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Hydrogen Spillover Phenomenon at the Interface of Metal-Supported Electrocatalysts for Hydrogen Evolution

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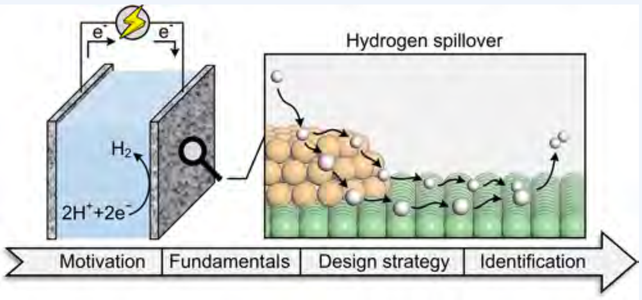

CONSPECTUS: Hydrogen spillover, as a well-known phenomenon for thermal hydrogenation, generally involves the migration of active hydrogen on the surface of metal-supported catalysts. For thermocatalytic hydrogenation, hydrogen spillover generally takes place from metals with superiority for dissociating hydrogen molecules to supports with strong hydrogen adsorption under a H_2 environment with high pressures. The former can bring high hydrogen chemical potential to largely reduce the kinetic barrier of the migration of active hydrogen species from metals to supports. At the same time, the latter can make H* migration thermodynamically spontaneous. For these reasons, hydrogen spillover is a common interfacial phenomenon occurring on metal-supported catalysts during thermocatalysis. Recently, this phenomenon has been observed for the exceptionally enhanced electrocatalytic performance for hydrogen evolution and other electrocatalytic organic synthesis. Different from hydrogen spillover for thermocatalysis under high H_2 pressure, hydrogen spillover for electrocatalysis involves the migration of active hydrogen species (H*) from metals with strong hydrogen adsorption to supports with weak hydrogen adsorption, thereby suffering from a thermodynamically unfavorable process accompanied by a high kinetic barrier. Thus, the occurrence of hydrogen spillover at the electrocatalytic interface is not easy, and successful cases are rare. Understanding the underlying nature of hydrogen spillover at the electrocatalytic interface of metal-supported catalysts is critical to the rational design of advanced electrocatalysts.

In this Account, we provide in-depth insights into recent advances in hydrogen spillover at the electrocatalytic interface for a significantly enhanced hydrogen evolution performance. Electron accumulation at the metal−support interface induces severe interfacial H* trapping and is recognized as the main factor in the failed hydrogen spillover. Given this, we developed two novel strategies to promote the occurrence of hydrogen spillover at the electrocatalytic interface. These strategies include (i) the introduction of ligand environments to enrich the local hydrogen coverage on metals and lower the barrier for interfacial hydrogen spillover and (ii) the minimization of work function difference between metals and supports ($\Delta\Phi$) to relieve electron accumulation and lower the kinetic barrier for hydrogen spillover. Also, we summarize the previously reported strategy of shortening the metal−support interface distance to lower the kinetic barrier for interfacial hydrogen spillover. Afterward, some criteria and methodologies are proposed to identify the hydrogen spillover phenomenon at the electrocatalytic interface. Finally, the remaining challenges and future perspectives are also discussed. Based on this Account, we aim to provide new insights into electrocatalysis, particularly the targeted control of hydrogen spillover at the electrocatalytic interface, and then to offer guidelines for the rational design of advanced electrocatalysts.

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This work proposed the ΔΦ as a key factor to determine the hydrogen spillover and HER activity in Pt alloys/CoP catalysts and revealed the underlying mechanism of ΔΦ.

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- Tan, Y.; Zhu, Y.; Cao, X.; Liu, Y.; Li, J.; Chen, Z.; Hu, J. Discovery of Hydrogen-Spillover-Based Binary Electrocatalysts for Hydrogen Evolution: from Theory to Experiment. *ACS Catal.* **2022**, *12*, 11821−11829.[4] This work reported the theoretical screening of the hydrogen-spillover-based HER electrocatalysts through ΔΦ.

1. INTRODUCTION

Hydrogen spillover is a well-known interfacial phenomenon generally occurring on metal-supported catalysts in thermocatalytic hydrogenations.[5−7] It refers to the process by which active hydrogen species generated through the H_2 dissociation on the metal surface migrate to the support surface and participate in the catalytic conversion of the substance adsorbed on supports. In 1964, Boudart et al. discovered this phenomenon in the platinum−tungsten trioxide (Pt/WO_3) catalyst.[8,9] They defined "spillover" as the migration of hydrogen species from the metal to support sites. Since then, this phenomenon has attracted dramatic interest, bringing about significant advances in hydrogen storage and thermocatalysis applications.

Recently, the discovery of the hydrogen spillover phenomenon in electrocatalysis has attracted significant attention. Based on this phenomenon, a new type of bicomponent metal/support catalyst has been proposed for electrocatalytic reactions. The combinations of rhodium nanoparticles and silicon nanowires (Rh/SiNWs) were explored as the electrocatalysts for the hydrogen evolution reaction (HER) with high performance, in which the proton was effectively adsorbed on rhodium and then spilled over to silicon for the facile desorption.[10] The classic Pt/WO_3 systems were also reported to be highly active toward the HER, which delivered a superior Pt utilization HER activity.[11] Hydrogen spillover from Pt to WO_3 was proposed to explain such high HER activity, which promoted hydrogen desorption, re-exposure of the Pt surface, and subsequent proton adsorption for the next cycle. Later, several hydrogen-spillover-based electrocatalysts have been reported and experimentally and theoretically demonstrated, including Ir/SiNWs, Ir/Rh metallene, $PtCu/WO_3$, Ru/WO_{3-x}, $Ru/W_{18}O_{49}$, $Pt/RuCeO_x$, $Pt/La_2Sr_2O_{7+\delta}$, Pt/MoO_3, OH^- modified NiO loaded on Cu, ethylene glycol (EG)-modified Pt loaded CoP, PtIr alloys loaded CoP, RuFe alloys loaded CoP, $MoS_2/NiPS_3$, Ni_3S_2/Cr_2S_3, $PtIr/MoS_2$, Cu nanodots-decorated Ni_3S_2, and $SrHf_{1-x}Ru_xO_{3-\delta}$.[1−4,12−24] In these cases, the hydrogen spillover phenomenon significantly enhances the HER electrocatalytic activity accompanied by reduced metal usage. Therefore, understanding how to enable this hydrogen spillover phenomenon at the electrocatalytic interface and its nature has been quintessential for creating a new paradigm for designing high-performance electrocatalysts.

