Activation of H$_2$O tailored by interfacial electronic states at nanoscale interface for enhanced electrocatalytic hydrogen evolution

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Abstract: Despite the fundamental and practical significance of the hydrogen evolution reaction (HER), the reaction kinetics at the molecular level is not clear, particularly in basic media. Here, with ZIF-67 derived Co-based carbon frameworks (Co/NC) as a model catalyst, we systematically investigated the effects of different reaction parameters on the HER kinetics, and surprise found that HER activity was not directly dependent on the type of nitrogen in the carbon framework, but on the relative content of surface hydroxyl and water (OH/H$_2$O) adsorbed on Co active sites embedded in carbon frameworks. When the ratio of the OH/H$_2$O was close to 1:1, Co/NC nanocatalyst showed the best reaction performance under the condition of high-pH electrolytes, e.g., with an overpotential of only 232 mV at a current density of 10 mA cm$^{-2}$ in 1 M KOH electrolyte. We unambiguously identified that, the structural water molecules (SWs) in the form of hydrous hydroxyl complex adsorbed on metal centers {OH–H$_2$O@M$^+$} were catalytic active sites for enhanced HER, where M$^+$ could be transition and/or alkaline metal cations. Different from the traditional hydrogen bonding of water, the hydroxyl (hydroxide) groups and water molecules in SWs were mainly transiently bonded together through the spatial interaction between the $p$ orbitals of O atoms, showing characteristics of delocalized $\pi$ bond with dynamic feature. These new formed surface bonds or transient states could be a new weak interaction, which can act as an alternative channel for concerted electron and proton transfer at electrode surface. The capturing of new surface states not only answers pH-, cation- and transition metal- dependent hydrogen evolution kinetics, but also provides completely new insights into the understanding of other electrocatalytic reduction involved by other small moleculesm, including CO$_2$, CO and N$_2$ etc.

Introduction

The energy crisis and environmental issues have stimulated extensive research on alternative energy storage and conversion systems$^{1,2}$. The hydrogen evolution (HER) holds the key to the future hydrogen economy by controlling efficient generation of hydrogen from water and the reverse direction to harvest clean energy$^{3,4}$. Despite their significance in both practical and fundamental aspects, the HER kinetics has been elusive and clouded by several long-standing puzzles, such as anomalous hydrogen evolution behavior in high-pH environment$^{5-9}$ (generally, most of the emerging HER electrocatalysts achieve high activities in acidic electrolytes)$^{10-13}$, extreme sensitivity of surface electronic structure on catalyst (for example, the physical origin of transition metal/oxide-doping and hydroxyl-adsorption induced catalytic enhancement)$^{14}$, promoter effects of alkali metal cations on the electrochemical reduction$^{15,17}$, and even unexpected hydrogen evolution reaction activity on metal-free electrocatalysts$^{8,11,18-21}$.
Scheme 1. (a) Surface chemisorption bond or noncovalent interaction dominated reaction kinetics of HER; (b) Metal centered $d$ band theory by tuning the $d$-band center relative to the Fermi level of metals to optimize the electrocatalytic activity as a classical model. (c) Structural water molecules (SWs) dominated $p$ band intermediate (or transient) state model to explain the reaction kinetics of HER by providing the alternative channels for proton-and-electron transfer. Herein, different from the traditional hydrogen bonding of water, the hydroxyl (hydroxide) groups and water molecules in structural water are mainly transiently bonded through the spatial interaction between the $p$ orbitals of O atoms, showing characteristics of delocalized $\pi$ bond with dynamic feature. (d) When the metal is present, the ultra-fast switching between surface chemical bonds can be written in a simple formula of $2H_{OM} = H_{OO} + H_{MM} = 1$, where $H$ means the orbital hybridizations between surface atoms and the subscripts of OM, OO and MM represent the chemical bond interactions between surface metal and O atom, O and O atom in SWS, and metal and metal atom, respectively. (e) Energy level diagram of atomic orbital hybridization at the interface of electrode. These new formed transient states provide the ideal alternative channels for surface electron-and-proton transfer.

