Electronic metal–support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction

Yi Shi1,8✉, Zhi-Rui Ma1,8, Yi-Ying Xiao1, Yun-Chao Yin2, Wen-Mao Huang3, Zhi-Chao Huang3, Yun-Zhe Zheng4, Fang-Ya Mu5, Rong Huang4, Guo-Yue Shi5, Yi-Yang Sun6, Xing-Hua Xia2✉ & Wei Chen1,3,7✉

Tuning metal–support interaction has been considered as an effective approach to modulate the electronic structure and catalytic activity of supported metal catalysts. At the atomic level, the understanding of the structure–activity relationship still remains obscure in heterogeneous catalysis, such as the conversion of water (alkaline) or hydronium ions (acid) to hydrogen (hydrogen evolution reaction, HER). Here, we reveal that the fine control over the oxidation states of single-atom Pt catalysts through electronic metal–support interaction significantly modulates the catalytic activities in either acidic or alkaline HER. Combined with detailed spectroscopic and electrochemical characterizations, the structure–activity relationship is established by correlating the acidic/alkaline HER activity with the average oxidation state of single-atom Pt and the Pt–H/Pt–OH interaction. This study sheds light on the atomic-level mechanistic understanding of acidic and alkaline HER, and further provides guidelines for the rational design of high-performance single-atom catalysts.

1 Department of Chemistry, National University of Singapore, Singapore, Singapore. 2 State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China. 3 Department of Physics, National University of Singapore, Singapore, Singapore. 4 Key Laboratory of Polar Materials and Devices (MOE), Department of Electronics, East China Normal University, Shanghai, China. 5 School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, China. 6 State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China. 7 Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou, China. 8 These authors contributed equally: Yi Shi, Zhi-Rui Ma.

✉email: sychemnju@foxmail.com; xhxia@nju.edu.cn; phycw@nus.edu.sg
Hydrogen has emerged as a green and sustainable fuel to meet the demand for future global energy. Nowadays, the majority of hydrogen is still produced from steam-reformed methane, which is derived from limited fossil resources and greatly increases CO₂ emission. Electrocatalytic hydrogen evolution reaction (HER) enabled by renewable electricity holds great promise as a safe, scalable, low-cost, and environmentally-friendly pathway for hydrogen production. To date, noble metals (e.g., Pt, Pd, and Rh) are regarded as the most efficient materials to catalyze the conversion of H₂O⁻ (acid) and H₂O (alkaline) to H₂. In order to maximize the utilization efficiency of noble metals, the rational design and controllable synthesis of catalysts based on the deep understanding of reaction mechanism and structure–activity relationship is crucial for cost-efficient HER catalytic process. An effective approach for mechanistic study of the structure–activity relationship is to modulate the electronic structure of catalysts and unravel the factors that govern their catalytic activities.

Several strategies—multimetallic construction that integrates metal components with distinct electronic properties, surface engineering of metal by organic modifiers, and metal–support interaction modulation—have been developed to tune the electronic structure of metal catalysts. In industrial heterogeneous catalysis, metal nanoparticles are immobilized on a support and the electronic structure of the active sites on metal nanocatalysts can be effectively regulated through the strong metal–support interactions, which is rationalized as the electronic metal–support interaction (EMSI) proposed by Rodriguez and colleagues. EMSI is associated with the orbital rehybridization and charge transfer across the metal–support interface, leading to the formation of new chemical bonds and the realignment of molecular energy levels. The electron transfer modulates the d-band structure of metal nanocatalysts, strengthens the adsorption of reaction intermediates, and hence lowers the energy barrier and facilitates the rate-limiting step. However, the rearrangement of electrons with considerable EMSI effect is only confined to a couple of atomic layers at the metal–support interface. For the conventional supported metal nanocatalysts consisting of few atomic layers near the interface and non-uniform atomic coordination sites (e.g., vacancies, step edges, kinks and corner sites), it is difficult to correlate the overall catalytic activity with the EMSI effect on the electronic structure of active sites.