Applying such a hydrogen spillover phenomenon stimulates the advances in detecting and recognizing methodologies at the electrocatalytic interface. Shao et al. theoretically predicted the Tafel slope and reaction order for the hydrogen-spillover-based HER electrocatalysts.[10] Subsequently, the coincidence between the measured kinetic parameters of the Rh/SiNWs and the predicted ones was proposed to support the existence of the hydrogen spillover phenomenon. Also, in the presence of the hydrogen spillover phenomenon, it was suggested that this process would affect the hydrogen adsorption and desorption behaviors on supports in the metal/support HER electrocatalysts.[2] Consequently, monitoring such hydrogen adsorption and desorption behaviors by *operando* electrochemical characterizations (e.g., cyclic voltammetry and the electrochemical impedance spectrum) could confirm the existence of hydrogen spillover. Nevertheless, the direct evidence for the hydrogen spillover phenomenon is still lacking. With the development of advanced *operando* spectroscopy techniques (e.g., X-ray photoelectron spectroscopy, infrared spectroscopy, and Raman spectroscopy), the facile tracking of the spilled-over H* becomes possible, directly benefiting in visualizing the hydrogen spillover phenomenon.

This Account highlights our recent progress and fundamental understanding of the hydrogen spillover phenomenon at the electrocatalytic interface. We first propose the motivation for introducing hydrogen spillover into electrocatalysis. Then, based on theoretical profiling, the difficulties and key aspects of hydrogen spillover at the electrocatalytic interface are further discussed. This work is followed by emphasizing two successful strategies to enable the hydrogen spillover pathway through introducing a ligand environment and lowering the work function difference between the metal and the support. Next, we discuss our recognition methods on hydrogen spillover at the electrocatalytic interface. Finally, challenges and the outlook for the applications of hydrogen spillover effects in electrocatalysis are underlined. All of the understanding we identify in this Account may help design novel electrocatalysts with high performance.

2. HYDROGEN SPILLOVER IN HER

2.1. Motivations

The generation of hydrogen as a clean energy resource in a viable manner demands efficient and sustainable catalysts.[25] One prospective method of hydrogen generation is electrocatalytic water splitting.[26] The "volcano" theory states that the ideal HER electrocatalyst displays neither too strong nor too weak hydrogen binding, that is, a Gibbs free energy that is close to zero ($\Delta G_H \approx 0$), affording both favorable hydrogen adsorption and desorption processes (Figure 1A).[27] If hydrogen binding is too strong ($\Delta G_H < 0$), it is advantageous for hydrogen adsorption while unfavorable for hydrogen desorption. Conversely, weak hydrogen binding ($\Delta G_H > 0$) is favorable for hydrogen desorption but unfavorable for hydrogen adsorption. Therefore, most state-of-the-art investigations focus on the design of electrocatalysts in the pursuit of $\Delta G_H \approx 0$. The platinum (Pt) and its alloyed electrocatalysts deliver the most promising application prospects among various catalysts.[28] Unfortunately, the high price and scarcity of noble metals limit their practical utilizations. In this context, different low-price transition-metal-based catalysts were constantly designed;[29] however, they displayed less competitiveness in HER performance due to their nonideal ΔG_H. This

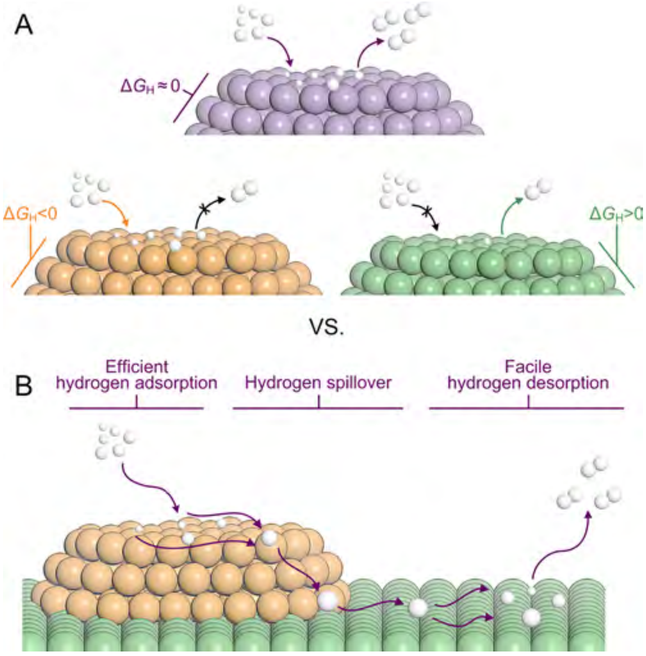

Figure 1. (A) The state-of-the-art design concept for HER electrocatalysts is based on ΔG_H. (B) The design of HER electrocatalysts based on hydrogen spillover effects.

dilemma stimulates us to develop HER electrocatalysts through conceptual innovation.

Fundamentally, the design limitations mentioned in the above concepts based on ΔG_H are due to hydrogen adsorption and desorption on a single active site, leading to a trade-off between them. To avoid this encountered trade-off, we seek, therefore, to separate these two critical steps of hydrogen adsorption and desorption into their respective ideal component, intending for both favorable hydrogen adsorption on one component with $\Delta G_H < 0$ and facile hydrogen desorption on another one with $\Delta G_H > 0$ (Figure 1B). The migration of active hydrogen species (H*) at the interface between two components, the aforementioned hydrogen spillover phenomenon, is a prerequisite to implementing this concept. As such, how to enable hydrogen spillover at the electrocatalytic interface needs to be understood and interpreted.

2.2. Fundamentals

For thermocatalytic hydrogenation, metal oxides generally serve as supports in metal-supported catalysts. These supports have a relatively negative ΔG_H in comparison with that of metals. This way, hydrogen spillover from metals to supports is exothermic and thermodynamically favorable. Therefore, the kinetic energy barrier of hydrogen spillover needs to be considered. Owing to the high capability of metals for dissociating H_2 molecules, especially under high pressure of H_2, a sufficient amount of H* can be generated on metal surfaces to reach high hydrogen chemical potential, which largely reduces the kinetic barrier of hydrogen spillover from metals to supports. For these reasons, hydrogen spillover is a common interfacial phenomenon occurring on metal-supported catalysts during thermocatalysis.