Recently, significant efforts have been focused on activity descriptors or designed principles
of catalysts by tuning the covalent and/or noncovalent interaction at electrical double layer (EDL) with surface electronic structure factor as a key parameter to elucidate the molecular-level origin of HER micro-kinetics\textsuperscript{24} (Scheme 1a). In the models of covalent interactions, $d$-band center theory was widely applied by tuning the $d$-band center relative to the Fermi level of metals, which could control the binding energy of surface adsorbates such as adsorbed hydrogen (H*) or hydroxyl (OH*) and consequently optimize the electrocatalytic activity (Scheme 1b). Thus, several important reaction descriptors were proposed for the rational catalyst design and development, including hydrogen binding energy\textsuperscript{25, 26}, OH–M bond strength (M denotes transition metal cation)\textsuperscript{27–29}, the $e_s$ occupancy\textsuperscript{30} etc. Even though case-to-case studies showed the paramount importance of tuning the reaction kinetics by electronic factors, so far, no descriptor could perfectly explain all the observed activity trends. Very recently, owing to the fast development of in-situ operando spectroscopic and computational techniques to investigate the interfacial water, more and more evidence showed that the structure of interfacial water dominated by weak non-covalent interactions played a key role in determining the reaction rate\textsuperscript{9, 15, 24, 28, 29, 31–34}. And some very important intermediate species at EDL region were captured, such as hydronium (H$_3$O$^+$) intermediate even in high-pH electrolytes\textsuperscript{10}, hydrogen-bonded and hydrated Na$^+$ ion water, OH$_{ad}$–M$^+$ (H$_2$O)$_x$ clusters\textsuperscript{28}, hydroxyl-water-cation adducts\textsuperscript{15, 35}. But it is still unclear how the interaction mode of the complexes formed by interfacial water and surface hydroxyl or both with alkali metal ions or transition metal ions and how the formed electronic states of these surface structures affect the proton and electron transfer process at nanoscale interface (Scheme 1c-e).

Recently, with the help of steady and transient absorption and emission spectrum, we unambiguously confirmed that SWs adsorbed or confined at nanoscale interface in the form of OH·H$_2$O could emit bright colors as non-conjugation luminophors\textsuperscript{36–39}, which answers a century of debate on that water is colored or colorless liquid\textsuperscript{40, 41}. Differing from the traditional hydrogen bonding of water, the hydroxyl (hydroxide) groups and water molecules in structural water are mainly combined through the spatial interaction between the $p$ orbitals of O atoms, which is a new kind of weak interaction with the characteristics of conjugated $\pi$ bond and transient feature (Scheme 1c). Very interestingly, when SWs are adsorbed onto the metal centers, due to the space interaction between the adjacent O atoms, a pair of chemical-sorption bonds of O-M (M could be different metals) perpendicular to the metal surface can be very quickly switched to two interface states or bonds parallel to the metal surface\textsuperscript{37}, concomitantly accompanying the surface proton transfer (scheme 1c-e). The interaction between two O atoms on the interface is called $p$ band intermediate or transient state (PBIS) by us\textsuperscript{42}, which has typical $\pi$ bond characteristics, and the interaction between two metal atoms is the well-known metallophilic interactions\textsuperscript{43–45}, for example aurophilic interaction of Au-Au bonds\textsuperscript{46}. It is importantly noted that the switching of these surface bonds or states is an ultra-fast process in a picosecond or even femtosecond time scale, which is evidenced by ultra-fast transient absorption spectrum\textsuperscript{37, 39}. According to quantum mechanics, its dynamic process can be expressed in a simple formula of $2H_{OM} = H_{oo} + H_{MM} = 1$, where H means the orbital hybridization of surface atoms (Scheme 1d). This new formed surface transient state could be acted as an alternative channel for concerted electron and proton transfer at nanoscale interface. In fact, using our newly developed PBIS model, we have successfully explained the catalytic conversion mechanism of selective hydrogenation of organic compounds containing unsaturated functional groups such as nitro and carbonyl groups involving multiple electron–proton transfer at the molecular level\textsuperscript{47–49}. Since the electron and proton transfer process of
traditional metal nanocatalysts for selective reduction of organic compounds containing nitro-groups is very similar to that of HER of electrocatalyst of metal nanoparticles, the working mechanism of micro-kinetics of both reactions should follow the same working mechanism. The only difference is that, in the HER, the cathode is the supplier of electrons, while in the hydride catalytic reduction of nitro groups, the adsorbed borohydride at metal surface is an electron donor. This exciting idea promotes us to study the reaction kinetics of HER at metal nanocatalysts, since it is considered as the simplest electrochemical reaction.