Single-atom metal catalyst (SAMC) minimizes the structure of metal components with the well-defined active sites, which are located at the metal–support interface and exposed to reactive species. The homogeneous atomic coordination environment makes SAMC an ideal and simplified model system for the mechanistic investigation of catalytic reactions. Strong EMSI not only stabilizes the single-atom metals owing to the formation of thermodynamically favorable metal–support bonds, but also leads to the charge redistribution induced via electron transfer. The net electron transfer from the single-atom metals to the electronegative atoms (e.g., C, N, O, S) on support positively charges the metal atoms with high oxidation state, and thus modulates the d state of single-atom metals. The d-orbital electrons of transition metal atoms participate directly in the catalytic redox reactions, and thus have close relationship with the adsorption strength of the catalytic reaction intermediates. Although SAMC has been widely used for catalyzing HER, comprehensive atomic-level insights into the structure–activity relationship of SAMC for a wide-pH-range HER are rarely reported.

Transition metal dichalcogenides (TMDs) have been widely used as the supports for immobilizing SAMC in heterogeneous catalysis. Compared with SAMC supported on carbon-based materials, the electronic structure of single-atom metals supported on TMDs is usually adjusted by both the anchoring atom and the neighboring transition metal atoms with relatively high atomic number, which affords a more flexible and complex coordination environment to regulate the catalytic activity. Owing to the various well-defined band structures of TMDs (e.g., MoS₂, WS₂, MoSe₂, and WSe₂), the core anchoring chalcogen (S, Se) and the neighboring transition metal (Mo, W) can synergistically regulate the electronic structure of SAMC through EMSI. The tuneable d-orbital state of single-atom Pt changes the adsorption energy of reactants on metal atoms and thus influences the catalytic activity of HER.

Herein, we used the previously reported site-specific electrodeposition technique to construct four kinds of single-atom Pt catalysts on different two-dimensional TMDs supports (MoS₂, WS₂, MoSe₂, and WSe₂) as a model system. Detailed spectroscopic and electrochemical characterizations show that the fine tuning of the oxidation state of single-atom Pt through EMSI affects the alkaline and acidic HER (mass activity) up to 73-fold (Pt-SAs/MoSe₂) and 43-fold (Pt-SAs/WS₂) higher than that of the commercial Pt/C, respectively, revealing the universality of the single-atom Pt system for the wide-pH-range HER investigations. With the decrease in oxidation state of single-atom Pt, the hydrogen binding energy decreases, and consequently the acidic HER activity increases to a record level. In the alkaline HER, the single-atom Pt catalyst with optimal oxidation state (ca. +2) shows neither too strong catalyst–H interaction for hydrogen release, nor too weak catalyst–OH interaction for water dissociation—exhibits exceptional catalytic activity.

Results

Synthesis and characterization of single-atom Pt catalysts. For the self-terminating growth of single-atom Pt on various TMDs supports (Fig. 1b), Cu atoms were first underpotentially deposited on the chemically exfoliated TMDs (ce-TMDs, Supplementary Figs. 1–3). The Cu atoms were then galvanically exchanged by Pt (II) (Supplementary Figs. 4 and 5), forming TMDs-supported single-atom Pt samples (denoted as Pt-SAs/TMDs: Pt-SAs/MoS₂, Pt-SAs/WS₂, Pt-SAs/MoSe₂, and Pt-SAs/WSe₂). The surface-limited underpotential deposition (UPD) technique enables the formation of energetically favorable metal–support bonds, and automatically terminates the sequential formation of metallic bonding, confirming the growth of single-atom Pt. The Pt loadings on ce-MoS₂, ce-WS₂, ce-MoSe₂, and ce-WSe₂ were 5.1, 4.1, 4.7, and 4.9 wt%, respectively, as revealed by inductively coupled plasma optical emission spectrometry. No Pt-containing clusters/nanoparticles or crystalline Pt phases were observed on the Pt-SAs/TMDs nanosheets (Supplementary Figs. 6, 7). Owing to the discrete distribution of Pt atoms, electrochemical cyclic voltamograms of all the Pt-SAs/TMDs samples did not show characteristic peaks of Pt in the regions of Pt-H adsorption/desorption (Supplementary Fig. 8). The similar Raman spectra of Pt-SAs/TMDs samples with those of the pure ce-TMDs imply that the metallic 1T phase of TMDs well retained after single-atom Pt decoration (Supplementary Figs. 3, 9). The aberration-corrected high-angle annular dark-field-scanning TEM (HAADF-STEM) images confirmed the atomically dispersed Pt atoms (bright spots) on the ce-TMDs nanosheets (Fig. 1c–f). The STEM-coupled energy-dispersive spectroscopy element mapping showed the homogeneous dispersion of atomic Pt over the whole samples (Fig. 1c–f).