For electrocatalytic HER, hydrogen spillover generally occurs at the interface between metals with $\Delta G_H < 0$ for efficient hydrogen adsorption and supports with $\Delta G_H > 0$ for facile hydrogen desorption. As disclosed in Figure 2, the significant difference in their intrinsic Fermi level (E_f) drives the electron transfer from metal to semiconductor until the Fermi level of the system reaches an equilibrium. As a result, a built-in electric field comes into being at the interface, inducing the band bending of the semiconductor near the interface. This event creates a Schottky barrier toward the subsequently transferred electrons, resulting in significant interfacial electron accumulation. With this electronic configuration, the interfacial sites are endowed with very strong H* adsorption, leading to the H* trapping at the interface. Consequently, hydrogen spillover across the interface is both a thermodynamically and kinetically unfavorable process that must overcome a high energy barrier. In this context, the key is to solve the kinetic issues of hydrogen spillover over these bicomponent metal/support catalysts for the HER.

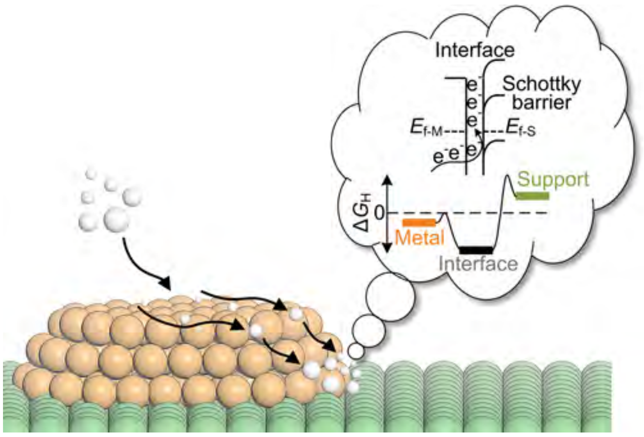

Figure 2. Fundamentals of the hydrogen spillover phenomenon in electrocatalysis. $E_{f\text{-}M}$ and $E_{f\text{-}S}$ represent the Fermi levels of the metal and the support, respectively.

With these in mind, we develop two novel strategies to promote the occurrence of hydrogen spillover at the electrocatalytic interface, which include (i) the introduction of ligand environments to enrich the hydrogen coverage on metals and (ii) the minimization of the work function difference between metals and supports to optimize the electronic configurations at the interface.

2.3. Hydrogen Spillover Enabled by Enriching H* on Metal Surfaces

Previous investigation suggests that the hydrogen coverage of metals determines the kinetic barrier for hydrogen spillover in metal-supported catalysts for thermocatalytic hydrogenations.[6] High hydrogen coverage induces almost instantaneous hydrogen spillover from metals to supports. Given that the ethylene glycol (EG) may serve as the proton concentrator to enrich protons because of the protonation of its −OH groups in acid media,[30,31] we recently proposed a strategy of introducing unique EG ligands to bicomponent Pt/CoP HER electrocatalysts to enhance the local H* concentration on the Pt surface, intending to facilitate the subsequent Pt-to-CoP hydrogen spillover.[1]

Cobalt phosphides (CoP) have been widely explored as HER electrocatalysts; however, most showed unsatisfactory HER activities due to their relatively positive ΔG_H (0.08−0.5 eV) and sluggish hydrogen adsorption kinetics. If H* can be preenriched on Pt ($\Delta G_H = -0.08$ eV) and then spills to CoP, the kinetic issues of CoP are expected to be resolved accordingly. On the other hand, the timely hydrogen desorption on CoP can re-expose Pt sites for the subsequent H* adsorption, significantly increasing their utilization and reducing their dosage. In this way, as a proof-of-concept, a few Pt species with unique EG ligand environments were partnered with CoP (Figure 3A). In this system, it has been demonstrated that EG can significantly improve the local H* concentration on Pt by a factor of 9.0 (Figure 3B), illustrating the proton concentration effect for the highly enhanced hydrogen chemical potential on Pt and benefiting the Pt-to-CoP hydrogen spillover. Besides, EG showed significant effects on the d-band centers of the catalytic sites, where the impacts are clearly illustrated in the data evolving from Pt to CoP (Figure 3C); one of the most important is the upshift of the d-band center of the interfacial sites (sites b and c). With these effects, the strong H* adsorption at the Pt/CoP interfacial sites (sites b and c) becomes moderate (Figure 3D). The thermoneutral free energy of H* at interface sites of EG-Pt/CoP favors both hydrogen adsorption and desorption. More importantly, with such active sites, a series of catalytic sites from Pt to CoP with steadily weakened H* adsorption come into being. In this case, the H* enriched on the metal surface by EG can be transferred to CoP with a low thermodynamic barrier (0.25 eV) and can be facilely released from CoP, thus affording high HER activities of EG-Pt/CoP with a low Pt loading of 1.5 wt % surpassing the Pt/C benchmarks (20 wt %) in acidic media (Figure 3E).

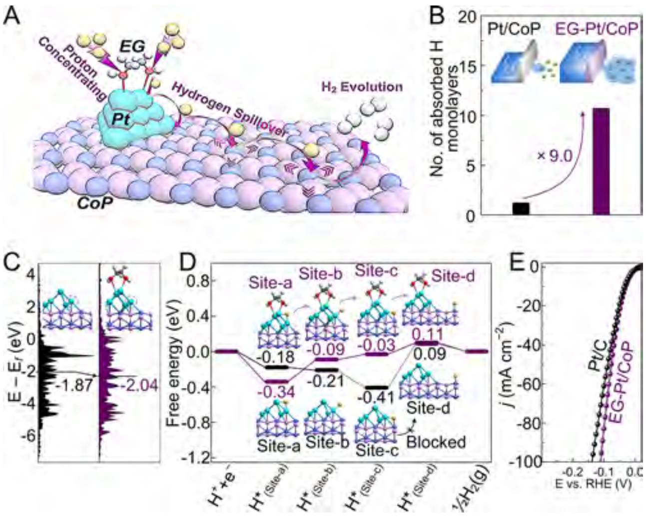

Figure 3. (A) Schematic illustration of triggering the hydrogen spillover phenomenon through EG ligand environments over Pt/CoP model catalysts. (B) The measured enriched H* on the Pt/CoP and EG-Pt/CoP during HER through the *operando* EIS investigation. (C) Calculated d-band centers at a series of catalytic sites from Pt to CoP over Pt/CoP and EG-Pt/CoP. (D) Calculated free energy diagram for the HER pathway based on hydrogen spillover for the Pt/CoP and EG-Pt/CoP interface. (E) The observed HER activities were for Pt/CoP and various EG-Pt/CoP catalysts. Adapted with permission from ref 1. Copyright 2019 Royal Society of Chemistry.