Herein, using ZIF-67 derived Co-based nanocarbon framework (Co/NC) as model catalysts, we systematically study the effects of different reaction parameters on the HER kinetics, mainly including the composition of nanocatalysts (content of N, degree of graphitization of carbon), pH value, type and concentration alkaline metal cation, and type of transition metal etc. We surprisingly find that HER activity is not directly dependent on the type of nitrogen in the carbon framework, but on the relative content of surface hydroxyl and water (OH/H2O) adsorbed on Co active sites embedded in carbon frameworks. Interestingly, when the ratio of the OH/H2O is close to 1:1, Co/NC nanocatalyst shows the best reaction performance under the condition of high-pH electrolytes, e.g., an overpotential of only 232 mV at a current density of 10 mA cm−2 in 1 M KOH electrolyte, even better than 5 wt.% Pt/C. Furthermore, the characterization by optical excitation and emission spectrum together with 1H NMR evidences the presence of SWs in the alkali metal hydroxide solution, which constructs unique surface states for bright color emission and proton activation, even in the absence of Co/NC nanocatalysts. Using SWs dominated surface transient state model within the double-layer region (Scheme 2), the pH-, alkali-metal cation- and transition metal- dependent reaction kinetics of HER can be easily elucidated. Our work provides a comprehensive understanding on the reaction kinetics of all the redox reaction involving the electron and proton transfer at nanoscale interface, not just limited to the electrocatalysis reaction, and thus provides opportunities to tune kinetics by subtly altering the interface states in addition to the catalyst electronic structure.

Results and Discussion

Preparation and characterization of Co-based carbon framework catalysts containing nitrogen atoms (Co/NC)

Co zeolitic imidazolate frameworks (ZIF-67) were synthesized according to reported method (SI). The obtained ZIF-67 showed the well-defined polyhedron morphology in a size of ca. 740 nm, which was confirmed by X-ray diffraction (XRD) pattern (Fig. S1 a) and scanning electron microscopy (SEM) images (Fig. S1 b). Then, by the high-temperature pyrolysis, ZIF-67 nanoparticles were transferred to Co based carbon framework catalysts (Fig. S2 and SI), which were named Co/NC-T (T stands for the pyrolysis temperature). XRD and TEM in Figure S3 showed that Co ions were self-reduced by carbonized organic linkers, yielding Co nanoparticles and atomically dispersed Co atoms that were anchored on nitrogen-doped porous carbon. Upon the acid leaching, most of Co NPs on the external surface of C framework (Co/NC-T catalysts) were removed, but some very smaller sized Co NPs less than 10 nm could also be observed by XRD patterns and the TEM images (Fig. S4 and Fig. S5). The close examination by TEM (Fig. S5) showed more structural information of carbon frameworks with the increase of pyrolysis temperature from 700 °C to 1000 °C. The size of Co/NC NPs was dramatically decreased up to ca. 400 nm due to the shrinkage of C frameworks, and at the same time, with the great improvement of reduction and graphitization, the content of Co in the C frameworks became lower, which was...
evidenced by the coupled plasma atomic emission spectrometry (ICP-AES) analysis (Table S1) and X-ray photoelectron spectroscopy (XPS) analysis (Fig. S6 and Table S2). But, the primitive polyhedron morphology of ZIF-67 NPs remained almost intact. In a word, using ZIF-67 as a carbon precursor, by high-temperature pyrolysis method, the Co-based carbon framework nanocatalysts (Co/NC-T) was successfully synthesized.

Figure 1. SEM image (Inset is particle size (PS) histogram) (a), TEM image (b), EFTEM image (c) and elemental mapping (d-g) of Co/NC-800 electrocatalyst.

Screening of best Co/NC-T catalyst and confirmation of catalytic active site for HER

We first investigated the effect of the pyrolysis temperature of catalysts on HER activity. We found that, under both acidic and base conditions, Co/NC pyrolyzed at 800 °C showed the best catalytic performance, even better than commercial catalyst of Pt/C (Fig. 2). It is importantly noted that, even though the Co/NC-800 was acid-leached, the Co NPs could not be completely removed, indicating that these Co NPs were embedded or sealed in the C frameworks (Fig. 1a-c), which certainly could not be diffusively accessible by water molecules (or hydronium). In addition, the CoNPs@Co/NC catalysts without acid-washing pre-treatment, showed the lower HER activity in both acidic and alkaline electrolytes (Fig. S7), which clearly precluded the contribution role of metallic cobalt or cobalt oxide nanoparticles as active sites for the HER$^{52-56}$. Thus, these
embedded Co NPs or cobalt oxide NPs could not be active sites for HER. Interestingly, the results of elemental mapping showed that, besides the N and O atoms, the Co atoms were also homogeneously atomically distributed into the carbon frameworks component (Fig. 1d-g), confirming that the Co-C-N was possible active sites of Co-based carbon catalysts for HER.\textsuperscript{6,57,58} But what was the precise composition of active sites and how it affected the reaction kinetics of HRE were yet clear, especially for such as pH- and alkali metal cation-dependent effect. Since the Co/NC-800 catalyst was the best catalyst, hereafter, we used it as a model catalyst to study reaction kinetics of HER.

