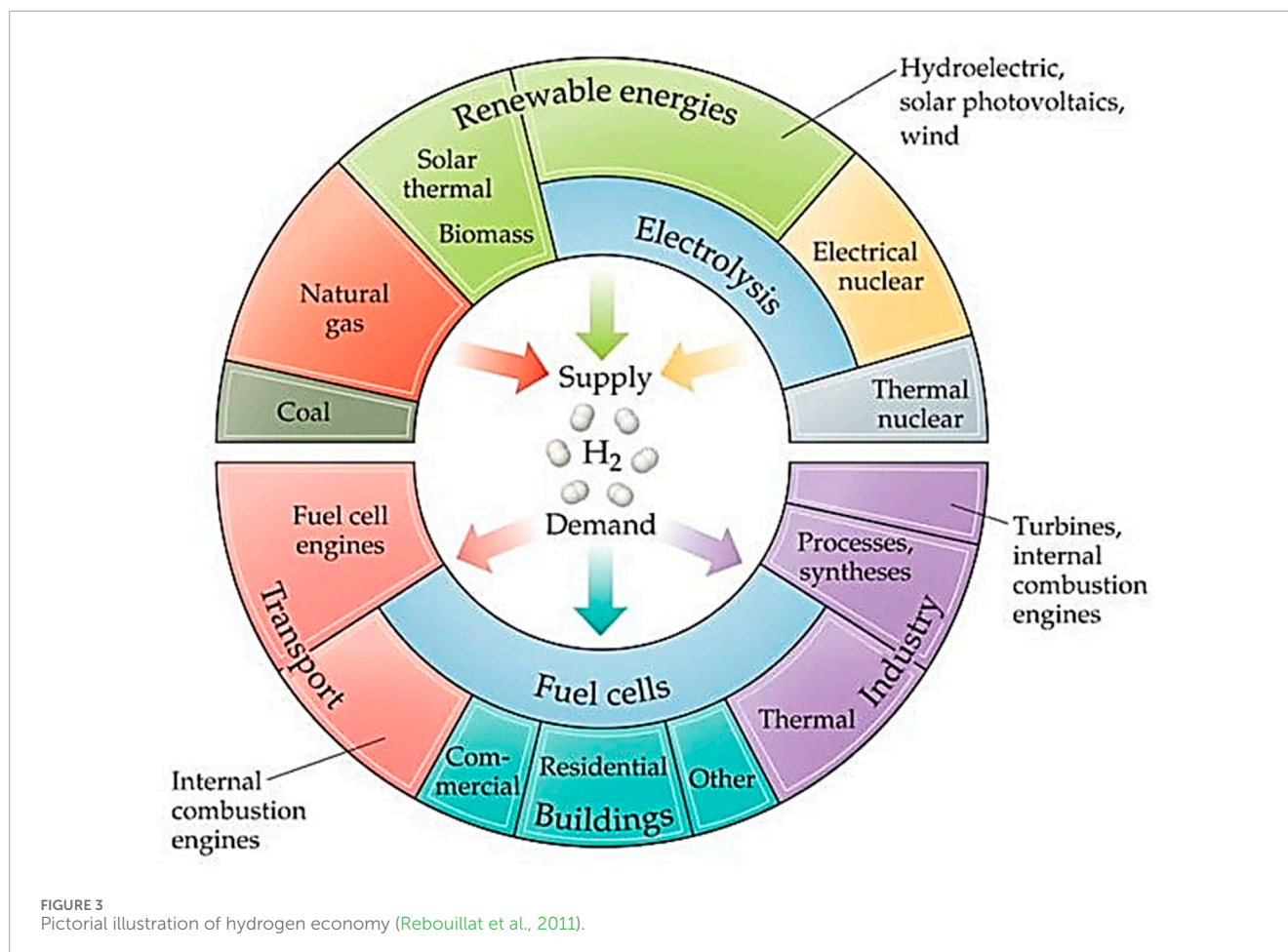




The electrocatalytic splitting of water offers a much more environment-conscious way to create hydrogen than these methods do (Gao et al., 2019; Gao et al., 2020). A prospective way to generate hydrogen with high purity and a carbon-neutral source for energy storage and recovery, as well as a starting point for commercial catalytic processes, is electrochemical water splitting (Kang et al., 2015; Liu et al., 2020; Pu et al., 2016; Wang et al.,

2016). For the electrolysis of water to function as a strategic initiative for storing sustainable power in the energy-dense bonding of  $H_2$ , both reactions must take place with high efficiency in the presence of affordable catalysts (Anantharaj and Noda, 2020). However, in contrast to the HER, the OER has slower electrode kinetics because of the four-electron transfer process (Butburee et al., 2018). On the other hand, the catalytic performance of oxygen evolution at the anode is crucial for the effectiveness of hydrogen production during the electrolysis of water. According to the pH level at which the electrolysis is performed, such half-equations vary a little (Figure 4B) (McHugh et al., 2020).

Adsorption of  $OH^-$  on the catalyst ( $M-OH$ ) and the adsorbed  $OH^-$  ions converting into oxygen moieties on the catalysts ( $M-O$ ) are the primary stages. There are two distinct ways to create  $O_2$  species from the adsorbed intermediates: either a peroxide ( $M-OOH$ ) intermediate is created during the third electron transfer and then decays after the fourth electron transfer step to release  $O_2$  gas or two neighboring  $M-O$  intermediates are directly combined to yield  $O_2$  gas under the alkaline electrolyte. Electrocatalytic OER in heterogeneous OER reactions depends on the bonding interactions ( $M-O$ ) in the intermediates of  $M-OH$ ,  $MO$ , and  $M-OOH$  (Gonçalves et al., 2021) (Figure 4C) (Guo et al., 2023; Raveendran et al., 2023; Xu et al., 2023). There are simple processes in the HER (Figure 4D) (Gonçalves et al., 2021). The HER process may be classified into two steps, where the first one, designated Volmer reaction, is proton reduction caused by creating  $H^*$  on the catalysts under alkaline media. The second step, the Heyrovsky reaction, is the formation of  $H_2$ . In addition to the Heyrovsky reaction,  $H_2$  may be formed via the Tafel reaction. There are two  $H^*$  in the vicinity combined on the surface of the electrode forming  $H_2$ . 1) On the surface, a proton first needs to be ingested by capturing an electron. 2) Two alternative mechanisms can be used to progress to the second aspect. When two adsorbed hydrogen atoms interact together, 3) utilizing a Langmuir process, either one of the hydrogen atoms that



has been adsorbed combines with a proton that has been dissolved in water by absorbing one electron, as follows the reaction mechanism.

The transition metal-derived nanostructures as emergent substitutes have been used for numerous electrocatalytic reactions due to their extraordinary catalytic activity, high earth-abundance, good conductivity, and ecological sociability (Farhan et al., 2024; He et al., 2024; Hegazy et al., 2024; Yao et al., 2023). High earth-abundance transition metal-derived catalysts are dispersed on carbon (C) or Ni conductive electrode substrates that have been generally stabilized through attachment with doped nitrogen (N) and/or an additional class of hetero-atomic molecules. It has been shown that the covalently synchronized transition metal centers could discover encouraging adsorption possession and durability for various electrocatalytic applications (Chen et al., 2024c; Sadeghi et al., 2023; Zhu et al., 2023). The intriguing benefit of the atomic- and nano-scale confinement of adsorption intermediates has also been utilized to engineer the catalytic performance through improved turnover rates and mass activity (employment of metal efficacy), which has provided an increase in divergent electrocatalytic performances since their bulk equivalent stating repetitive active site (Mao et al., 2023; Sadeghi et al., 2023; Sheng et al., 2023; Xu et al., 2023). Such nanotechnology-based techniques further enable the development of electrocatalysts and assist the production of nanomaterials mostly with improved efficacy, enhanced specificity, and preferred

electrochemical performance by manipulating their surface energy, electrochemically active surface area, and physiochemical characteristics at the molecular or atomic level. Extensive dimension- and shape-controlled nanostructured transition metals and metal oxide materials such as Pt-Fe<sub>3</sub>O<sub>4</sub>, metal oxides of FeCoNiO, FeOOH/Co/FeOOH, Fe-doped NiSe<sub>2</sub>, and Fe<sub>2</sub>C are demonstrated for improved electrochemical properties (Mao et al., 2023; Mekete Meshesha et al., 2023; Reddy et al., 2023; Ren et al., 2023; Sabir et al., 2023; Sadeghi et al., 2023).