2.4. Hydrogen Spillover Enabled by Minimizing the Work Function Difference between Metals and Supports

Fundamentally, the high kinetic barriers of hydrogen spillover over bicomponent metal/support HER catalysts are due to the unaligned Fermi levels between metals and supports, resulting in charge accumulation and hydrogen trapping at the interface. Given that $E_f = E_{vac} - \Phi$, minimizing the work function difference between the metal and support ($\Delta\Phi = |\Phi_{Metal} - \Phi_{Support}|$) for Fermi level alignment ($|E_{f\text{-}M} - E_{f\text{-}S} \approx 0|$) can alleviate charge accumulation and avoid hydrogen trapping at the interface (Figure 4).[2] In this way, the kinetic barrier for the interfacial hydrogen spillover can be minimized spontaneously, leading to successful hydrogen spillover and efficient synergetic HER between metals and supports.

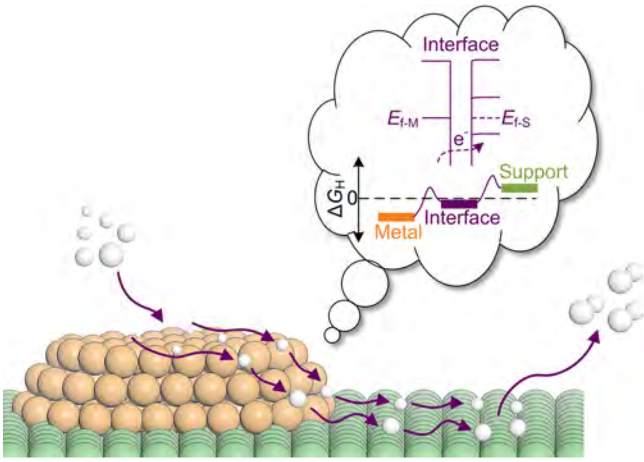

Figure 4. Fundamentals of the hydrogen spillover phenomenon in electrocatalysis. $E_{f\text{-}M}$ and $E_{f\text{-}S}$ represent the Fermi levels of the metal and the support, respectively.

Taking Pt/CoP as a paradigm, alloying Pt with Ir can observably decrease the ΔΦ value from 0.19 to 0.02 eV (Figure 5A). As expected, a significant electron dilution was observed at the interface of PtIr/CoP compared to that at the interface of Pt/CoP (Figures 5B and 5C). Accordingly, H* adsorption at the PtIr/CoP interface sites becomes moderate compared to that at the Pt/CoP interface sites (Figure 5D).

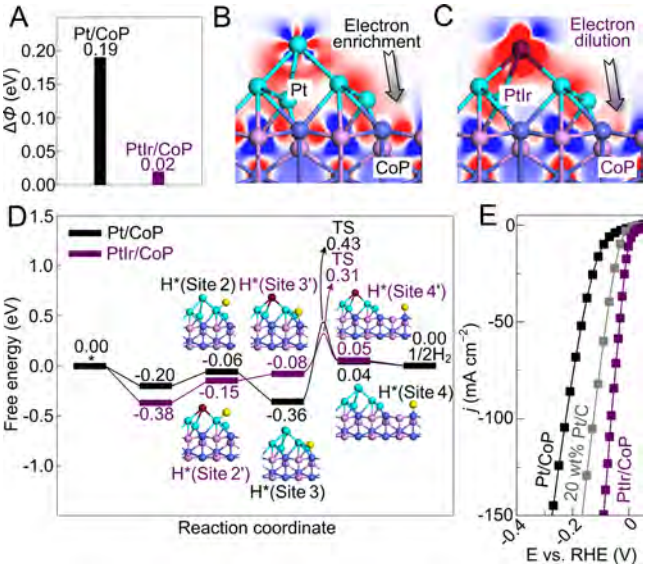

Figure 5. (A) The measured ΔΦ values were for Pt/CoP and PtIr/CoP. (B and C) Electron density difference map of the Pt/CoP and PtIr/CoP interfaces, where a loss of electrons is indicated in blue and electron enrichment is indicated in red. (D) Calculated free energy diagram for HER on Pt/CoP and PtIr/CoP. (E) The observed HER activities for Pt/CoP and PtIr/CoP. Adapted with permission from ref 2. Copyright 2021 Springer Nature.

Consequently, the kinetic barrier for the H* migration from the PtIr/CoP interface site-3′ to site-4′ (0.39 eV) was declined compared with that for the H* migration from the Pt/CoP interface site-3 to site-4 (0.79 eV). Different from the failed hydrogen spillover on Pt/CoP, the successful hydrogen spillover integrates efficient hydrogen adsorption on PtIr alloys and facile hydrogen desorption on CoP, eventually resulting in a significantly improved HER performance (Figures 5E).

The above design concept is further examined over the Ru_xFe_y alloy-loaded CoP catalysts (Ru_xFe_y/CoP).[3] Compared with Ru/CoP with a large $\Delta\Phi$ (0.43 eV), RuFe/CoP with the minimized $\Delta\Phi$ value of 0.05 eV (Figure 6A) showed an obvious electron dilution (Figures 6B−6C) and weakened H* adsorption at the interface, thereby declining the kinetic barrier (0.25 eV) for the interfacial hydrogen spillover from RuFe to CoP in comparison with that at the interface of Pt and CoP (0.54 eV, Figure 6D). Therefore, the energetically favorable interfacial hydrogen spillover comes into being over RuFe/CoP catalysts, integrating efficient hydrogen adsorption on RuFe and facile desorption on CoP and thus leading to their high electrocatalytic performance for HER (Figure 6E). Based on the above two examples, $\Delta\Phi$ is proposed as a descriptor for identifying the hydrogen spillover phenomenon in the electrocatalytic HER.