In fact, it is really challenging to establish direct correlations between the electronic structure and the trend of catalytic activity of Co/NC materials since the delicate change of microenvironment of Co/NC,\textsuperscript{59} such as the graphitization degree of carbon frameworks,\textsuperscript{60} and the valence state of N atoms\textsuperscript{52,61-64}. Graphitized carbon, which was usually formed via catalysis over Co, Fe, etc., was vital for electrical conductivity of catalyst. Yes, it was right that, with the increase of pyrolysis temperature, the graphitization degree of carbon frameworks was gradually increased, which was evidenced by thermogravimetric (TG) analysis (Fig. S8), C1s of XPS (Fig. S6 i-l and Table S2) and XRD (Fig. S3a and Fig. S4). However, with the increase of graphitization degree, the reaction activity first increased and decreased, and reached the top at the medium pyrolysis temperature of 800 °C under both acidic and base conditions (Fig. 2). Obviously, our observation showed that the graphitization degree of carbon frameworks, although important, was not the decisive factor to determine HER reaction activity.\textsuperscript{53}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{The HER polarization curves and Tafel plots of Co/NC-T catalysts in 1.0 M KOH (a, c), 0.5 M H\textsubscript{2}SO\textsubscript{4} (b, d).}
\end{figure}
Recently, solid evidences showed that the HER activity of transition metal (TM) based carbon catalysts was dependent on the type and valence state of N atoms in carbon frameworks, and the reaction activity showed a monotonic increasing trend with the increase of N content in a specific valence, such as pyridine-N, pyrrole-N and graphite-N\(^8,65-68\). XPS analysis of the N 1s peak allowed the identification of different concentrations of the N functionalities on the Co/NC-T catalysts. The high-resolution N 1s spectra of the Co/NC composite (Fig. 3 e-h) were deconvoluted into four peaks at 397.6, 398.5, 399.9 and 401.5 eV, which correspond to pyridinic-N, Co-N, pyrrolic-N and graphitic-N, respectively. With the increase of pyrolysis temperature from 700 to 1000 °C, the content of pyridinic-N was gradually decreased, while the contents of pyrrolic-N and graphitic-N were monotonically increased as expectedly due to the transformation of pyridinic-N with a almost constant value of Co-N in 24.0% (Table S2).

Several research groups had reported that the pyridinic-N was the active site to enhance activity of the N-doped carbon materials\(^61,62\), whereas some others suggested that more graphitic nitrogen atoms, rather than the pyridinic ones, were important for the activity\(^63,64\). Hence, the exact catalytic role for each of the nitrogen forms in nanocarbon HER catalysts was still a matter of controversy\(^69\). But, our results of N 1s XPS spectrum of Co/NC-T did not build a direct correlation of the type and content of N atoms in carbon framework with the catalytic activity of HER (Fig. 2 and Table S2). Nevertheless, one must not neglect their influence on the catalytic activity. Since more reports showed that, the adsorption of hydroxyl groups on the metal center significantly promoted the reaction kinetics HER\(^9,10,15,28,29,31-33,35,70\). We shifted our concentration to the analysis of oxygen-associated species by the O 1s XPS spectra. For Co/NC catalysts, the spectrum could be deconvoluted into four peaks centered at 530.0, 531.3, 532.5 and 534.3 eV (Fig. 3 a-d), which were assigned to Co-O, OH*, H\(_2\)O* and C-O, respectively\(^71-73\). The XPS O 1s spectra analyses verified the presence of hydrous hydroxide complex on the Co metal centers of the Co/NC-T catalysts, and very interestingly, when the ratio of OH* to H\(_2\)O was close to 1:1 (Table S2), Co/NC-800 catalyst exhibited the best catalytic performance of HER (Fig. 2 a-b). This hydrous hydroxide complex was recently proposed to be structural water molecules (SWs), which could be acted as the intermediate species to tune the surface electron and proton transfer by space interaction (Scheme 1d)\(^36-39,47-49\). Thus, we hypothesized that the interfacial adsorbed SWs probably provide alternative channel for electron and proton transfer, which
promoted the dissociation (or activation) of water at the electrode and consequently accelerated the HER reaction kinetics. This also probably answered the important role of doping N atoms (type and content of N atoms in the carbon frameworks) to tune the catalytic activity by changing the alkaline micro-environment of Co coordination sphere.