Elakkiya et al. developed a durable and efficient bi-functional electrocatalyst using hierarchical flower-like nickel cobalt oxide nanoporous (NiCo<sub>2</sub>O<sub>4</sub>-NP) materials for the overall electrocatalytic water splitting (Elakkiya et al., 2019). The NiCo<sub>2</sub>O<sub>4</sub>-NP materials are synthesized through a hydrothermal method using nickel nitrate and cobalt nitrate in a 1:3 ratio as the precursors. The NiCo<sub>2</sub>O<sub>4</sub>-NP materials displayed a flower-like surface morphology with a pore size of ~11.2 nm (Figures 5A,B). Cubic NiO had a flower-like morphology that measured a few microns in length (Figures 5C,D), whereas spinel Co<sub>3</sub>O<sub>4</sub> had a rice-flower-like structure that measured a few nanometers ((Figures 5E,F)). The crystalline nature of NiCo<sub>2</sub>O<sub>4</sub>-NP nanostructures can be indexed to the (111), (220), (311), (200), (511), and (440) planes, suggesting a spinel crystalline structure (Farhan et al. 2024). The developed NiCo<sub>2</sub>O<sub>4</sub>-NP, NiO, and Co<sub>3</sub>O<sub>4</sub> nanostructures showed polycrystallinity, and the corresponding crystalline planes also agreed well with the XRD

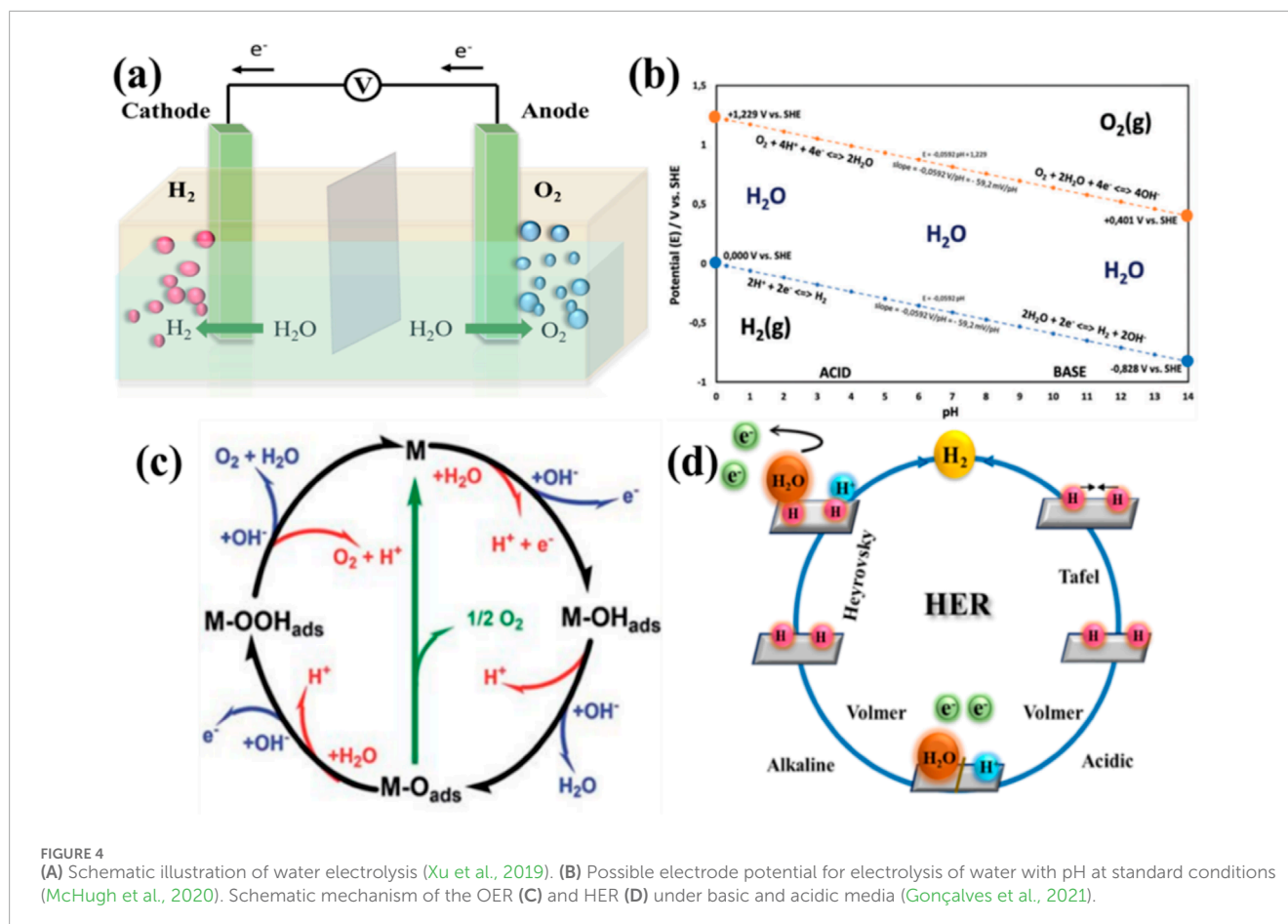


FIGURE 4

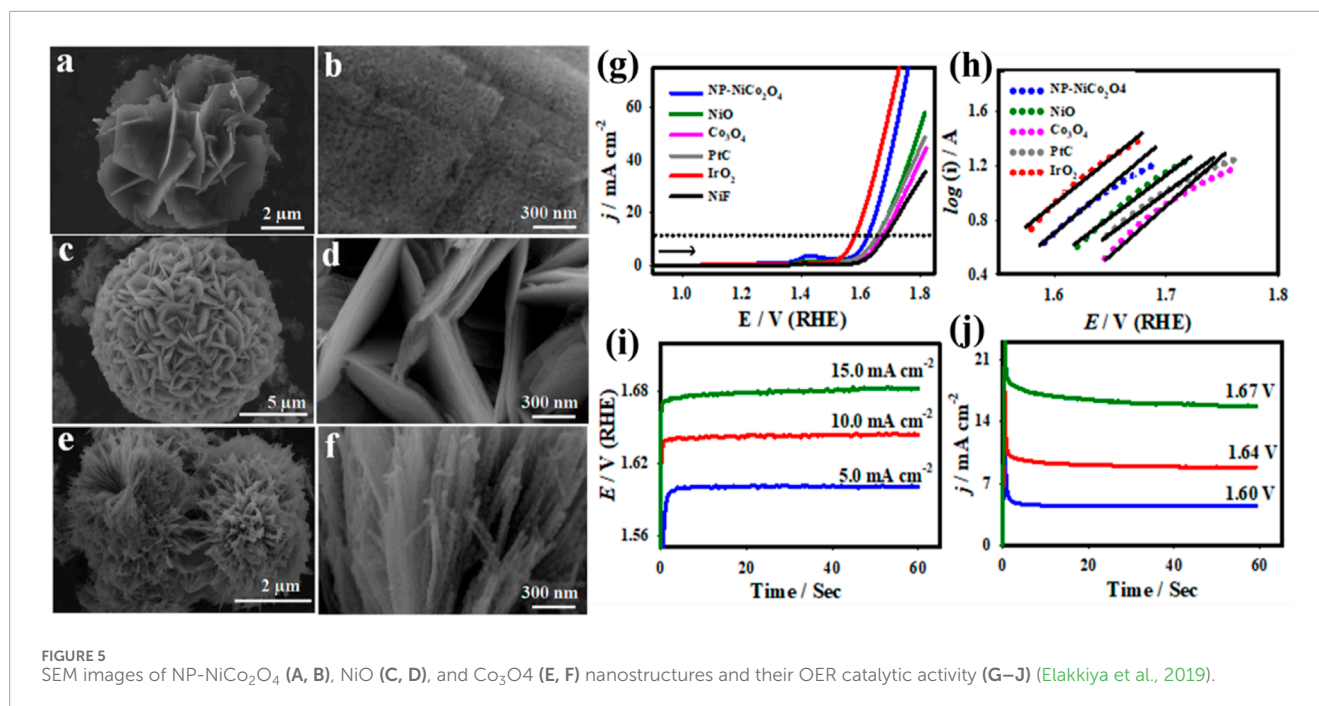
(A) Schematic illustration of water electrolysis (Xu et al., 2019). (B) Possible electrode potential for electrolysis of water with pH at standard conditions (McHugh et al., 2020). Schematic mechanism of the OER (C) and HER (D) under basic and acidic media (Gonçalves et al., 2021).