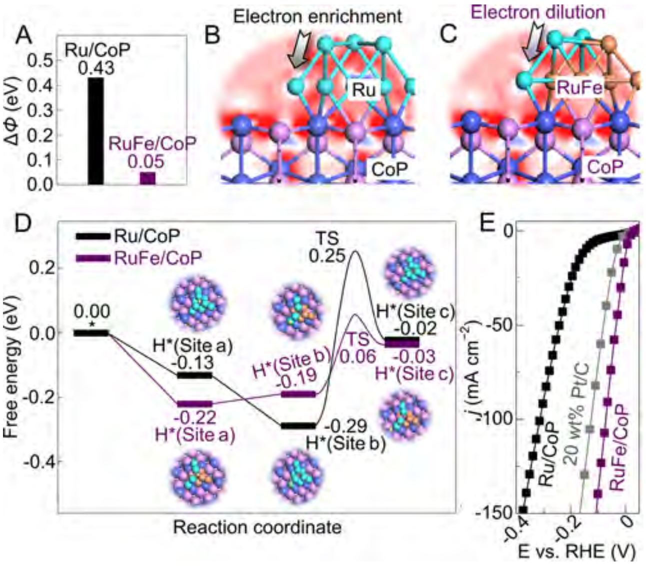

Figure 6. (A) The measured $\Delta\Phi$ values were for Ru/CoP and RuFe/CoP. (B and C) Electron density difference map of the Ru/CoP and RuFe/CoP interfaces, where a loss of electrons is indicated in blue and electron enrichment is indicated in red. (D) Calculated free energy diagram for HER on Ru/CoP and RuFe/CoP. (E) The observed HER activities for Ru/CoP, RuFe/CoP, and 20 wt % Pt/C. Adapted with permission from ref 3. Copyright 2022 American Chemical Society.

To further verify the roles of $\Delta\Phi$, we rapidly screened the bicomponent metal-supported HER electrocatalysts of 5000 candidates (Figure 7A).[4] In the procedures, ΔG_H and $\Delta\Phi$ served as the two descriptors. The metal and support were screened with ΔG_H to ensure favorable hydrogen adsorption on metals (-0.30 eV $\leq \Delta G_H \leq 0$ eV) as well as facile hydrogen desorption ($|\Delta G_H| \leq 0.15$ eV) on supports. A value of $\Delta\Phi \leq 0.05$ eV was used to ensure the energetic metal-to-support hydrogen spillover, yielding a total of 11 candidates (WRe/MoS_2, Co/MoS_2, FeCo/MoS_2, OsIr/MoS_2, RuIr/MoS_2, NiCo/MoS_2, PtAu/MoS_2, Ir/MoS_2, CoNi/MoS_2, RuRe/MoS_2, and PtIr/MoS_2). Taking PtIr/MoS_2 with a metal loading of 2.0 wt % as a paradigm, it theoretically showed the visibly lower kinetic barrier for interfacial hydrogen spillover (Figure 7B). It also experimentally displayed the significantly higher HER activity close to the 20 wt % Pt/C benchmark (Figure 7C), indicating the success of the catalyst screening. At this point, we describe a unique concept for designing hydrogen-spillover-based HER electrocatalysts by simply optimizing $\Delta\Phi$.

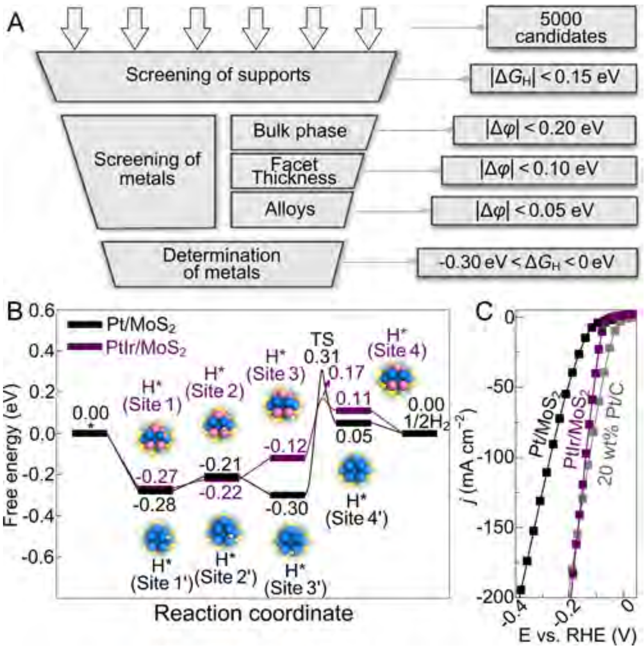

Figure 7. (A) Tiered screening pipeline for accelerated discovery of hydrogen-spillover-based catalysts from 5000 candidates. (B) Calculated free energy diagram for the HER on Pt/MoS_2 and PtIr/MoS_2. (C) The observed HER activities for Pt/MoS_2, PtIr/MoS_2, and 20 wt % Pt/C. Adapted with permission from ref 4. Copyright 2022 American Chemical Society.

2.5. Hydrogen Spillover Enabled by Shortening the Interface Distance

The kinetic barrier for hydrogen spillover has also been reported to be related to the transport distance. Short hydrogen spillover distances bring a much lower spillover barrier, thus enabling efficient hydrogen spillover. Inspired by the above recognitions, efforts have focused on reducing the size of loaded metals to shorten the interfacial hydrogen spillover distance. Taking the Pt/metal oxide catalysts as an example,[18,32] when replacing Pt nanoparticles with Pt single atom, a successful hydrogen spillover from Pt to metal oxides was triggered. Such a short distance of hydrogen spillover promoted hydrogen desorption, re-exposure of the Pt surface, and subsequent H* adsorption for the next cycle.

3. BASIS OF JUDGEMENTS FOR HYDROGEN SPILLOVER

The increasing reports of the hydrogen spillover phenomenon in electrocatalytic HER have called for its recognition. In principle, for thermocatalytic hydrogenation involving the hydrogen spillover phenomenon, the dissociative adsorption of H_2 is not typically observed on the support to yield H* intermediates during the reaction.[6] Thus, monitoring the H* intermediates on supports by *operando* spectroscopy can provide convincing evidence of the occurrence of hydrogen spillover from metals to supports. Inspired by these facts, we proposed various methods to support the existence of hydrogen spillover in electrocatalytic HER.

3.1. Comparison of the Theoretical and Experimental Kinetic Parameters

For the hydrogen-spillover-based HER electrocatalysts, a Volmer−Spillover−Heyrovsky reaction pathway takes place, which is described as (i) Metal/Support + H^+ + e^- ↔ H*−Metal/Support; (ii) H*−Metal/Support ↔ Metal/Support−H*; and (iii) Metal/Support−H* + H^+ + e^- ↔ H_2 + Metal/Support.[10,27] The reaction velocity of hydrogen evolution could be written as $r = k_3\theta_{\mathrm{CoP-H^*}}C_{\mathrm{H^+}}$, where r is the reaction rate, k is the rate constant, θ is the hydrogen coverage of active sites, and $C_{\mathrm{H^+}}$ is the concentration of hydrogen ions.