Electronic and coordination structure. We then investigated the chemical configuration and local coordination of Pt-SAs/TMDs through the combination of X-ray photoelectron spectroscopy
Fig. 1 Rational design and construction of single-atom Pt catalysts. **a** Electronic metal–support interactions (EMSI) modulation of single-atom Pt for catalyzing HER. Left: schematic structure of single-atom Pt on TMDs material. The gray, purple, and green spheres represent the chalcogen (sulfur/selenium), transition metal (molybdenum/tungsten), and platinum, respectively. The electronic structure of single-atom Pt was modulated by two-dimensional TMDs through charge delocalization, enabling the single-atom Pt to take slightly positive charge (Pt$^{\delta+}$). The structural unit of single-atom Pt was circled by the orange dashed line and further enlarged above. Top right: schematic diagram of the band edges of TMDs. The conduction band minimum (CBM)/valence-band maximum (VBM) band edges of TMDs (theoretical values) refer to ref. 42. The schematic band structure—showing the electron affinity and ionization potential of various TMDs—provides a guideline for rationalizing the EMSI modulation of single-atom Pt. Bottom right: schematic illustrating that the $d$-state shift of single-atom Pt induced by EMSI regulates the catalytic performance of HER. **b** Fabrication of TMDs-supported single-atom Pt. The gray, purple, brown, and green spheres represent chalcogen (sulfur/selenium), transition metal (molybdenum/tungsten), copper, and platinum, respectively. After site-specific electrodeposition of Cu adatoms on the support, galvanic replacement of Cu adatoms with PtCl$_4^{2-}$ is carried out to produce TMDs-supported single-atom Pt. Atomic-resolution HAADF-STEM images for (c) Pt-SAs/MoS$_2$, (d) Pt-SAs/MoSe$_2$, (e) Pt-SAs/WS$_2$, (f) Pt-SAs/WSe$_2$ (scale bars: 5 nm) and the corresponding elemental mappings (right side, scale bars: 100 nm).
respectively) of the geometric con
average oxidation states of Pt, the Pt4
that the Pt species in Pt-SAs/TMDs were partially oxidized with
also shown in Supplementary Fig. 10. These results demonstrated
for Pt-SAs/MoS2 (2.205), indicative of the increased
hole for Pt-SAs/MoSe2 was estimated to be 2.590, higher than that
(Fig. 2b) showed that the white-line intensity for Pt-SAs/MoS2
integrated XPS analysis showed that the average oxidation states
Pt-SAs/WS2, Pt-SAs/MoSe2, and Pt-SAs/MoSe2 were 1.24, 1.71, 2.11, and
2.61, respectively (Fig. 2a, and Supplementary Table 1). The
binding energies of Mo 3d and S 2p/Se 3d of the supports
decreased slightly (Supplementary Fig. 11) while the binding energy
Pt 4f increased, indicating that the electrons were
transferred from Pt to ce-TMDs supports. In X-ray absorption
near-edge spectroscopy (XANES), the Pt L3-edge analysis
showed that the white-line intensity for Pt-SAs/MoS2 and
Pt-SAs/MoSe2 were higher than that for Pt foil, indicating more unoccupied 5d orbitals for single-atom Pt. The oxidation
states of single-atom Pt in Pt-SAs/MoS2 and Pt-SAs/MoSe2 samples were 1.61 and 2.07 (Fig. 2c and Supplementary Fig. 12), respectively, in line with the XPS analysis. According to Pt0 foil (5d6s1) and PtIV O2 (5d6s0) standards, the number of d-band hole for Pt-SAs/MoSe2 was estimated to be 2.590, higher than that
for Pt-SAs/MoS2 (2.205), indicative of the increased d vacancy29
(Fig. 2d). Because of the interference of W k-edge signal, the Pt L3
edges of Pt-SAs/WS2 and Pt-SAs/WSe2 could not be well
recorded45.