results. The high-resolution XPS spectrum of Ni 2p, Co 2p, and O 1s species for the NiCo<sub>2</sub>O<sub>4</sub>-NP materials is reported to assess the chemical state of nickel (Ni<sup>2+</sup> and Ni<sup>3+</sup>), cobalt (Co<sup>3+</sup> and Co<sup>2+</sup>), and oxygen (M–O bonds and defect spots with little O). It is highly understood that the imperfect O-sites may expedite the electrocatalytic OER activity of the spinel oxide nanomaterials. The electrocatalytic measurements of NiCo<sub>2</sub>O<sub>4</sub>-NP materials for the OER and HER were examined in 1.0 M KOH. The LSV curves of the NiCo<sub>2</sub>O<sub>4</sub>-NP nanomaterial were compared to those of NiO, Co<sub>3</sub>O<sub>4</sub>, commercial IrO<sub>2</sub>, bare NiF, and commercial Pt/C (Figure 5G). In particular, the NiCo<sub>2</sub>O<sub>4</sub>-NP material shows a reduced overpotential of ~360 mV and increased OER activity at 10 mA cm<sup>-2</sup>. The NiCo<sub>2</sub>O<sub>4</sub>-NP materials produced a low onset potential and a Tafel slope of approximately 1.52 V and 150 mV dec<sup>-1</sup>, respectively (Figure 5H). It was discovered that the maximal mass activity of the NiCo<sub>2</sub>O<sub>4</sub>-NP nanomaterial was approximately 112.3 Ag<sup>-1</sup>, and its TOF value was 0.103 s<sup>-1</sup>. The electrocatalytic OER activity of the NiCo<sub>2</sub>O<sub>4</sub>-NP materials was investigated further using the EIS, potentiometric, and chronoamperometric techniques (Figures 5I,J). The electrode potentials of ~-0.32, ~-0.38, and ~-0.42 V were delivered by the NiCo<sub>2</sub>O<sub>4</sub>-NP nanomaterials for the applied constant current densities of -5.0, -10.0, and -15.0 mA cm<sup>-2</sup>, respectively, as seen in Figures 5I,J. On the other hand, by providing constant applied potentials of -0.33, -0.38, and -0.43 V, respectively, the NiCo<sub>2</sub>O<sub>4</sub>-NP nanomaterials displayed the current densities of ~-3.3, ~-9.9, and ~-17.7. The potential of 1.96 V and 1.70 V

was revealed by NiCo<sub>2</sub>O<sub>4</sub>||NiCo<sub>2</sub>O<sub>4</sub> and Pt/C||IrO<sub>2</sub>, indicating that the well-established hierarchical NiCo<sub>2</sub>O<sub>4</sub> nanostructures found on Earth had nearly the same potential as cutting-edge Pt/C catalysts for the alkaline water electrolyzer.

Santos et al. fabricated the NiMo–NiCu<sub>0.06</sub> nanostructures by a simple electrodeposition method that exhibited a low overpotential of ~86 mV (@ *j* of ~10 mA cm<sup>-2</sup>) toward HER (Santos et al., 2020). Interestingly, the single atomic catalyst of cobalt and nitrogen co-doped with graphene was successfully developed by the annealing method, which delivers the overpotential ~384 mV (@ *j* of ~20 mA cm<sup>-2</sup>) in 1.0 M KOH (Zhang Q. et al., 2020). Bose et al. reported the preparation of CoSe<sub>2</sub>|CoP-DO electrode materials grown on carbon fiber paper using the two-step process (solothermal and phosphidation). The synthesized CoSe<sub>2</sub>|CoP-DO showed excellent performance in the OER with a low overpotential ( $\eta$ ) of ~240 mV (@ current density (*j*) of ~10 mA cm<sup>-2</sup>) and outstanding stability for ~120 h (Bose et al., 2018). A facile preparation of earth-abundant two-dimensional (2D) transition metal oxide (TMO) nanosheets such as cobalt oxide (Co<sub>3</sub>O<sub>4</sub>-NS), nickel oxide (NiO-NS), copper oxide (CuO-NS), and iron oxide (Fe<sub>3</sub>O<sub>4</sub>-NS) for the OER under alkaline electrolyte was developed by Elakkiya and Maduraiveeran (2020). These TMO nanosheets are synthesized using chemical reduction accompanied by annealing treatment. Because 2D metal oxides have high surface-to-volume ratios and electron confinement, there has been significant interest in developing a generic synthetic technique for them. When