In the steady state,

$$\begin{aligned}\frac{d\theta_{\mathrm{Support-H^*}}}{dt} &= k_2\theta_{\mathrm{Metal-H^*}}(1-\theta_{\mathrm{Support-H^*}}) \\ &\quad - k_{-2}\theta_{\mathrm{Support-H^*}}(1-\theta_{\mathrm{Metal-H^*}}) \\ &\quad - k_3\theta_{\mathrm{Support-H^*}}C_{\mathrm{H^+}}\end{aligned}$$

$$\begin{aligned}\frac{d\theta_{\mathrm{Metal-H^*}}}{dt} &= k_1(1-\theta_{\mathrm{Metal-H^*}})C_{\mathrm{H^+}} - k_{-1}\theta_{\mathrm{Metal-H^*}} \\ &\quad - k_{-2}\theta_{\mathrm{Metal-H^*}}(1-\theta_{\mathrm{Support-H^*}}) \\ &\quad + k_{-2}\theta_{\mathrm{Support-H^*}}(1-\theta_{\mathrm{Metal-H^*}})\end{aligned}$$

At the low overpotential,

$$\begin{aligned}\theta_{\mathrm{Support-H^*}} &\approx \frac{k_2\theta_{\mathrm{Metal-H^*}}}{k_2\theta_{\mathrm{Metal-H^*}} + k_{-2} - k_{-2}\theta_{\mathrm{Metal-H^*}} + k_3C_{\mathrm{H^+}}} \\ &\approx \frac{k_2}{k_{-2}}\theta_{\mathrm{Metal-H^*}}e^{-F\Delta\phi/RT}\end{aligned}$$

$$\begin{aligned}\theta_{\mathrm{Metal-H^*}} &\approx \\ &\frac{k_1C_{\mathrm{H^+}} + k_{-2}\theta_{\mathrm{Support-H^*}}}{k_1C_{\mathrm{H^+}} + k_{-1} + k_2 + k_{-2}\theta_{\mathrm{Support-H^*}} - k_2\theta_{\mathrm{Support-H^*}}} \\ &\approx \frac{k_1}{k_{-1}}C_{\mathrm{H^+}}e^{-F\Delta\phi/RT}\end{aligned}$$

Thus,

$$r \approx k_3\theta_{\mathrm{Support-H^*}}C_{\mathrm{H^+}} = \frac{k_1k_2k_3}{k_{-1}k_{-2}}C_{\mathrm{H^+}}^2e^{-(2+\alpha)F\Delta\phi/RT}$$

And,

$$-j = Fr = \frac{k_1k_2k_3}{k_{-1}k_{-2}}FC_{\mathrm{H^+}}^2e^{-(2+\alpha)F\Delta\varphi/RT}$$

$$\lg(-j) = \mathrm{Constant} + 2\lg C_{\mathrm{H^+}} - \frac{(2+\alpha)F}{2.303RT}\Delta\varphi$$

Therefore, the theoretical kinetic parameters of the Tafel slope and reaction order for the hydrogen-spillover-based metal/support catalysts are 0.023 V dec^{-1} and 2, respectively (assuming $\alpha = 0.5$, F is the Faraday constant, R is the Rydberg gas constant, and T is the absolute temperature). Various hydrogen-spillover-based electrocatalysts in previous works, such as Pt_2Ir_1/CoP, Ru_1Fe_1/CoP, Rh/Si, Rh/MoS_2, and Ir/Si, are measured with similar Tafel slopes and reaction orders in comparison with the theoretical values,[2,3,10,12,33] suggesting that the hydrogen-spillover-based process is the most likely HER pathway.

3.2. Hydrogen Adsorption/Desorption Behaviors

Monitoring H* adsorption and desorption on catalyst surfaces can provide crucial clues in recognizing hydrogen spillover. Considering the adsorption/desorption of H* on supports and their migration across the interface in electrocatalytic HER, it is expected that the hydrogen adsorption and desorption behaviors on supports should be substantially different if hydrogen spillover indeed exists. Taking the Ru_xFe_y/CoP catalysts as an example, the hydrogen adsorption capacitance (C_φ) and resistance (R_2) derived from the electrochemical impedance spectra (EIS) results can be understood by analyzing the hydrogen adsorption behavior.[34−36] When integrating the C_φ vs overpotential (η), the hydrogen adsorption charge (Q_H) reflects the amount of the adsorbed H* (Figure 8A). Thus, the similar Q_H values on CoP (Q_H[CoP] = 1547 μC) and on Ru/CoP (Q_H[Ru/CoP] − Q_H[Ru/rGO] = 1530 μC) embody a similar quantity of adsorbed hydrogen on CoP and Ru/CoP, justifying the negligible Ru-to-CoP hydrogen spillover. It is noted that the

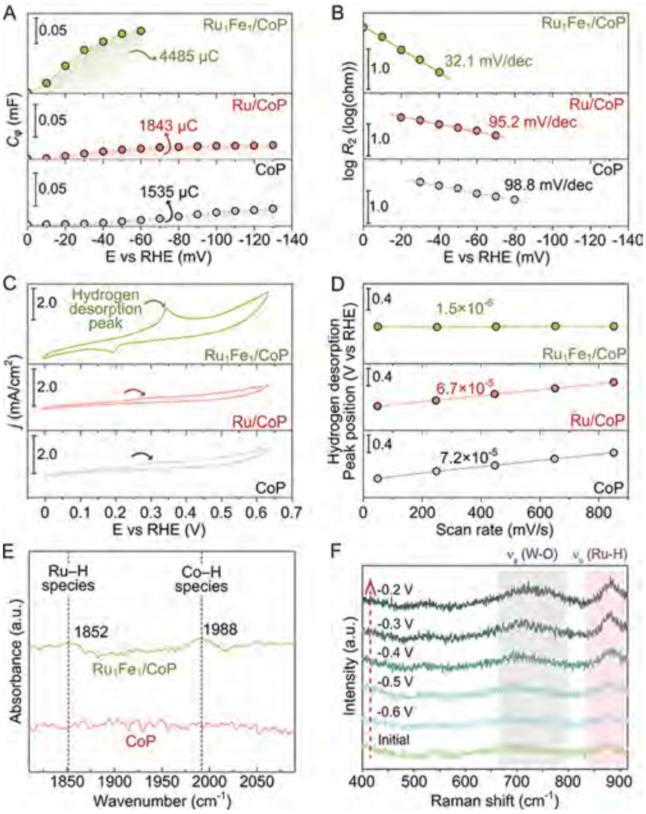

Figure 8. (A) Plots of C_φ vs η of the bare CoP, Ru/CoP, Ru_1Fe_1/CoP, Ru/rGO, and Ru_1Fe_1/rGO catalysts during HER. (B) EIS-derived Tafel plots of the bare CoP, Ru/CoP, and Ru_1Fe_1/CoP catalysts. (C) CV of the bare CoP, Ru/CoP, and Ru_1Fe_1/CoP catalysts. (D) Plots of hydrogen desorption peak position vs scan rates of the bare CoP, Ru/CoP, and Ru_1Fe_1/CoP. (E) *Operando* ATR-IR spectra for the bare CoP and Ru_1Fe_1/CoP catalysts at a HER potential of −0.04 V vs RHE. Adapted with permission from ref 3. Copyright 2022 American Chemical Society. (F) *Operando* Raman spectra for the Ru/WO_{3-x} catalysts at various HER potentials. Adapted with permission from ref 15. Copyright 2022 Springer Nature.