In addition, the capturing of SWs at the Co center also answered the higher activity of Co/NC in the basic media (1.0 M KOH) than in the acidic electrolyte (0.5 M H₂SO₄), as displayed in Figure 2 a-b by the linear sweep voltammetry (LSV) polarization curve. Accordingly, Co/NC electrocatalytic activity in 1.0 M KOH gave a smaller overpotential (232 mV at 10 mA cm⁻²) and Tafel slope (99 mV decade⁻¹) compared with 0.5 M H₂SO₄ (308 mV at 10 mA cm⁻² and Tafel slope=215 mV decade⁻¹) (Fig. 2). When compared with Pt/C’s overpotential in basic media, interestingly, at slightly higher applied potentials than their onset potential (< 0.25 V vs. RHE), Pt/C actually gave higher current density, otherwise, Co/NC catalyst showed smaller overpotential which meant greater electrocatalytic activity even than the commercially available Pt/C catalyst (Fig. 2a). It is importantly noted that, in fact, our Co/NC-800 catalyst also exhibited superior HER performance with a very smaller overpotential (308 mV) in 0.5 M H₂SO₄, very close to that of Pt/C catalyst (228 mV) at 10 mA cm⁻² (Fig. 2b). Our results were in strong contrast with the previous reports that activity was higher in an acidic electrolyte than in an alkaline electrolyte⁶,⁷⁴, implying that the chemically adsorbed SWs at the electrode interface may play a determinant role in the HER. Although the performance of Co/NC is not the best among the reported HER catalysts including non-precious and precious catalysts⁸,⁷⁵-⁷⁹, the concept of SWs as an intermediate to tune the surface coupled proton and electron transfer provides completely new insights for the understanding mechanism of HER at the molecule level.

**Figure 4.** The HER polarization curves and Tafel plots of Co/NC-800 catalyst under different concentrations of KOH (a-b) and 1.0 M AMOH (c-d) (AM⁺ = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺).
Next, to further verify the effect of adsorbed hydroxyl on HER, the activity in different concentrations of KOH electrolyte was tested. As can be seen in Fig. 4a, the activities of catalyst in different electrolytes followed the order of $1.0 \text{ M KOH} \approx 2.0 \text{ M KOH} \approx 3.0 \text{ M KOH} > 0.1 \text{ M KOH} > 0.01 \text{ M KOH}$. This suggested that the density of surface hydroxyl groups adsorbed on the metal surface strongly affect the reaction kinetics of HER: the adsorption of a small amount of OH$^-$ was not conducive to the construction of interface state; On the contrary, the introduction of excessive OH$^-$ inhibited the formation of interfacial active H species (or adsorbed H species, Fig. S14b). In addition, the introduction of OH$^-$ significantly changed the rate-determining step (RDS) of HER as shown in Tafel slopes (Fig. 4b). Tafel slopes in different electrolytes were compared in a similar range to avoid the influence from the high overpotential polarization and formed bubbles. It can be seen that the Tafel slope of Co/NC in low [OH$^-$] environment was greater than 120 mV dec$^{-1}$ (Fig. 4b), indicating that the RDS of HER was water dissociation step. However, when [OH$^-$] increased to 1.0 M, the Tafel slope reduced to 99 mV dec$^{-1}$ and even less in higher concentration of KOH solution (~ 92 mV dec$^{-1}$ in 2.0 M KOH solution and ~ 85 mV dec$^{-1}$ in 3.0 M KOH solution), suggesting that the RDS was either proton recombination (Volmer–Tafel) step or electrochemical desorption (Volmer–Heyrovsky) step. Such base concentration-dependent reaction kinetics was also observed in LiOH-based electrolytes (Fig. S9), indicating the similar reaction mechanism in high concentration of alkaline solutions.

Scheme 2. Adsorption mode of hydrated alkaline metal cations ($AM^+$) of Li$^+$ (a) and Cs$^+$ (b) in the electrical double layer (EDL) region on the electrode surface. In the alkaline conditions, due to the adsorption of hydroxide groups (OH$^-$), the negatively charged electrode surface strongly binds the $AM^+$ with electrostatic interactions in the EDL region: In the inner Helmholtz plane (IHP), SWs are strongly bound to the Co active sites, which show the negatively charged surface; in the outer Helmholtz plane (OHP), Li$^+$ and Cs$^+$ are both densely adsorbed onto the electrode surface, while K$^+$ cations with the medium hydration ability are loosely adsorbed on the electrode surface (not shown).