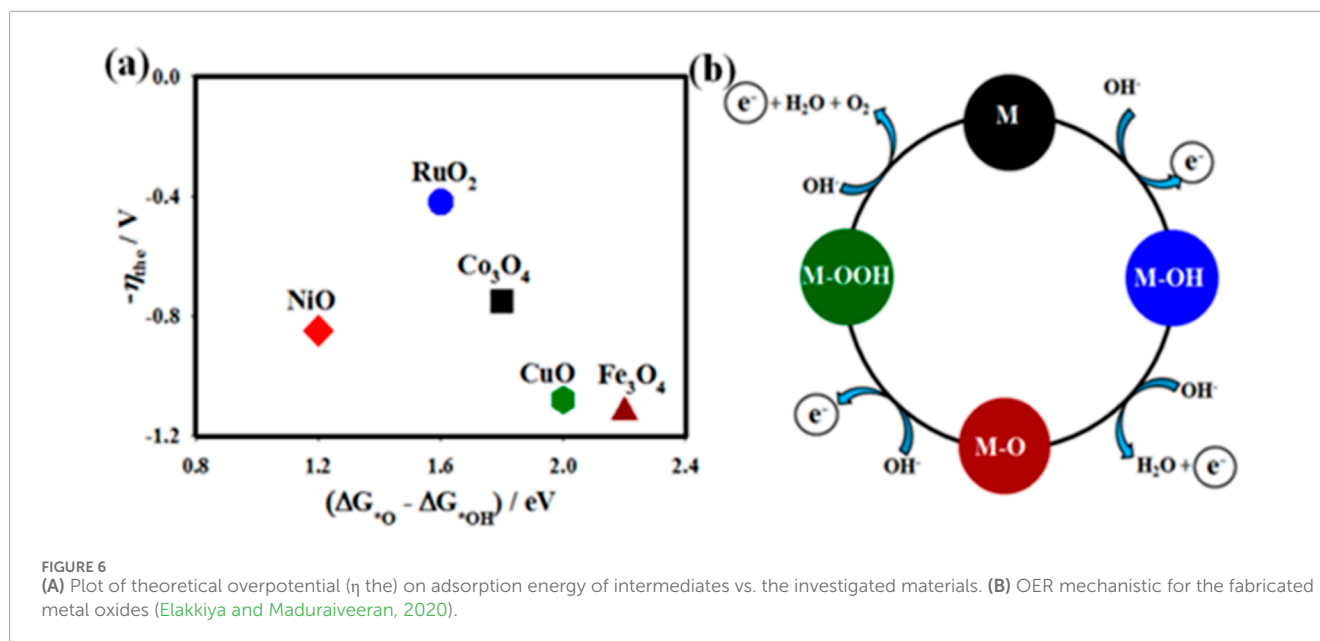


comparing 2D metal oxides to graphene and/or metal hydroxides, it is much easier to grasp how the intrinsic layered atomic structures of these compounds form. One possible explanation for the construction of 2D layered nanosheets of metal oxide is that, even before the calcination process, the facets with strong energy in the lateral path may have progressed to a greater degree than the low-energy facets in the vertical direction. By selectively changing some aspects' energy or initiating the directed attachment of primary blocks, the resulting NH<sub>3</sub>- molecules can function as a template agent for the formation of 2D nanosheets. From the volcano plot, RuO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> adsorb oxygen OER intermediates at almost ideal binding energy, while CuO and Fe<sub>3</sub>O<sub>4</sub> nanosheets bind to the intermediates weakly, and NiO binds with them strongly. The created 2D Co<sub>3</sub>O<sub>4</sub> nanosheet was shown to have suitable adsorption energy, indicating its potential as an effective OER catalyst (Figure 6A). The most frequently generated intermediates, as shown in Figure 6B, are M–OH and M–O, which are most likely centered on the OER that generates oxygen. The bonding interactions (M–O) in the intermediates of M–OH, MO, and M–OOH are essential for the electrocatalytic OER. Due to its high BET-specific surface area, 2D morphological architecture, organized thin-sheet-like nanostructures with homogenous mesopores, and enormously abundant active sites, the Co<sub>3</sub>O<sub>4</sub>-NS significantly outperformed the other materials investigated in this work in terms of OER activity, as shown by all the results. Alnaser co-workers prepared the laser-induced NiCoCr(V) electrode materials, with their richness of oxidation states, and exhibited high-performance electrochemical water splitting that is comparable to those of commercial electrodes (Ahmad et al., 2024). The NiCoCr(V) electrode demonstrated an overall water splitting potential of 1.61 V@10 mA cm<sup>-2</sup>, which is very close to 1.56 V of Pt/C||Ir/C electrodes. By constructing laser-induced periodic structures on the surface, femtosecond laser surface structuring has been utilized

to expand the electrochemically active surface area and further enhance the oxidation states through customized laser–matter interactions.

The development of several nanostructured iron sulfide (FeS) materials, including rice grains (RGS), nanoflowers (NFS), and nanoparticles (NPS), has been accomplished by electrodeposition, solvothermal, and chemical techniques, respectively (Elakkiya and Maduraiveeran, 2021a). The systematic investigation of the connection between the morphology-controlled nanostructure FeS production processes (Figures 7A–C) and the electrocatalytic OER activity is examined (Figures 7D–G). As the common S-source for all the preparation techniques used in this work, DMSO was specifically used to generate different nanostructured FeS as the emerging OER electrocatalysts. The solvothermal-supported FeS nanomaterials revealed a flower-like morphology, the chemically assisted production of FeS particles showed a high distribution of sphere-like surface morphology, and the electrochemically produced FeS nanomaterials appeared to have a rice grain-like morphology according to the SEM and TEM images (Figures 7A–C). In comparison with the developed nanostructures in this work, the electrodeposited FeS-RGS|NF electrode demonstrated high OER catalytic activity with low onset potential of ~1.37 V, low overpotential of ~0.20 V at 10 mA cm<sup>-2</sup>, small Tafel slope of ~54.2 mV dec<sup>-1</sup>, and high mass activity of ~5.4 Ag<sup>-1</sup>, as displayed in Figures 7D–G. The FeS-RGS nanostructures also showed excellent durability and ECASA during 24 h at a constant current density of 17 mA cm<sup>-2</sup>. The FeS-RGS || PtC shows the stable OER current density that was reached. The real-world capability of FeS-RGS nanostructures was found, as evidenced by the minimal fluctuation in the overpotential of approximately 4 mV. The high mass activity and low overpotential of the as-developed FeS-RGS nanostructures were demonstrated. Thanks to the constructive *in situ* oxidation of Fe-species, synergistic effects, numerous accessible electrochemical active sites, direct growth of rice grain structures, and constructive *in situ*





oxidation, the nanostructured FeS–RGS electrode exhibited improved OER catalytic activity.

### 3 Water–CO<sub>2</sub> electrolysis

The electrochemical conversion of CO<sub>2</sub> in the atmosphere (CO<sub>2</sub>) into extremely energy-dense carbon molecules that could be used as energy and feedstocks, such as a leading “carbon-neutral” energy source, is one of the most viable methods (Bhargava et al., 2021). Worldwide, the energy economy and chemical industry rely heavily on fossil fuels, such as carbon dioxide (CO<sub>2</sub>), which are powered by renewable resources. This puts environmental safety at risk since it increases the atmospheric concentration of CO<sub>2</sub> (Dinges et al., 2024; Hua et al., 2024; Jiang et al., 2024; Pei et al., 2021). The electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR) must be optimized for high-performance and low-cost electrocatalysts to produce value-added chemicals and fuels (Liu Y. et al., 2024; Yang et al., 2024; Yu et al., 2024; Zhang Y. et al., 2024).

The application of CO<sub>2</sub> in an electrochemical reduction process yields hydrocarbon and alcohol (Timoshenko et al., 2022). Research and enhancement of heterogeneous and homogeneous catalysts for the CO<sub>2</sub>RR under organic electrolytes and alkaline electrolytes have received much attention in scientific research (Bagemihl et al., 2023; Barecka et al., 2021; Bi et al., 2023). The primary benefits of converting CO<sub>2</sub> electro-catalytically to value-added chemicals are as follows: 1) reusing its supporting electrolyte is conceivable, 2) limiting the carbon dioxide emissions, 3) possible modifications to the electrochemical cell, and 4) regulating the mechanism using voltage and temperature. The efficiency and selectivity of the electrochemical reduction of carbon dioxide are primarily influenced by the CO<sub>2</sub> concentration in the electrolyte, the form of the electrode and electrolyte, and the applied current or voltage (Song et al., 2019; Ye et al., 2017; Zheng et al., 2017).

When the CO<sub>2</sub>RR is combined with electrochemical water splitting, the energy conversion technologies do not necessitate

an extra hydrogen feedstock (Hua et al., 2024; Jiang et al., 2024; Pimlott et al., 2023). Water might provide the protons required to reduce CO<sub>2</sub> in its place. The term “water–CO<sub>2</sub> co-electrolysis” is often used to describe the combination of the anode process (OER) and the cathode process (CO<sub>2</sub>RR) (Figure 8A) (Meng et al., 2019). Several criteria, including the Faradaic efficiency, current density, onset potential, and energy efficiency, related to core electrochemical performance may be systematically determined. Three key phases in the CO<sub>2</sub>RR mechanism take place at the cathode and electrolyte interaction. The chemical adsorption or the activation of carbon dioxide molecules onto the interface of the catalysts is the initial step. Although it has a greater energy boundary, it is typically a rate-determining step throughout the reduction process of CO<sub>2</sub>. The C–O bonds are then broken, causing related reaction products to develop as protons and electrons are transferred (Figure 8B) (Kortlever et al., 2015). These mediators are crucial for producing hydrocarbon products. Finally, these products undergo a rearrangement to become products and separate into the electrolyte from the catalytic surface. The anodic process takes place on the anode surface concurrently with the charge carrier of the whole electrochemical reaction. Figure 8C shows the pictorial representation of CO<sub>2</sub>RR at homogeneous, heterogeneous electrocatalysts, and when immobilized (Varela et al., 2018). A variety of nanomaterials comprising several elements, including nitrogen, carbon, and non-noble metals, extending from distinct restrained complexes to carbon materials doping have been considered as appropriate substitutes.