value of $Q_H[Ru_1Fe_1/CoP] - Q_H[Ru_1Fe_1/rGO]$ (4150 μC) is significantly higher than that of $Q_H[Ru/CoP] - Q_H[Ru/rGO]$ (1530 μC), suggesting a considerably enhanced hydrogen adsorption on CoP of Ru_1Fe_1/CoP and implying the successful Ru_1Fe_1-to-CoP hydrogen spillover.

Moreover, when plotting the log R_2 vs η, the corresponding EIS-calculated Tafel slope reflects the hydrogen adsorption kinetics (Figure 8B). In this way, the similar EIS-calculated Tafel slopes between Ru/CoP (95.2 mV dec^{-1}) and CoP (98.8 mV dec^{-1}) indicate the unaltered kinetics of hydrogen adsorption on Ru/CoP and CoP. In contrast, the significantly decreased EIS-derived Tafel slope (32.1 mV dec^{-1}) of Ru_1Fe_1/CoP illustrates the kinetic acceleration of hydrogen adsorption, revealing the successful Ru_1Fe_1-to-CoP hydrogen spillover and thus significantly enhancing the quantity of adsorbed H* on CoP.

The *operando* cyclic voltammetry (CV) is further employed to determine the hydrogen desorption behavior (Figure 8C). For the bare CoP and Ru/CoP, the hydrogen desorption peak intensities are weak, revealing no increased quantity of the desorbed hydrogen on Ru/CoP and in that way implying the insignificant Ru-to-CoP hydrogen spillover. Meanwhile, the sharply high hydrogen desorption peak for Ru_1Fe_1/CoP doubtlessly indicates the highly facilitated Ru_1Fe_1-to-CoP hydrogen spillover, providing a massive amount of H* on CoP for desorption.

As it requires more time for the current to vary with the applied potentials in catalysts, the peak shifts of the CV curves (i.e., hydrogen desorption) of different catalysts as the function of scan rates are proposed to quantify their hydrogen desorption kinetics.[37] As shown in Figure 8D, the comparable fitted slopes of Ru/CoP (6.7×10^{-5}) and CoP alone (7.2×10^{-5}) reveal the unchanged hydrogen desorption kinetics. On the other hand, a sharply declined slope (1.5×10^{-6}) for Ru_1Fe_1/CoP is ascribed to a significant acceleration in hydrogen desorption kinetics owing to the successful Ru_1Fe_1-to-CoP hydrogen spillover.[32] Overall, the significantly improved hydrogen adsorption and desorption behaviors on CoP in Ru_1Fe_1/CoP provide strong evidence for the occurrence of hydrogen spillover phenomena in electrocatalytic HER. These identification criteria can also apply to other hydrogen-spillover-based electrocatalysts.

The hydrogen adsorption behavior was monitored through *operando* spectroscopy, as well. Generally, for the hydrogen-spillover-based HER electrocatalysts, the support itself ($\Delta G_H > 0$) displayed negligible hydrogen adsorption, while metal ($\Delta G_H < 0$) showed significant hydrogen adsorption under low overpotentials. If an existing hydrogen spillover phenomenon exists, the spillover H* signal on supports could be detected by *operando* spectroscopy at low overpotentials. The *operando* attenuated total reflection infrared spectra (ATR-IR) were collected for the bare CoP and Ru_1Fe_1/CoP catalysts at −0.04 V vs RHE (Figure 8E). The former curve showed almost no characteristic peak at ~2000 cm^{-1} (Co−H species), while the latter one showed obvious peaks at 1858 cm^{-1} (Ru−H species) and ~1992 cm^{-1} (Co−H species). In this way, these findings provided direct evidence to confirm the existence of the spillover H* from Ru_1Fe_1 to CoP. Besides, the *operando* Raman spectra were measured on the Ru/WO_{3-x} catalysts. Clearly, at a low overpotential (−0.2 V vs Ag/AgCl), these catalysts still displayed a very high Raman peak intensity of Ru−H at 878 cm^{-1} (Figure 8F). These observations suggested a significant increase in hydrogen coverage on Ru, which supports the existence of hydrogen spillover from WO_{3-x} to Ru.

3.3. Density Functional Theory (DFT) Simulations

As a powerful tool, DFT calculations can reveal the reaction intermediates, predict the reaction pathway, and provide insights into the catalytic mechanism. This calculation always identifies the hydrogen spillover phenomenon in the metal-supported electrocatalysts. In general, the model of the catalyst is constructed with a metal cluster on a support slab. The ΔG_H at the catalytic sites from metals to supports, especially at the interface sites, is the focus of attention. Suppose that the interfacial sites display a significantly negative ΔG_H. In that case, it brings a very high thermodynamic and kinetic energy barrier for hydrogen migration across the interface, suggesting a failed hydrogen spillover. Comparatively, when the ΔG_H of catalytic sites from metals to supports is uphill stepwise, the kinetic energy barrier of hydrogen migration from metals to supports is significantly lowered.[1−4] These results are generally considered criterion for the occurrence of the hydrogen spillover phenomenon.

4. CONCLUSIONS AND OUTLOOK

In this Account, we demonstrate the hydrogen spillover phenomenon at the electrocatalytic interface for HER. We begin with the limitations of the state-of-the-art design concept for HER electrocatalysts to point out the motivations for introducing hydrogen spillover effects into electrocatalysis. Theoretically profiling further discusses the difficulties and keys to the hydrogen spillover phenomenon at the electrocatalytic interface. As a proof-of-concept, we next provide the successful implementation of hydrogen spillover effects at the electrocatalytic interface by introducing ligand environments and lowering the $\Delta\Phi$. We also discuss our recognition methods for the hydrogen spillover in electrocatalytic HER. Despite the significant progress, challenges remain to be addressed, and opportunities await discovery. Here, we lay out three research directions that are worth pursuing.

