Highlight

Solar Fuels

Asymmetric electronic modulation for synchronised proton-coupled electron transfer in CO_2 reduction

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Single-atom catalysts (SACs) offer an attractive route to the conversion of renewable electricity and CO_2 into value-added chemicals via the electrochemical CO_2 reduction reaction (CO_2RR) [1,2]. Among the various products, CO is particularly important because it is a key component of syngas and a versatile feedstock for downstream chemical synthesis [3,4]. However, achieving highly selective CO_2-to-CO conversion becomes increasingly challenging at strongly negative potentials, where high reaction rates are desirable. The origin of this dilemma lies in the kinetic mismatch between proton and electron supply at the catalyst–electrolyte interface. Increasing the cathodic bias accelerates electron delivery, whereas proton delivery is governed by local proton availability, interfacial water structure, and hydrogen-bonded transport networks. The competing hydrogen evolution reaction (HER) consumes interfacial protons and aggravates local proton depletion. This kinetic mismatch can slow the proton-coupled electron transfer (PCET) required for *COOH formation while simultaneously favouring the HER [5]. Thus, maintaining synchronised proton and electron delivery under high-current-density conditions is a central challenge for practical CO_2 electrolysis.

Ni–N–C SACs are among the most effective platforms for CO_2-to-CO conversion because the isolated Ni sites provide a favourable balance between CO_2 activation and CO desorption [6]. However, the electronically symmetric M–N_4 environment of conventional SACs offers limited flexibility for the independent optimisation of different elementary steps. In particular, the same local electronic structure must accommodate both CO_2-derived intermediates and proton-related species, inevitably resulting in an intrinsic adsorption-energy trade-off [7]. Heteronuclear dual-atom catalysts offer an attractive route to breaking this symmetry by constructing neighbouring, chemically distinct metal centres with divergent electronic properties. Rather than requiring a single site to simultaneously manage CO_2 activation and proton transfer, heteronuclear dimers can spatially divide these catalytic functions, potentially enabling spatially decoupled yet temporally synchronised PCET [8].

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A recent study by Yu et al. (China University of Geosciences), published in *Advanced Materials* (2026, 38, e73766; DOI: 10.1002/adma.73766), reported an asymmetric Ni–Fe dual-atom electrocatalyst supported on N-doped mesoporous hollow carbon spheres (NiFe/NMHCS) to address this long-standing challenge [9]. The core concept relies on spontaneous electron redistribution between adjacent Ni and Fe atoms within the dimer. Specifically, electrons migrate from Fe to Ni, generating an electron-rich Ni site and an electron-deficient Fe site within a single Ni–Fe dimer. This heterometallic electron polarisation establishes a locally asymmetric electronic environment without introducing additional components. Rather than treating the two metals as equivalent active centres, the catalyst deliberately assigns distinct functions to the neighbouring Ni and Fe atoms: Ni preferentially activates CO_2, whereas Fe regulates proton adsorption and delivery. Such a spatial division of catalytic functions provides a compelling strategy to decouple, yet kinetically synchronise, the proton and electron components of PCET. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) directly visualises atomically paired bright spots with an average Ni–Fe interatomic distance of approximately 2.5 Å (Figure 1a,b). Complementary X-ray absorption near-edge structure and extended X-ray absorption fine structure (EXAFS) analyses further supports the formation of N_3Ni–FeN_3 heteronuclear dual-atom moieties, together with the absence of discernible Ni–Ni or Fe–Fe features (Figure 1c,d).

In situ attenuated total-reflection- surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) in N_2-saturated- electrolyte reveals substantially suppressed Fe–H vibrational bands in NiFe/NMHCS compared with monometallic Fe/NMHCS (Figure 2a–c). This finding demonstrates that Ni–Fe electronic coupling effectively moderates excessive H adsorption on Fe sites. Upon switching to a CO_2-saturated- atmosphere, intensified vibrational signals assigned to the key intermediates *COOH and *CO were observed for NiFe/NMHCS. More strikingly, the surface coverage increased monotonically as the potential shifted towards more negative values (Figure 2d–f). In sharp contrast, monometallic Ni-SAC and Fe-SAC exhibited rise-and-fall profiles in the intermediate signals, reflecting increasing competition from the HER and destabilisation of the