A key tactic in the creation of high-performance electrocatalysts for enhanced CO<sub>2</sub>RR is the morphology- and dimension-controlled production of nanostructured electrode materials based on transition metals, oxides, and chalcogenides (Zhang Z. et al., 2024; Zhang M. et al., 2024; Zhang et al., 2019). Several research studies have been conducted to create high-efficiency electrode substances with the selective synthesis of compounds with added value, high mass activity, long-term durability, low onset potential, and overpotential (Li J. et al., 2023; Li P. et al., 2023; Lu et al., 2024).

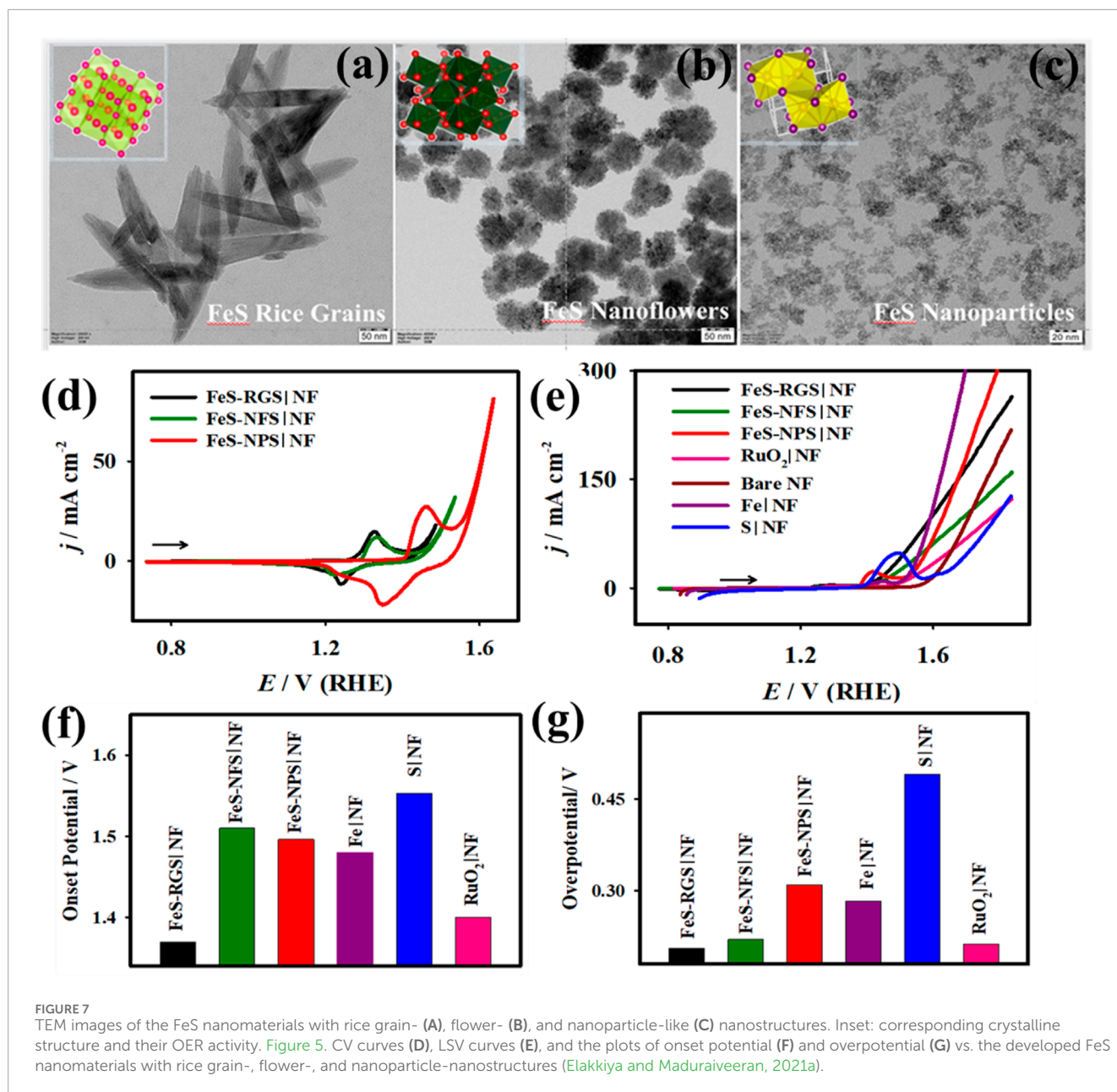


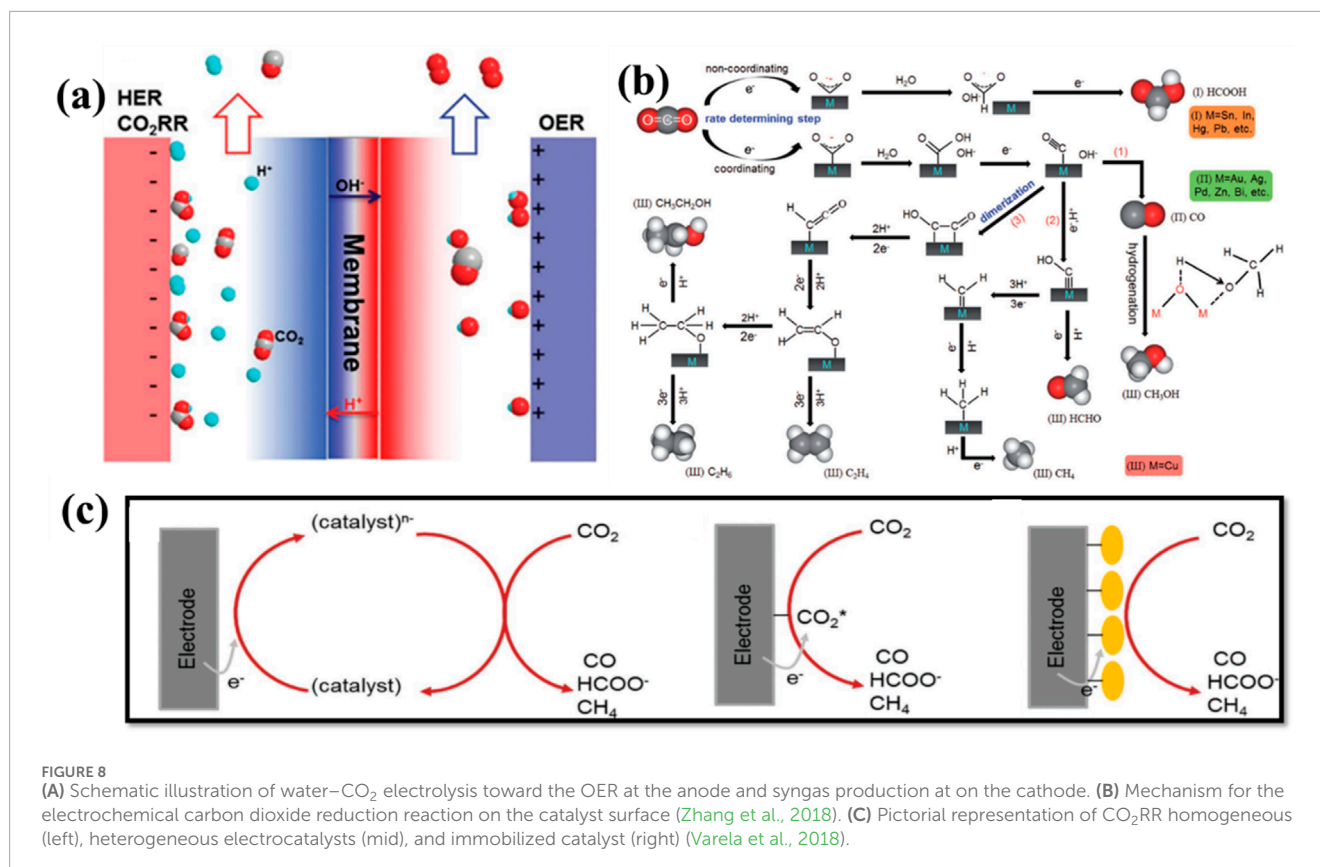
FIGURE 7

TEM images of the FeS nanomaterials with rice grain- (A), flower- (B), and nanoparticle-like (C) nanostructures. Inset: corresponding crystalline structure and their OER activity. Figure 5. CV curves (D), LSV curves (E), and the plots of onset potential (F) and overpotential (G) vs. the developed FeS nanomaterials with rice grain-, flower-, and nanoparticle-nanostructures (Elakkiya and Maduraiveeran, 2021a).