To further demonstrate the homogeneous coordination
environment of the model system, we further evaluated the local
atomic structure of single-atom Pt by extended X-ray absorption
fine structure (EXAFS), density functional theory (DFT)-
optimized structural models, as well as magnified HAADF-
STEM images. The EXAFS spectra of Pt-SAs/MoS2 and Pt-SAs/
MoSe2 showed a similar peak at approximately 2.3 Å, ascribed to
the Pt–S and Pt–Se bonds with coordination numbers of 3.2 and
3.5, respectively (Fig. 2e, Supplementary Figs. 13, 14, and 15, and fitting parameters shown in Supplementary Table 2)23,43. No appreciable Pt–Pt bond (2.8 Å) was detected in Pt-SAs/MoS2 and Pt-SAs/
MoSe2 (Fig. 2e), further verifying the dominant existence of
single-atom Pt. No observation of Pt–Mo coordination ruled out
the covalent attachment of Pt atom on Mo edge site or S vacancy.
Combined with the coordination numbers, the magnified HAADF-STEM images implied that Pt atoms, coordinating with
three nearest neighboring S or Se, were straddled atop Mo
(Supplementary Fig. 15). In line with these results, the theoretical
Pt–S (2.22, 2.22, and 2.47 Å) and Pt–Se distance (2.28, 2.28, and
2.56 Å) obtained from the optimized Mo atom model (Supplementary Fig. 16) agreed well with the EXAFS analysis (average
bond length 2.27 and 2.35 Å for Pt–S and Pt–Se, respectively),
which further confirmed Pt attachment on the Mo top site
(Fig. 2f). The high-energy barrier for Pt diffusion between the
nearest adsorption sites demonstrated the structural stability of
the single-atom catalysts (Supplementary Fig. 16).

Electrochemical HER study. The structural characterizations have shown that the electronic structure of single-atom Pt could be fine-
tuned by different TMDs supports through EMSI. We then
attempted to demonstrate the effect of EMSI modulation on the
catalytic performance of single-atom Pt. Considering the different HER reactants in alkaline (H₂O) and acidic (H₂O²⁻) media (detailed mechanisms shown in Supplementary Fig. 17), we investigated the electrocatalytic HER activity of Pt-SAs/TMDs using a typical three-electrode configuration in wide-pH-range electrolytes, including 1.0 M KOH and 0.5 M H₂SO₄ solutions (Supplementary Fig. 18).