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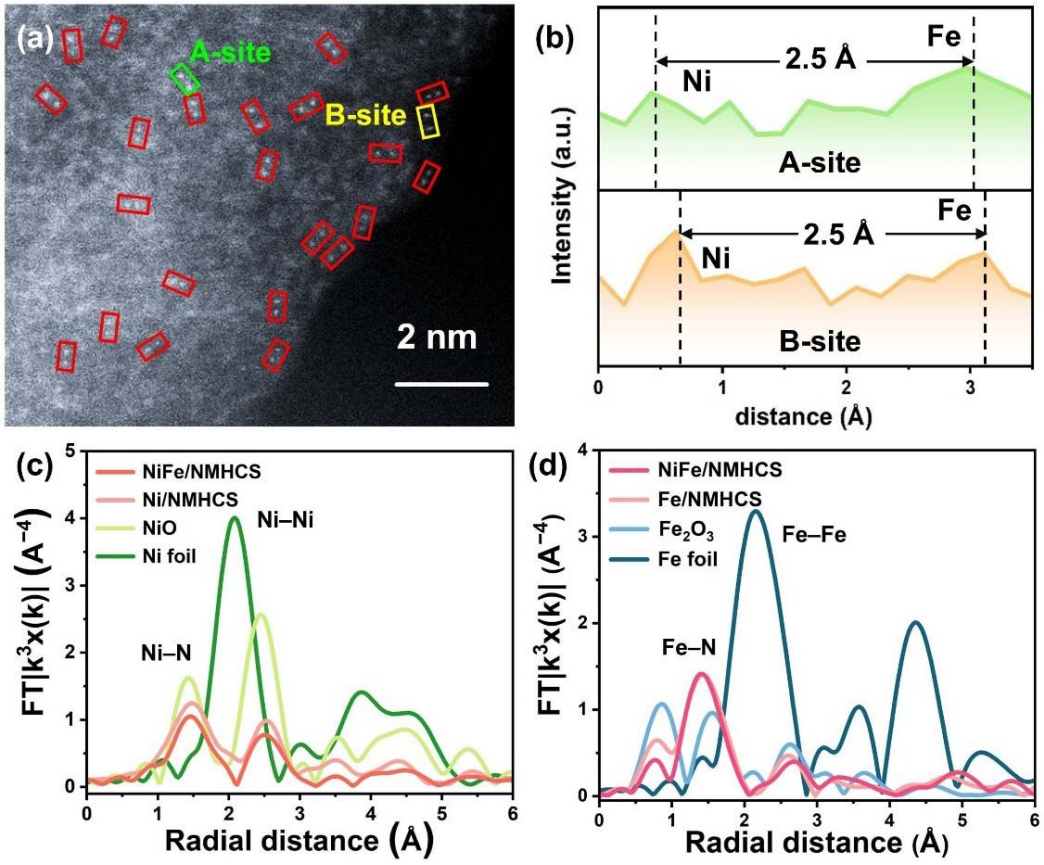


Figure 1 (a) HAADF-STEM image of NiFe/NMHCS. (b) Line-scanning intensity profile obtained along sites A and B highlighted in panel (a). (c) Ni *K*-edge EXAFS spectra and (d) Fe *K*-edge EXAFS spectra of NiFe/NMHCS and the corresponding reference samples. Reproduced with permission from Ref. [9]. Copyright 2026 Wiley.

reaction intermediates. These in situ spectroscopic observations support efficient cross-site PCET on Ni–Fe, accounting for the exceptional retention of CO selectivity even under strongly cathodic conditions.

Theoretical calculations further elucidate the origin of the cooperative PCET mechanism. Calculations of the electron localisation function and differential charge- density- revealed an asymmetric electron distribution within the Ni–Fe dimer, with electron density being partially transferred from Fe to Ni, producing an electron-rich Ni centre and an electron-deficient Fe centre. Projected density of states- analysis further shows that Ni–Fe orbital coupling upshifts the Ni *3d*-band- centre while simultaneously downshifting the Fe *3d*-band- centre (Figure 2g,h). Such *d-band* centre modulation strengthens the Ni–C interaction for CO_2 activation while appropriately weakening Fe–H bonding. Crystal orbital Hamilton population analysis quantitatively corroborated these changes in the bonding strengths of Ni–C and Fe–H. Consequently, the electron-rich Ni site preferentially promoted CO_2 adsorption and molecular bending, lowering the energy barrier for *COOH formation, whereas the electron-deficient Fe site acted as a transient proton reservoir with moderate H-binding strength, suppressing the HER while supplying nearby protons to Ni-bound CO_2 intermediates. Therefore, spatially separated yet temporally synchronised PCET could be achieved across adjacent Ni and Fe sites, accelerating the rate-determining CO_2-to-*COOH transformation.

Benefiting from this asymmetric cross-site PCET mechanism, the NiFe/NMHCS dual-atom catalyst maintains a CO Faradaic efficiency above 95% over an unusually broad potential window from −0.9 to −1.4 V vs. the reversible hydrogen electrode, reaching a maximum of 99.1% at −1.2 V. In sharp contrast, monometallic Ni/NMHCS and Fe/NMHCS exhibited typical volcano-type selectivity profiles and pronounced HER interference at high overpotentials. Thus, this work establishes a clear design paradigm that moves away from pursuing a single active site capable of simultaneously optimising the adsorption of all relevant intermediates. Instead, assigning differentiated catalytic tasks to electronically non-equivalent neighbouring metal centres in heteronuclear dual-atom motifs can effectively decouple conflicting PCET requirements.