Modern noble metal-based catalysts (Au, Pt, Ag, Pd, etc.) have limited commercial application due to their high cost, low selectivity, and less earth abundance (Kim et al., 2020; Ko et al., 2024; Lv et al., 2021). Numerous catalysts, including semiconductors, organic compounds, proteins, ionic liquids, and organometallic complexes, for CO<sub>2</sub>RR have been studied in the past (Patra and Gopinath, 2023; Pimlott et al., 2024; Roy et al., 2024). Recently, Zhao et al. produced the Cu/ZnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>@ Cu/ZnO/MgO electrocatalysts for the formation of methanol during CO<sub>2</sub> hydrogenation using a template-assisted chemical deposition process, followed by an incipient wetness impregnation method (Guo et al., 2019). Huang and colleagues created partially oxidized 5-nm cobalt nanoparticles scattered on single-layer nitrogen-doped graphene (PO-5 nm Co/SL-NG) to manufacture methanol with a maximum faradaic efficiency of 71.4% at the potential of -0.90 V vs. RHE

(Huang et al., 2018). Zhang et al. developed the MOF-derived nanostructures of Cu GNC-VL to achieve a high faradaic efficiency of 70.52% at -0.87 V against RHE in the electro-reduction of CO<sub>2</sub> to ethanol (Zhang Y. et al., 2020). Recent research demonstrates that copper (Cu) nanoparticles are among the most highly electrically conductive and catalytically active, and they inhibit the HER activity (Mavrokefalos et al., 2020).

Moreover, metallic Cu or Cu-based compounds have been extensively employed for diverse purposes such as photo-thermal, electrical, organic transformation and for electronic devices (Li L. et al., 2022). Researchers are particularly interested in copper chalcogenides because of their fascinating mechanical, electrical, optical, and catalytic properties (Shin et al., 2015; Song et al., 2024; Song et al., 2019). Better electrochemical properties were provided by the CuSe-based electrode materials, which had various

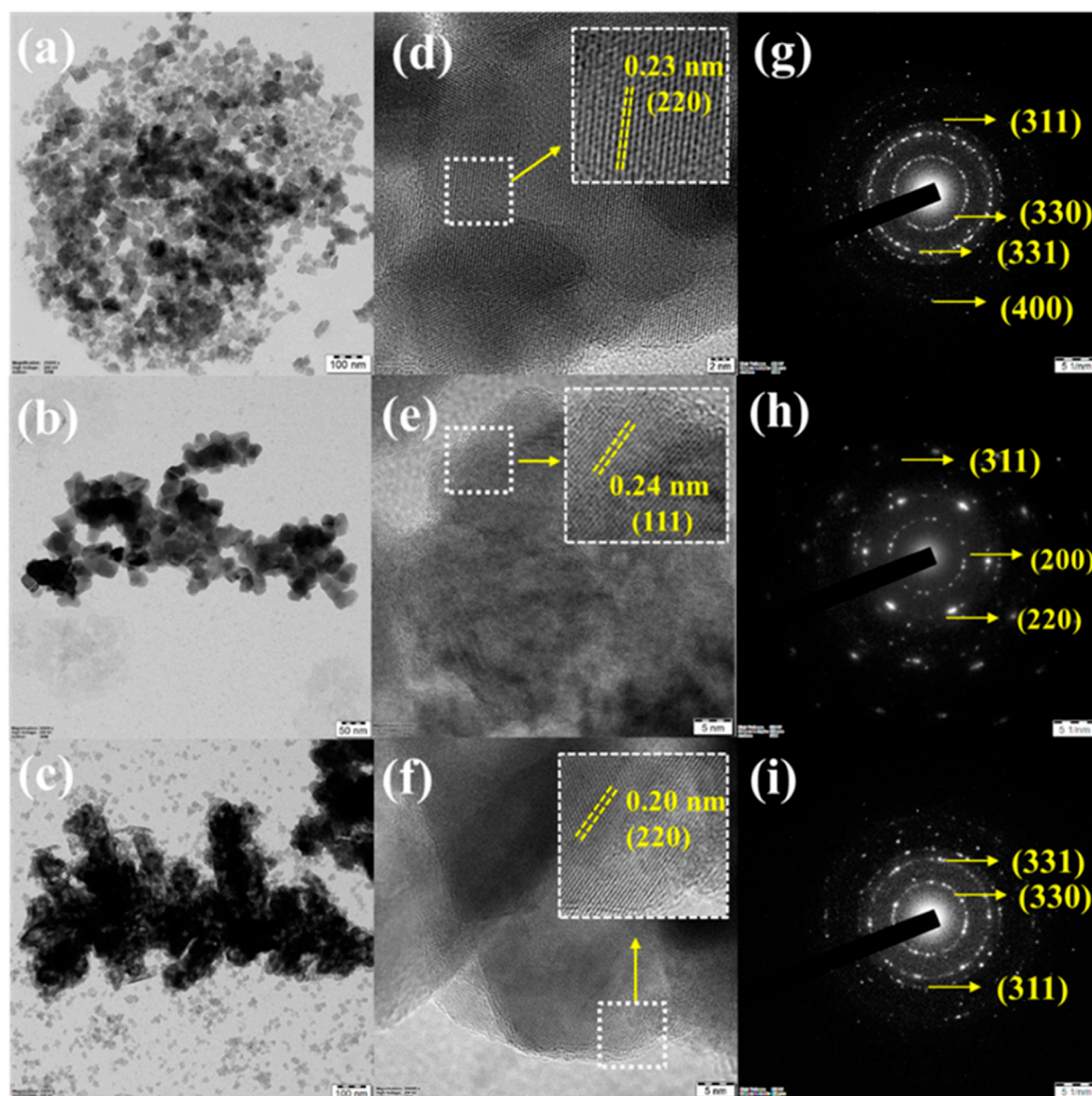


oxidation states and good electrical conductivity. Furthermore, the heterostructures including unsaturated Se atoms and their edges might increase the number of the exposed active sites and electrocatalytic activity in CO<sub>2</sub>RR. To create materials with Cu-derived chalcogenides, several synthetic methods have been established. In addition to having a variety of crystallographic patterns (monoclinic, hexagonal, tetragonal, and cubic), it can exist in a broad range of stoichiometric (Cu<sub>3</sub>Se<sub>2</sub>, Cu<sub>2</sub>Se, Cu<sub>7</sub>Se<sub>4</sub>, CuSe<sub>2</sub>, and Cu<sub>5</sub>Se<sub>4</sub>) and nonstoichiometric (Cu<sub>2-x</sub>Se) compositions (Wang, 2023; Wen et al., 2023; Woldu et al., 2023).