In the alkaline condition, all the Pt-SAs/TMDs samples showed much superior electrocatalytic HER activity with negligible overpotential, compared to the pristine ce-TMDs supports (Supplementary Fig. 19). It should be noted that these supported single-atom Pt samples exhibited various alkaline HER activities, with the order of Pt-SAs/MoS₂ > Pt-SAs/MoSe₂ > Pt-SAs/WSe₂ > Pt-SAs/WS₂ (Fig. 3a). Specifically, Pt-SAs/MoSe₂ displayed the overpotential value of approximately 29 mV at a current density of 10 mA cm⁻² (left axis of Fig. 3b) and exceptional mass activity of 34.4 A mg⁻¹ under an overpotential of 100 mV (right axis of Fig. 3b, details of calculation shown in Supplementary Note 1), which was the best among all four samples. The electrocatalytic HER activity of Pt-SAs/MoSe₂ was remarkably 73.4-fold higher than that of commercial Pt/C, and exceeds most of the state-of-the-art SAMCs or Pt-based electrocatalysts (Fig. 3b, Supplementary Fig. 20, and references shown in Supplementary Tables 3, 4). Gas chromatography analysis was applied to verify the catalytic production of H₂ (Supplementary Fig. 21).

To investigate the mechanistic insights into the alkaline HER activity of Pt-SAs/TMDs samples, we evaluated the catalysis kinetics from Tafel plots (Fig. 3c). Compared to the other Pt-SAs/TMDs samples (50, 59, and 65 mV dec⁻¹), Pt-SAs/MoSe₂ exhibited the smallest Tafel slope of 41 mV dec⁻¹, implying the fastest HER kinetics. Tafel slopes were much lower than 120 mV dec⁻¹ in all Pt-SAs/TMDs samples, suggesting that the prior sluggish Volmer reaction was greatly accelerated. The turnover frequency (TOF) value of the Pt sites on Pt-SAs/MoSe₂ was 6.21 s⁻¹ (at −50 mV; details of the calculation shown in Supplementary Note 2), which strikingly surpasses the other three Pt-SAs/TMDs samples (Fig. 3d) and previously reported single-atom electrocatalysts (references shown in Supplementary Table 3). The negligible degradation of Pt-SAs/TMDs after 1000 cycles stability tests demonstrated the high stability of the supported single-atom Pt (Supplementary Fig. 22), which is an essential prerequisite for mechanism investigation. The HAADF-STEM and XPS characterizations of Pt-SAs/TMDs after HER measurements suggested the unchanged morphology and valence state of single-atom Pt during HER, further confirming the stability of the Pt-SAs/TMDs catalysts (Supplementary Figs. 23, 24, and Supplementary Table 5).

Similarly, we also showed the various acidic HER activities on different supported single-atom Pt samples, which followed the order distinctive from that in alkaline HER: Pt-SAs/WS₂ > Pt-SAs/MoS₂ > Pt-SAs/MoSe₂ > Pt-SAs/WSe₂ (Figs. 3e and 3f), consistent with the previously reported results[43]. For instance, compared to the other three samples, Pt-SAs/WS₂ displayed much lower overpotential value (32 mV; left axis of Fig. 3f) at a current density of 10 mA cm⁻² and exceptional mass activity of 130.2 A mg⁻¹ under an overpotential of 100 mV (43.1-fold higher than commercial Pt/C; right axis of Fig. 3f; details of the calculation shown in Supplementary Note 1). The Tafel slope and TOF values of Pt-SAs/WS₂ were 28 mV dec⁻¹ and 273 s⁻¹ (at −200 mV; details of the calculation shown in Supplementary Note 2), respectively, much better than the other three Pt-SAs/TMDs samples and most of the state-of-the-art SAMCs or Pt-based electrocatalysts (Figs. 3g, 3h, Supplementary Fig. 25, and references shown in Supplementary Tables 6, 7).