Obviously, according to the $p$ band intermediate (or transient) state model (Scheme 1c), owing to the ultra-fast switching between surface bonding (scheme 1d), the stability of SWs on the electrode surface is very sensitive to the delicate change of micro-environment of catalytic active sites, for example the influence of the type of alkali metal cations on the kinetic of HER. Thus, we further studied the HER performance in varied $AM^+$OH solution ($AM^+ = Li^+, Na^+, K^+, Ru^+$ and Cs$^+$). To our surprise, the trend of HER activity did not follow the structure-making (or hydration)
tendency of alkali metal cations (AM\(^{+}\)) in alkaline solutions of 1.0 M AMOH (in the order of Cs\(^{+}\) < Rb\(^{+}\) < K\(^{+}\) < Na\(^{+}\) < Li\(^{+}\)), since in 1.0 M KOH solution, our Co/NC-800 catalyst showed the highest activity. Obviously, just considering the hydration ability of AM\(^{+}\) on catalytic activity is not enough to under the micro-kinetics of HER. Another overcrowding effect of the AM\(^{+}\) bound on the electrode surface to block the active sites at the electrical double layer (EDL) region of electrode have to be also considered\(^{24}\).

Combining the SWs dominated \(p\) band surface transient state (PBIS) with the overcrowding effect of AM\(^{+}\) cations, we proposed a simple model to understand the alkali metal cation-dependent kinetics of HER (Scheme 2). In the alkaline conditions, due to the adsorption of hydroxide groups (OH\(^{-}\)), the negatively charged electrode surface strongly binds the AM\(^{+}\) with electrostatic interactions in the EDL region: in the inner Helmholtz plane (IHP), SWs are strongly bound to the Co active sites, which show the negatively charged surface; in the outer Helmholtz plane (OHP), Li\(^{+}\) and Cs\(^{+}\) are both densely adsorbed onto the electrode surface (Scheme 2 a and b), while K\(^{+}\) cations with the medium hydration ability are loosely adsorbed on the electrode surface (not shown). Owing to the weak hydration capacity, the bulky Cs\(^{+}\) cations are strongly naked adsorbed with more free water at the electrode surface (a local hydrophobic surface is formed like the hydrophobic nanocavity in the metalloenzymes), which blocks the diffusion of water to the Co active site with SWs and consequently lowers the activity of HER. In fact, if we just consider the electrostatic interaction, upon the introduction of Li\(^{+}\) with strongest structure-making tendency, the electrode surface should be more densely covered (or packed) by Li\(^{+}\) formed a local “Water-in-salt” structure at nanoscale interface\(^{80}\), and thus it should show the lowest chemical reactivity due to the blocking of Co active site. However, this is not the case. There are two reasons to explain this abnormal observation of HER activity. One reason is that, even though Li\(^{+}\) cation is densely covered on the electrode surface, its own strong hydration ability can continuously supply the water to the Co active sites, leading to the high activity. If this is true, from the perspective of more conducive to mass transfer, it should show the best catalytic performance even than that in KOH solution. The other reason is that, owing to the stronger hydration ability of Li\(^{+}\), in the alkaline solution, it can build the similar interface state of SWs by itself to the Co active site with a common formula of \(\{\text{OH}_{\text{ad}}\text{H}_{2}\text{O}\text{H}_{\text{ad}}\text{H}_{2}\text{O}\text{H}_{\text{ad}}\text{H}_{2}\text{O}\text{@M}^{+}\}\), where M\(^{+}\) can be transition metals or alkali metals. Since the catalyst in the KOH solution shows the best catalytic activity (Fig. 4 c), the later explanation is obviously more reasonable, i.e, \(\{\text{OH}_{\text{ad}}\text{H}_{2}\text{O}\text{H}_{\text{ad}}\text{H}_{2}\text{O}\text{@Li}^{+}\}\) is active site for HER owing to the strong hydration capacity, but its activity is less than \(\{\text{OH}_{\text{ad}}\text{H}_{2}\text{O}\text{H}_{\text{ad}}\text{H}_{2}\text{O}\text{@Co}^{6\text{+}}\}\).
Figure 5. Fluorescence spectra of different AMOH (AM$^+$ = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) solution with DMSO as solvent (a) and at varied concentration of KOH (b); Time-resolved luminescence decay profiles of KOH (c) and LiOH solution (d).