Importantly, this principle is not limited to Ni–Fe combinations. Other heteronuclear systems, including Cu–Co and Fe–Co, as well as related transition-metal combinations, also highlight the potential of coupling chemically distinct metal centres to generate complementary catalytic functions. More broadly, heteronuclear dual-atom catalysts provide a platform for engineering not only adsorption thermodynamics but also the spatial organisation and temporal coordination of elementary reaction events [10]. For the CO_2RR, the cross-site PCET regulation demonstrated here provides a conceptual framework that may be extended to other heteronuclear metal combina-

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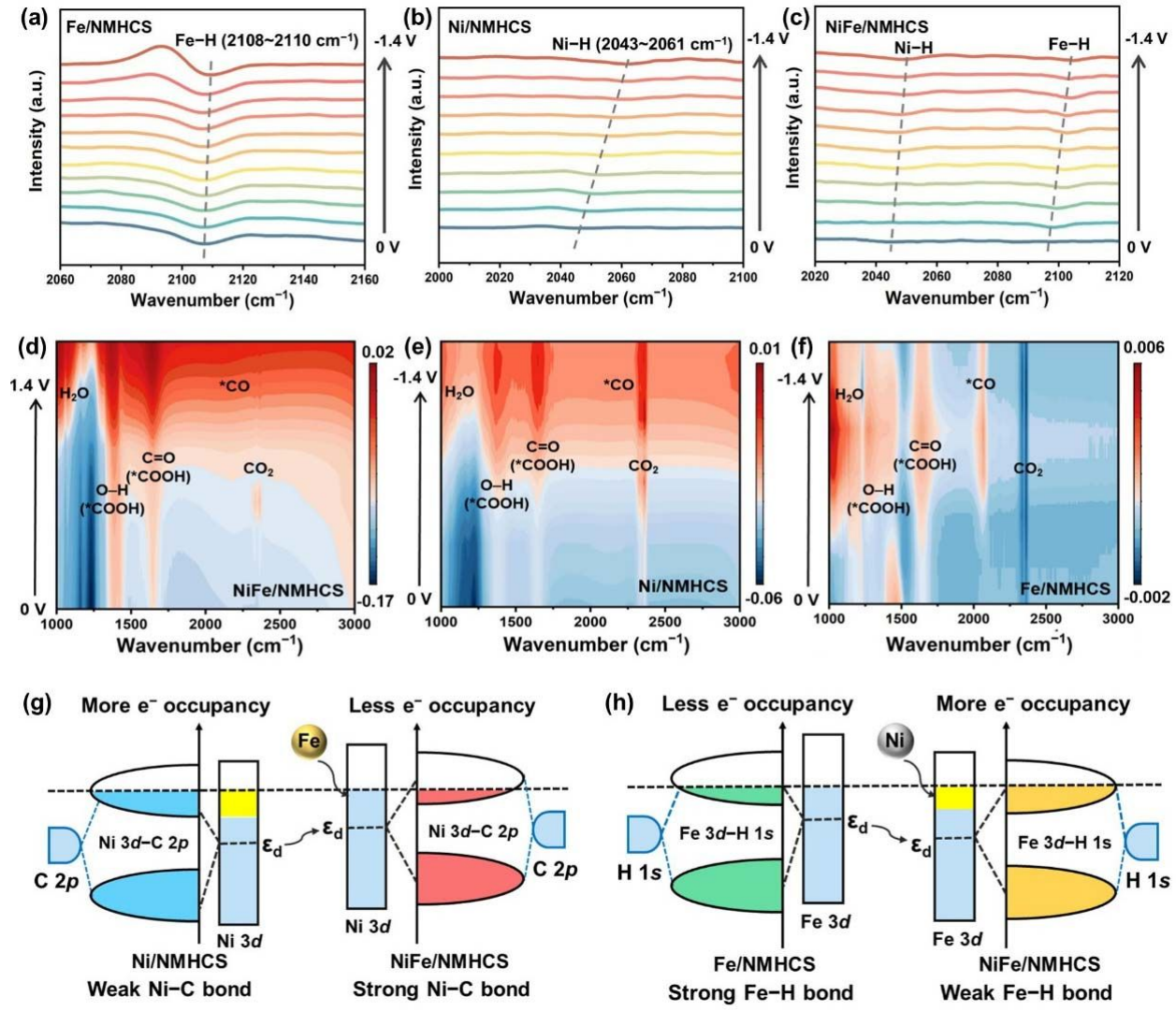


Figure 2 In situ ATR-SEIRAS spectra of (a) Fe/NMHCS, (b) Ni/NMHCS, and (c) NiFe/NMHCS in N_2-saturated 0.5 M $KHCO_3$. In situ ATR-SEIRAS spectra of (d) NiFe/NMHCS, (e) Ni/NMHCS, and (f) Fe/NMHCS in CO_2-saturated 0.5 M $KHCO_3$. Schematic illustrations of (g) enhanced CO_2 adsorption at the Ni site and (h) weakened H adsorption at the Fe site through engineered antibonding-orbital occupancy. Reproduced with permission from Ref. [9]. Copyright 2026 Wiley.

tions, offering a route to maintaining high selectivity under the strongly cathodic potentials and high current densities required for practical electrolysers. Nevertheless, challenges remain in precisely controlling heteronuclear site configurations, identifying their dynamic structures under operating conditions, and establishing predictive relationships between asymmetric electronic structures and catalytic functions. Addressing these issues through integrated synthesis, operando characterisation, and theoretical analysis is important for translating these insights into broadly applicable catalyst design principles.

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