We further verified the active sites for HER and the negligible contribution of TMDs support to HER. The thiocyanate ions (SCN⁻) poison experiment of the Pt-SAs/TMDs samples was conducted to efficiently block the Pt sites for acidic HER[34,43]. Upon the addition of SCN⁻, the HER current of all the Pt-SAs/TMDs samples decreased dramatically approaching near zero, confirming that HER activity dominantly derives from the single-atom Pt and the catalytic performance enhancement is mainly attributed to the EMSI modulation of Pt (Supplementary Fig. 26). This phenomenon is distinct from the Pt-doping case, where Pt atoms are incorporated into the TMD lattice and chalcogen atoms are reported as the active sites of HER[33] (Supplementary Note 3, and Supplementary Table 8). Additionally, the Tafel behavior of Pt-SAs/TMDs in acidic HER (~30 mV dec⁻¹) resembles that of the commercial Pt, indicating that the catalytic reaction on single-atom Pt contributed mostly to the HER. In contrast, it has been reported that Pt-doped MoS₂ showed a Tafel slope of 96 mV dec⁻¹, close to that of pure MoS₂ (~100 mV dec⁻¹)[33].

Structure and activity relationship. To evaluate the EMSI effect on the hydrogen adsorption ability of different single-atom Pt catalysts, the highly surface-sensitive ultraviolet photoelectron spectroscopy (UPS) was conducted to probe the occupied electronic states of single Pt atoms on different supports (Fig. 4a). For a free-state single-atom metal, no metallic bonding is formed and thus only the d level exists. The p–d hybridization between single Pt atom and coordinating atom (e.g., S and Se) on the support broadens the d level of single-atom Pt, leading to the formation of a narrower d band around 0–4 eV compared to that of bulk Pt (Fig. 4a and Supplementary Fig. 27)[36–49]. The positions of d-band center for Pt-SAs/WS₂, Pt-SAs/MoS₂, Pt-SAs/MoSe₂, and Pt-SAs/WSe₂ were −2.58 eV, −2.39 eV, −2.24 eV, and −2.06 eV, respectively (Fig. 4a), higher than that of Pt nanocrystal (−2.94 eV)[50]. Due to the EMSI modulation, various density of states patterns were obtained from the DFT calculation for the Pt-d orbitals of the four Pt-SAs/TMDs (Supplementary Fig. 28). The d-band model developed by Norskov and colleagues has been widely used in relating adsorption properties of rate-limiting intermediates to the electronic structure of catalysts[28,50]. According to the d-band theory, when the Pt d band experiences an upward shift, more antibonding states of hydrogen are pulled above the Fermi level, and hence strengthens the affinity of Pt towards hydrogen (Fig. 4b)[28,50]. On the basis of the experimental UPS valence-band spectra (VBS), the H adsorption ability of these single-atom Pt samples can be proposed following the order: Pt-SAs/WS₂ < Pt-SAs/MoS₂ < Pt-SAs/MoSe₂ < Pt-SAs/WSe₂. This trend predicted by the d-band theory also agreed well with the Gibbs free energy of atomic hydrogen adsorption (ΔG₁), Supplementary Fig. 29) obtained from the DFT simulation.

The correlation of electronic structure, hydrogen binding energy (HBE) and acidic HER activity is shown (Fig. 4c) with the average oxidation state of single-atom Pt (determined by XPS and XANES) as x-axis while hydrogen adsorption ability (represented by the d-band center from VBS) as left y-axis and the overpotential required to achieve a current density of 10 mA cm⁻² as the right y-axis. With the increase of average oxidation state of single-atom Pt, the hydrogen adsorption ability also increased in a nearly linear relation (Fig. 4c), implying the EMSI modulation on the adsorption energy of H⁺ intermediates during HER. We showed that the HER activity of the single-atom Pt catalyst decreased monotonically with the increase of average oxidation state and H adsorption ability (Fig. 4c), thus providing solid evidence supporting that HBE is the dominant descriptor in the acidic HER of single-atom Pt. The near ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) further demonstrated that stronger hydrogen adsorption on single-atom Pt with higher valence state (Pt-SAs/WSe₂) led to active site poisoning and slow hydrogen desorption, greatly limiting the overall HER activity (Supplementary Figs. 30, 31).
**Alkaline HER**