Excitation and emission spectrum of varied alkali metal hydroxide DMSO solution verified the above assumption that Li$^+$ could form more stable SWs for photoluminescence emission due to its stronger hydration ability, which could provide additional reaction channels for surface electron and proton transfer (Scheme 1c). As we earlier reported$^{36-39}$, in fact the PL emission of SWs was independent on the type of adsorbed metal, herein the alkali metal cations, and that, all the AMOH solution with DMSO as solvent showed a very broad emission peak centered at ca. 450 nm with a shoulder at ca. 420 nm (Fig. 5a, solid lines) under the UV irradiation of 370 nm wavelength, accompanying the observation of two excitation bands centered at ca. 295 nm and ca. 370 nm on excitation spectrum (Fig. 5a, dash lines), which were featured bands of SWs confined in the nanospaces or at the nanoscale interfaces$^{36-39}$. Very interestingly, with the increase of the concentration of KOH, the intensity of PL emission at ca. 420 nm and 450 nm showed a trend of first increase and then decrease (Fig. 5b and Fig. S10), which completely followed the trend of HER activity with the increase of the concentration of KOH (Fig. 4a and b), suggesting the key role of SWs to tune the kinetics of HER. However, differing from other AM$^+$, the close inspection of the excitation-emission two-dimensional plots of the LiOH solution in DMSO solvent showed that, with the increasing of LiOH concentration, the intensity of PL at ca. 420–440 nm was significantly increased (Fig. 6). Most interestingly, the growth of new excitation band centered at ca. 295 nm also corresponding to the PL at ca. 420 nm, indicating the formation of a new specie for PL emission (Fig. 6 and Fig. S11), but with the similar structure of free SWs as in other AMOH solution, such as Na$^+$, K$^+$, Rb$^+$ and Cs$^+$. It is importantly noted that, although free SWs could emit strong fluorescence, they did not contribute to HER due to their intrinsic instability.
Considering the super hydration capacity of Li$^+$ with smallest ionic radius in the alkali metal cations group, we assigned the new formed species for excitation band at ca. 295 nm to Li$^+$ bound SWs, $\{\text{OH}_\text{ad}\cdot\text{H}_2\text{O}@\text{Li}^+\}$, where Li$^+$ as an anchoring site for SWs. Li$^+$ bound SWs could act as catalytic active sites for HER, but the catalytic activity was lower than that of Co bound SWs, $\{\text{OH}_\text{ad}\cdot\text{H}_2\text{O}@\text{Co}^{\delta+}\}$. Obviously, the Li$^+$ bound SWs showed stronger stability than free SWs, which was evidenced by the lifetime measurement by time-resolved luminescence decay profiles of KOH (Fig. 5c, 1.28 ns) and LiOH solution (Fig. 5d, 1.59 ns). Thus, the observation of optical spectrum answered that Co/NC-800 catalyst in KOH solution showed the best catalytic performance of HER, in fact, which was the result of compromise between the electronic effect of Co active centers and overcrowding effect of alkali metal ion adsorbed on the electrode surface.

In fact, the catalytic activity of $\{\text{OH}_\text{ad}\cdot\text{H}_2\text{O}@\text{M}^{+}\}$ active sites are dependent on the binding strength of SWs with metal cations at the electrode. Too strong or too weak bonding of OH$^-$ group to metal is not conducive to the construction of interface p band transient state (Scheme 1c-e), i.e., it is not conducive to the overlap of p orbitals of space oxygen atoms by space interaction, consequently, slowing down the reaction kinetic of HER following the Sabatier principle. This also answers that, in the first row of transition metal groups (Mn/Co/Ni), Co/NC-oPD catalyst showed the best catalytic activity of HER owing to the medium binding strength of OH$^-$ to Co ions (Fig. S12). These results thus shed new lights on the rational design of electrocatalysts that the HER (and OER) activity can be attributed to differences in stabilization of p band transient states which is tailored by the nature of cations in the electrolyte or doping of multiple transition metals. These phenomena underscore the indispensable role of OH$_{ad}$ in triggering the catalytic roles of AM$^+$, thus favoring the notion of the formation of $\{\text{OH}_\text{ad}\cdot\text{H}_2\text{O}@\text{M}^{+}\}$ adducts within the double-layer region, where M$^+$ can be transition metals or alkali metal cations, answering the transition metals are not necessary for HER or OER.

**Figure 6.** Excitation (EX)–emission (EM) two-dimensional plots of the varied concentration LiOH solution in DMSO solvent showing that the growth of new excitation band centered at ca. 295 nm with increasing concentration of LiOH.