Several techniques have been successfully employed for the preparation of CuSe nanomaterials: microwave, colloidal, electrodeposition, chemical bath, sputtering, hot-injection, sol-gel, spin coating, solid-state reaction, hydrothermal, dip coating, and vapor-based methods. Maduraiveeran et al. established a one-step electrochemical strategy for the fabrication of highly efficient and stable nanocube-like copper selenide nanostructures (CuSe NCs) for the enhanced electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR), representing a new path for environmental and energy sustainability concerns (Elakkiya and Maduraiveeran, 2021b). A sequence of highly ordered 3D CuSe NCs gathered as domain nanocube-, branched nanocube-, and dendrite nanocube-like surface morphology on copper microelectrodes is developed (Figure 9). The as-fabricated nanostructures were chosen as CuSe NCs-A, CuSe NCs-B, and CuSe NCs-C for the Cu/Se molar ratios of 1:1, 1:3, and 3:1, respectively. Moreover, the major electrocatalytic CO<sub>2</sub>RR was examined at the modified hierarchically arranged 3D CuSe NCs

under both aqueous (KHCO<sub>3</sub>) and organic ([Bmim]PF<sub>6</sub>/MeCN) electrolytes. In 1.0 M aqueous KHCO<sub>3</sub>, the CuSe NCs-B-based Cu microelectrodes showed a less negative onset potential of  $-0.5$  V vs. RHE, a high catalytic current density of  $-120.3$  mA cm<sup>-2</sup>, a low cathodic potential of  $-0.65$  V vs. RHE, and a high mass activity of  $41.6$  mA g<sup>-1</sup> (Figure 10). In [Bmim]PF<sub>6</sub> in the MeCN electrolyte, the CuSe NCs-B based Cu microelectrodes exhibited a less negative onset potential of  $-1.1$  V vs. Ag/AgCl and high catalytic current density of  $-23.4$  mA cm<sup>-2</sup>. These results indicated that the 3D CuSe-B nanocube electrode possessed many electrochemical active sites, which led to enhanced CO<sub>2</sub>RR activity. The initial intermediate of absorbed CO can be improved by including appropriate Cu and Se active sites on the catalysts. This allows the intermediate to absorb protons and electrons, becoming absorbed CHO, which is then reduced to methanol. According to all the electrochemical reaction results, CuSe NCs-B/CuMEs were the most developed CuSe nanocube microelectrodes. They demonstrated the highest catalytic CO<sub>2</sub>RR activity in both aqueous and organic electrolytes, with a less negative onset potential and cathodic potential to reach  $-10$  mA cm<sup>-2</sup> and low polarization resistance, high mass activity, and stability. Due to the CuSe NCs-B-based Cu microelectrodes' high crystallinity, large volume of electrochemical active sites, low polarization resistance, hierarchical 3D nanocube-like morphology, and integrated intrinsic catalytic activity, they were able to achieve high electrocatalytic performance. Recently, Alnaser co-workers reported femtosecond laser-assisted tuning of the selectivity Cu for generating ethane and propanol (Ali et al., 2024). The





**FIGURE 9** TEM images for CuSe NCs-A (A), CuSe NCs-B (B), and CuSe NCs-C (C). HRTEM images for CuSe NCs-A (D), CuSe NCs-B (E), and CuSe NCs-C (F). SAED patterns of CuSe NCs-A (G), CuSe NCs-B (H), and CuSe NCs-C (I). The as-fabricated nanostructures were called CuSe NCs-A, CuSe NCs-B, and CuSe NCs-C for the Cu/Se molar ratios of 1:1, 1:3, and 3:1, respectively (Elakkiya and Maduraiveeran, 2021b).

conversion from C1 products to ethane and propanol is mainly triggered by the laser-assisted modification of the surface of Cu. Simultaneously, the so-formed hierarchical porous structures may cause the [111], [200], and [220]  $\text{Cu}_2\text{O}$  facets for the stabilization. These processes are responsible for the change in the product composition. Furthermore, the adsorption strength is enhanced, which increases the tendency for C–C coupling and, as a result, the selectivity for  $\text{C}_{2+}$  products.

Chen and co-workers carried out co-electrolysis of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to generate hydrocarbon with proton-conducting electrolysis cells (PCECs) (Figure 11) (Ye et al., 2023). The rough surface

of  $\text{CeO}_2$  modified with the  $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (BZCYYb) electrode was employed for the production of  $\text{CH}_4$  at a low current density. The  $\text{CeO}_2$ -modified electrode showed low polarization resistance and possessed a high-intensity interface process on the solid–gas interface. In particular, at low current density, the additional hydrogen-induced component analysis interference may be effectively removed. On the other hand, the hydrogen gas produced during electrolysis may prevent  $\text{CO}_2$  from oxidizing the fuel electrode. The adsorption of CO and proton bonding on the surface of  $\text{CeO}_2$  was weak compared to that on the BZCYYb surface. Although the first factor results in a more robust hydrogen bond



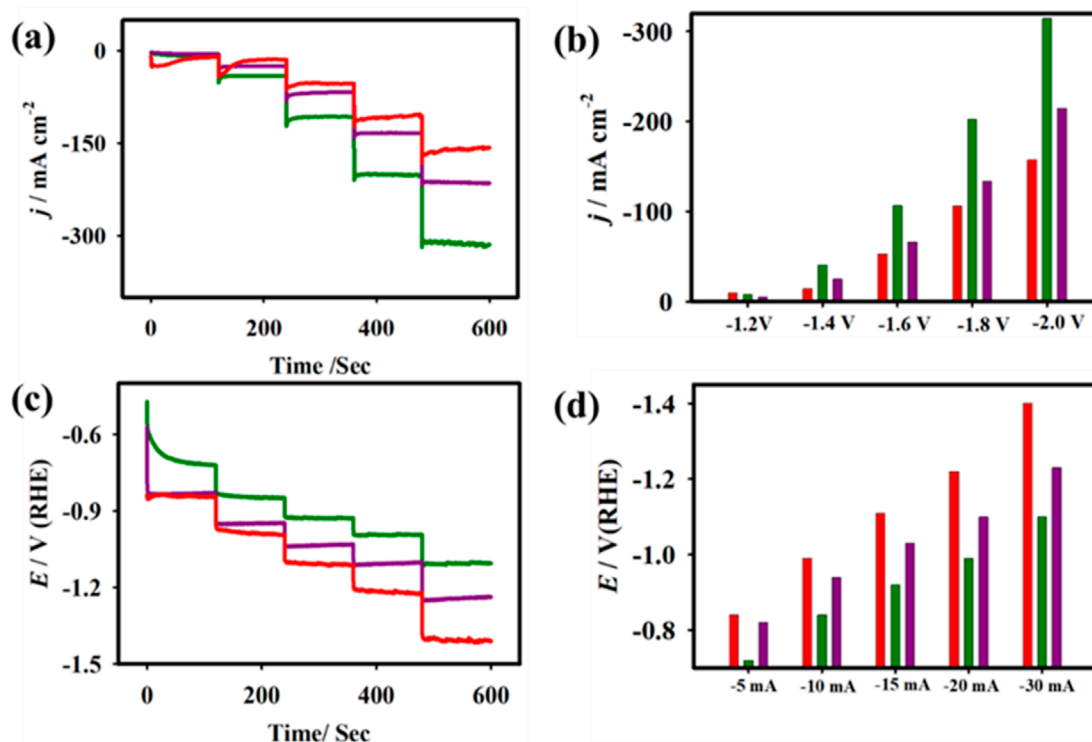


FIGURE 10

Chronoamperometric studies (A) and the plot of  $j$  vs.  $E_{app}$  (B). Chronopotentiometric studies (C) and the plot of electrode potential vs.  $j_{app}$  (D) for the CuSe NCs-A (red), CuSe NCs-B (green), and CuSe NCs-C (violet) electrodes. Electrolyte: 1.0 M aqueous KHCO<sub>3</sub> solution under saturated CO<sub>2</sub> (Elakkiya and Maduraiveeran, 2021a).

with CO and makes it easy for CO hydrogenation, the second factor encourages the protons to migrate after being driven to the electrode surface. The higher CH<sub>4</sub> selectivity is attained on the CeO<sub>2</sub>-modified electrode, majorly lowering the energy barrier for further CO hydrogenation. The advanced spectroscopic measurements integrated with density functional theory computations reveal that the modified CeO<sub>2</sub> improves the formation of CH<sub>4</sub> by modifying reactant adsorption and facilitating proton transport during the hydrogenation process.