Fig. 3 Electrochemical analysis in 1.0 M KOH and 0.5 M H₂SO₄. **a, e** HER polarization curves of various Pt-SAs/TMDs samples. **b, f** HER comparison of overpotentials required to achieve a current density of 10 mA cm⁻² (black arrow, left axis) and mass activities (normalized by the Pt loading, red arrow, right axis) at −100 mV versus RHE for various Pt-SAs/TMDs samples. **c, g** Tafel plots derived from the early stage of the corresponding HER polarization curves. **d, h** Turnover frequency (TOF) curves of various Pt-SAs/TMDs samples and a comparison with the previously reported state-of-the-art values for single-atom HER catalysts.
It is generally accepted that the HER process in acidic and alkaline conditions shares a similar reaction pathway, except for the generation of H* intermediates in alkaline HER through a water dissociation step (Supplementary Fig. 17). We correlated the hydrogen adsorption ability with the HER activity of four single-atom Pt catalysts in alkaline condition. We noted that with increased HBE, the alkaline HER activity of single-atom Pt catalyst increased at low oxidation states (<2.0), which was opposite to that observed in acidic HER (Supplementary Fig. 32). These results partially demonstrate that HBE of single-atom Pt — although is one of the influential factors — is not critical for the single-atom catalytic activity in alkaline HER9. Considering the sluggish water dissociation in the Volmer and Heyrovsky steps (H2O + e− → H* + OH− and H* + H2O + e− → H2 + OH−), which represents an adsorption site during alkaline HER38, we then focused on the contribution of water dissociation.

We propose that such single-atom Pt with high oxidation state is energetically favorable for the adsorption and activation of electron-rich H2O and adsorbed OH intermediates (OH*). The deuterated effect in alkaline HER indicated that water dissociation on single-atom Pt was dominant, as evidenced by the inferior HER activities in D2O than H2O (Supplementary Fig. 33)51,52, which was in good agreement with the Tafel slope analysis. It is well-known that the strong interaction between OH* species and surface of catalysts accelerates the water dissociation process53. Since OH* facilitates the removal of adsorbed CO intermediate53, we used CO stripping voltammetry tests to measure the ability of single-atom Pt catalysts for the water dissociation (Fig. 4d).
Compared to the commercial Pt/C (0.53 V, Supplementary Fig. 34), electron-deficient single-atom Pt catalysts showed much lower onset potential of CO oxidation (0.28–0.46 V), indicating stronger Pt–OH interaction of single-atom Pt and accelerated kinetics of water dissociation (Fig. 4d). On the other hand, single-atom Pt catalyst with higher oxidation state led to a smaller contribution of back-donation of Pt 5d electrons to the 2π* orbitals of CO molecule10,34, thus weakening CO adsorption. The different CO oxidation potential also in turn reflects the variation in the electronic structure of different single-atom Pt catalysts, in line with the XPS and XANES analysis. Additionally, the d-band upshifts of the four Pt-SAs/TMDs samples (Fig. 4a and Supplementary Fig. 2b) also imply an improved water dissociation ability due to the increased OH* binding energy35–37, consistent with the CO stripping measurement (Fig. 4d). With an increase of the average oxidation state of single-atom Pt, the Pt–OH interaction became stronger while the alkaline HER activity showed a volcano-type relationship (Fig. 4e). The single-atom Pt catalyst with the average oxidation state of approximately +2 (volcano’s top) exhibited exceptional alkaline HER activity.

Discussion

In this work, we demonstrate that EMSI modulation of single-atom Pt significantly regulates the HER activity over a wide-pH range, and systematically unravel the relationship between oxidation state and HER activity of single-atom Pt. The EMSI—acting as a bridge between electronic study and catalyst design—provides a detailed explanation of the enhanced properties of supported catalysts at the electronic scale. With the length scale of catalysts shrinking to the atomic level, the EMSI effect becomes stronger and can predominate the reaction rate24,41. The strong EMSI between the single-atom Pt and TMDs support redistributes the electron density around the metal center with the direct formation of metal–support bonds, facilitating the electron transfer from the active metal center to the reactant. The changes in the oxidation state of single-atom Pt can be the direct effect from EMSI, which acts as a useful approach to quantitatively determine the strength of EMSI. The technical characterizations (e.g., XPS, XAS; Fig. 2) of the oxidation state pave the way for revealing the underlying mechanism of the target reaction, which in turn enhances the comprehensive understanding of EMSI and electronic structures across the length scales. Apart from changes in the electronic structure of active sites, the stabilization effect is also a basic influence of EMSI, which suppresses the migration of single-atom metals even under operating conditions (Supplementary Figs. 23 and 24).