First, the current technologies still limit the thorough characterizations of the hydrogen spillover phenomenon in electrocatalysis. Appropriate methods or techniques that can provide direct evidence of the occurrence of hydrogen spillover are the prerequisites to evaluating the success of hydrogen-spillover-based electrocatalysts and understanding their catalytic mechanism. Although several examples of hydrogen-spillover-based electrocatalysts have been proposed, the existence of hydrogen spillover is mainly assessed based on (i) the comparison of the theoretical and experimental kinetic parameters, (ii) electrochemical investigations on the hydrogen adsorption/desorption behaviors, (iii) *operando* spectroscopy, and (iv) DFT simulations. However, these characterizations can provide only indirect evidence, and there is still no practical approach to visualize the hydrogen spillover pathway in electrocatalysis so far. Thus, it is highly desirable that advanced techniques can be developed to probe the hydrogen spillover, directly envisioning the hydrogen spillover phenomenon. To achieve this goal, the following aspects should be considered in the future. (i) Developing the transient imaging technology: For the existing efficient hydrogen spillover, large amounts of spilled hydrogen may accumulate on supports to form nanobubbles. Recently, the total internal reflection fluorescence microscopy has been reported to image transient formation and growth of single hydrogen nanobubbles at the electrode/solution interface during electrocatalytic water splitting.[38] The ability to image a single nanobubble on an electrode enables the possibility of observing the hydrogen spillover process. Nevertheless, this technique still requires a very high spatial resolution to identify the metals and supports. (ii) Developing the nanosized electrochemical system: The limitations of our *operando* electrochemical investigations are derived from the much larger size of the electrode device compared to that of the catalysts. Developing the nanosized electrode device may allow for investigating the local electrochemical response on the catalyst surface. This way, a transient electrochemical response at the interface will be detected during hydrogen spillover. (iii) Developing the special techniques to avoid the interference of solvents and electrolytes: The common issues of utilizing the state-of-the-art *operando* spectroscopy (EXFAS, FT-IR, and Raman) to trace the spilled hydrogen in HER electrocatalysts are the interference of adsorbed hydrogen of supports and various ions/molecules in ambiance (H_2O, H_3O^+, SO_4^{2-}, H^+, OH^-, and K^+) when using the common catalytic system (H_2SO_4 or KOH aqueous electrolyte). Thus, developing a special system may solve the above common issues without influencing the HER process of the catalysts, which may significantly increase the signals of *operando* spectroscopy to trace the spilled hydrogen.

Second, the fundamental understanding of hydrogen spillover in electrocatalysis is still lacking. Although the $\Delta\Phi$ is demonstrated as a critical factor for the hydrogen spillover in electrocatalytic HER, its action mechanism is based on the Schottky contact between metals and semiconductors that leads to charge accumulation at the interface. Considering that Schottky contact cannot occur between a metal and another metal, questions such as how the interfacial hydrogen spillover occurs over such bimetal systems is still unclear. We herein proposed a hypothesis on this question (Figure 9). Generally, there will be no excess charge accumulation at the interface for such bimetal systems, thus endowing catalytically interfacial sites with moderate hydrogen adsorption. At this point, to enable hydrogen spillover, the metal ($\Delta G_H < 0$) and support ($\Delta G_H > 0$) need to have ΔG_H values as close as possible, which can minimize the hydrogen spillover barrier. According to the d-band theory, the chemisorption strength of H* on metals was determined by their d-band centers (ε_d). The ε_d is closer to the Fermi level; fewer antibonding electronic states are occupied, leading to the strengthened H* adsorption. This way, the above target can be achieved by lowering the d-band center difference between the metals and supports ($\Delta\varepsilon_d$). If this hypothesis is verified on one model catalyst, the hydrogen-spillover-based HER electrocatalysts can be rationally designed based on the $\Delta\Phi$ and $\Delta\varepsilon_d$.

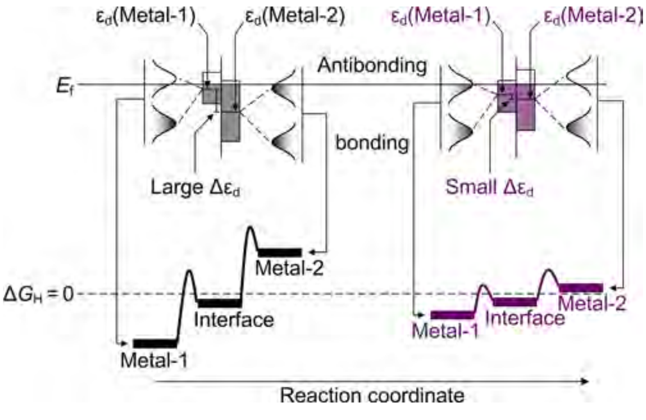

Figure 9. Schematic illustration of the interfacial hydrogen spillover phenomenon in bimetal systems.

Third, the reaction scope that benefited from the hydrogen spillover phenomenon is often limited. Currently, this effect is employed to bridge the metals with strong hydrogen adsorption ($\Delta G_H < 0$) and the supports with easy hydrogen desorption ($\Delta G_H > 0$), resulting in their limited applications in electrocatalytic HER. In heterogeneous hydrogenation reactions, the hydrogen spillover effects can integrate the metals with strong H_2 adsorption/activation and support with strong substrate adsorption/activation, leading to significantly enhanced hydrogenation efficiency under mild conditions. Inspired by these efforts, the hydrogen spillover effects are expected to apply to the recently emerging electrocatalytic hydrogenation of various unsaturated compounds (e.g., nitrates, alkynes, carbon dioxide, and nitriles). Such a design would integrate a component with strong water dissociation capability under low overpotentials to afford sufficient active hydrogen species and the second active sites with high ability for activation of those unsaturated substrates, in which hydrogenation is realized through hydrogen spillover across the interface of bicomponent catalysts.[39] Furthermore, hydrogen spillover effects have also been applied to the electrocatalytic alcohol oxidation reactions.[40] Nickel-based catalysts can catalyze these reactions due to the in-situ-generated NiOOH species on their surface during reactions. By promoting the hydrogen transfer from NiOOH to a proton acceptor, a highly reactive NiOO species emerged, which effectively activated the α-C−H bond in alcohols and greatly enhanced the catalytic activity.

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