## 4 Conclusion

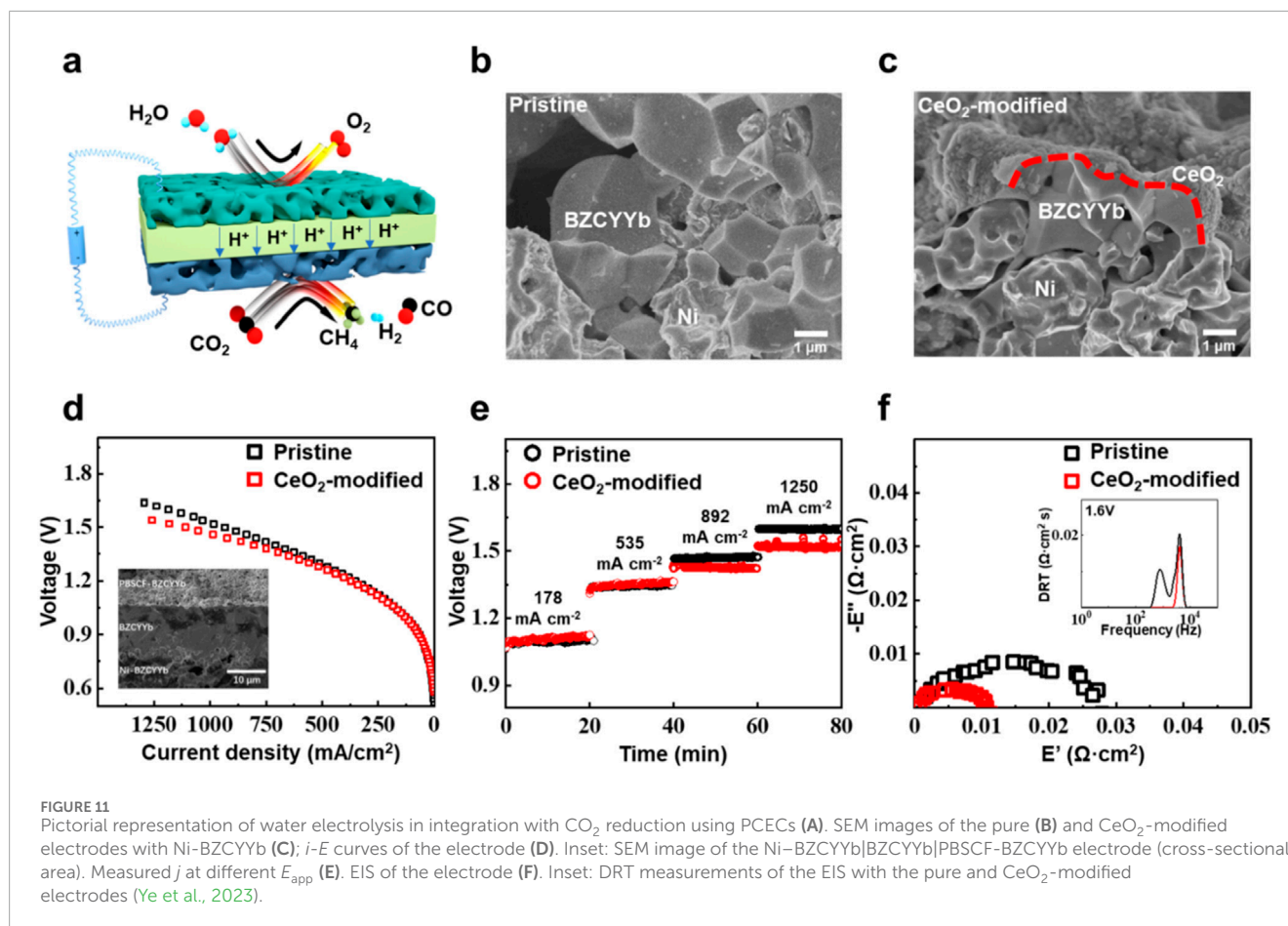
Owing to future socio-economic development, the replacement of fossil fuels with sustainable energy sources and carriers that are environment-friendly and inexpensive is crucial. The generation of hydrogen and hydrocarbon through water electrolysis (OER/HER) and water-CO<sub>2</sub> co-electrolysis (OER/CO<sub>2</sub>RR) is supposed to be the emergent energy carrier (Li W. et al., 2022). These electrochemical reactions are key chemical conversion courses that facilitate renewable energy transformations. Thus, the establishment of alternative low-cost, high earth-abundance, great catalytic activity, and durable electrocatalysts for the possible renewable technologies is both highly preferred and a grand challenge (Marimuthu et al., 2024; Yao et al., 2024). The search for renewable energy motivates the establishment of progressive nanostructured

catalysts for various electrocatalytic reactions, including OER, HER, and CO<sub>2</sub>RR, for efficient energy conversion and storage systems. In the present review, a variety of low-cost and high-performance electrocatalysts based on transition metal-based nanomaterials are discussed for water electrolysis (OER/HER) and water-CO<sub>2</sub> co-electrolysis (OER/CO<sub>2</sub>RR).

## 5 Challenges and outlook

The advantages of the catalysts mentioned in this study include the employability at room pressure and temperature, the utilization of plentiful water molecules rather than complex and costly H<sub>2</sub> for hydrogenation reactions, an extremely dispersed infrastructure, and the capability to attain good specificity toward the optimal products limiting the development of wasteful/toxic co-products. The as-developed nanostructured transition metal-based catalysts in this study demonstrated good catalytic activity in terms of low onset potential, high current densities, low overpotential, high mass activities, and long-term stability. The improved catalytic performance is attributed to the collective effect of heterostructures, a substantial volume of electrochemical active sites, and the establishment of fast electrode kinetics of the nanostructured catalytic materials.

In general, the design of electrocatalysts based on non-metals can still not compete with metal-based candidates



concerning efficiency for OER, HER, and CO<sub>2</sub>RR electrocatalysis. Thus, the establishment of nanocomposites as multifunctional electrocatalysts warrants a deep synergistic interaction among the catalytic sites, increasing the number of active sites, and interfaces is a practical approach that should be pursued. The incorporation of S, P, and Se on transition metal nanomaterials is an effective strategy for engineering the electronic structure and electrochemical properties for improved catalytic activity and durability. In addition to the optimization of nanostructured electrode materials, there are several approaches for reducing the overpotential, increase of current density, and total Ohmic resistance in energy systems through enhanced ionic movement (using ultrasonography at the gas-evolving electrodes and electrolyte, centrifugal acceleration field, mechanical stirring, and gravity). Most of these non-homogenous electrochemical processes share certain features, such as occurring at solid-liquid interfaces and consisting of multi-step ion/electron coupled electron flow, which leads to extremely slow electron transfer kinetics and highly demanding efficient electrocatalysts, even though the precise mechanism varies. The restricted functionality, capacity, effectiveness, and durability of the catalysts prevent them from being industrialized, even though great efforts have been made to improve the kinetics of electrochemical reactions. Moreover, the interchange of issues faced in the various domains of devices among these groups is greatly needed and stimulated.

## Author contributions

GM: conceptualization, funding acquisition, validation, writing—original draft, and writing—review and editing.

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## Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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