Based on the above electrochemical kinetic and optical spectrum analysis, a new SWs dominated p band transient state (PBIS) model was proposed to understand the reaction kinetics of the nanostructured Co/NC electrocatalysts for HER (Scheme 1c-e). According to p band transient state (PBIS) theory, in alkaline electrolyte, an ensemble of surface transient states formed through space overlap of p orbitals of O atoms of SWs can act as an alternative channel for concerted electron and proton transfer. Under high [OH$^-$], large amounts of OH$^-$ are available in the
electrolyte and can be easily formed to the p band, strongly promoting the water dissociation process to form the active *H species, which are confirmed by *H NMR (Fig. S14). With more electrons being transferred on the surface, *H combines with each other to form H$_2$ gas. However, the same process cannot take place in less-alkaline solutions due to the low [OH$^-$] in the environment cannot form stabilized p band transient states to facilitate the key water dissociation process. In this case, Volmer step (H$_2$O + e$^-$→H$^*$ + OH$^-$) becomes the RDS of the overall reaction as indicated by Tafel slope is greater than 120 mV dec$^{-1}$ (Fig. 4 b). Higher overpotential is needed for the catalyst to interact with water to start water dissociation under such a low [OH$^-$] environment. This also answers why Co/NC catalyst with higher component of *OH is the most active (Table S2). In addition, the cation-dependent can be explained by the formation of {OH$_{ad}$ • H$_2$O@AM$^+$} adducts within the double-layer region (Scheme 2). The nature of {OH$_{ad}$ • H$_2$O} adducts near the interface can significantly impact the activity of HER, thus altering the kinetics of HER by changing the unique interaction of SWs at the electrified interface. The hydration of alkaline metal ion decreases in the order Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$ and the interaction between AM$^+$ and water molecules within the hydration shell also decreases from Li$^+$ to Cs$^+$. The strongest interaction between Li$^+$ cations and their hydration water can be demonstrated by the smallest Li$^+$–O distance between the Li$^+$ ion and water in its hydration shell, ~2 Å compared to ~2.4 Å for Na$^+$, ~2.8 Å for K$^+$ ~3.0 Å for Rb$^+$ and ~3.1 Å for Cs$^+$ [84]. Therefore, interfacial OH$^-$ ions in the case of KOH form moderate interaction with surrounding water molecules compared to in the case of LiOH having stronger interaction with water molecules in the interface and RbOH, CsOH having weaker interaction with water molecules in the interface (Scheme 2). And then it’s easy to understand that the activity trend in the order K$^+$ > Na$^+$ ~ Li$^+$ > Rb$^+$ > Cs$^+$ with a comprise between the electronic effect of {OH$_{ad}$H$_2$O@M$^+$} catalytic active sites and overcrowding effect of AM$^+$. Thus, our work demonstrates how the kinetics of the water reduction reaction can be regulated by the SWs dominated p band transient state (PBIS) model at the electrified interface (Scheme 1). The unique interaction of oxygen atoms of {OH$_{ad}$H$_2$O} adducts in the interface can play a significant role in activating water molecules at the electrified interface, resulting in interesting pH- and cation-dependent effects on HER kinetics. Such understanding that goes beyond tuning the binding energetics of the active site by chemical covalent bonding (Scheme 1a-b) is critical to designing more active electrochemical interfaces.

**Conclusion**

So far, there is no unified model to explain the micro kinetics of electrocatalytic hydrogen evolution, such as the pH-, alkaline metal ions- and transition metal dependent reaction kinetics. Using ZIF-67 derived nanostructured carbons as a prototype electrocatalyst, we first provide solid evidence and confirm that the interfacial structural water molecules (SWs) in the form of hydrous hydroxyl complex absorbed on metals {OH$_{ad}$H$_2$O@M$^+$}, M$^+$ are transition and/or alkaline metal cations) are active sites for water activation (or dissociation) and subsequent proton reduction. The space interaction of two O atoms of SWs could be a new type of weak interaction with a strength between hydrogen bond and chemical covalent bond. Furthermore, owing to the spatial overlap of the $p$ orbitals of two O atoms in SWs, an ensemble of surface transient states is formed (Scheme 1c-e), which provides a new channel for the cooperative transfer of protons and electrons at the nanoscale interface. It should be emphasized that these surface transient states are not stable with dynamic features, which answers the extremely susceptible sensitivity of HER (even OER and ORR) on microenvironments, such as pH- and cation- dependent effect. The concept of SWS
dominated surface transient states to tune the concerted electron and proton enables optimization of the entire electrochemical interface as opposed to only catalysts structure to improve activity for the hydrogen evolution reaction, which is critical to designing more active electrochemical interfaces for energy storage and conversion reactions. This unique reaction mechanism may not only provide an important guidance for the design/selection of catalysts/electrolytes for the nanomaterial-catalyzed reactions in an aqueous environment, including CO₂/CO reduction, nitrogen reduction, and other electrocatalytic reduction reactions, but also shed new light on the nanoscale-range electron and proton transfer through the water-line ‘bridge’ in the biological macromolecule system, which could follow the out sphere electron transfer model of Marcus theory with connected SWs as a bridge.

Author Contributions
PYW and JFZ performed the main experiments and equally contribute to this research. BP performed the SEM and TEM measurements. HC performed the test of catalytic performance of HER partly. KZ conceived and directed the project, and proposed the p band dominated transient state model to understand the nature of electrocatalytic reactions. KZ designed the figures and wrote the manuscript with the help of PYW and BP. All authors have read and agreed to the published version of the manuscript.

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