Figure 5 shows the EMSI modulation mechanism of electrocatalytic HER on the single-atom Pt. a Surface intermediate on single-atom Pt modified electrode in the acidic condition. k represents the kinetics rate of H2 desorption. With the increase in oxidation state of single-atom Pt, the kinetics rate of H2 desorption (k) decreases. b Surface intermediate on single-atom Pt modified electrode in the alkaline condition. k1 and k2 represent the kinetics rates of water dissociation and H2 desorption, respectively. With the increase in oxidation state of single-atom Pt, the kinetics rate of water dissociation (k1) increases while the kinetics rate of H2 desorption (k2) decreases. EDL represents the electric double layer.

From the structure–activity relationship, the fine control over the oxidation state of single-atom Pt catalysts enables to achieve the optimal catalytic activity in either acidic or alkaline HER. In acidic environment, the HER performance could be well optimized through properly decreasing the oxidation state of single-atom Pt (Fig. 5a), accelerating the hydrogen desorption process. Similar to our finding, Liang’s and Yao’s groups have recently reported that the electron-enriched or near-zero-valence atomically dispersed Pt species are more active than the high-valence single-atom Pt for catalyzing acidic HER39,40. In alkaline environment, as the oxidation state of single-atom Pt increases, the HER activity also increases initially (left side of the volcano plot, Fig. 4e). Under the electrochemical condition, the charge of the metal plays a decisive role with regard to water dissociation38,39. Choi’s group reported the counterintuitive promoting effect of CO molecule on alkaline HER of single-atom Pt25, which could be also explained by our proposed model (Fig. 5b). After the coordination of CO (strong electron acceptor), metal-to-ligand charge transfer from Pt was increased, endowing the single-atom Pt site with higher oxidation state (ca. +2–2.3). Such single-atom Pt site was more electrophilic and favorable for the water dissociation, thus accelerating the alkaline HER. The opposite trends in acidic and alkaline HER (Fig. 4c, 4e) indicate the different mechanistic pathways of HER depending on the pH conditions, consistent with the previously reported works25,60.

We further suggest that single-atom Pt with optimal valence state is simultaneously favorable for water dissociation, adsorption/desorption of OH* and H* (Fig. 5b, and Supplementary Fig. 35). It should be noted that with the increased oxidation state of single-atom Pt, the adsorption of H* and OH* on the catalyst were both strengthened. Although single-atom Pt with high oxidation state energetically favors the adsorption of electron-rich H2O and OH*, too strong hydrogen adsorption will also lead to the slow release of active sites and hence the sluggish HER kinetics. From a fundamental point of view, the present work reveals the atomic-level enhancement of HER thermodynamically and kinetically by optimizing the catalyst–H interaction and accelerating the water dissociation, respectively. The single-atom Pt catalyst with optimal oxidation state (+2), showed neither
too strong Pt–H interaction to release hydrogen, nor too weak Pt–OH interaction to dissociate water, which dramatically contributes to the overall alkaline HER.

To date, three widely adopted theories have emerged to explain the alkaline HER mechanism: water dissociation theory (hydroxyl binding energy, OHBE), hydrogen binding energy (HBE) theory, or interface water and/or anion transfer theory29. It still remains unclear which descriptor governs the alkaline HER. At the atomic level, our results show that the two descriptors (OH* and H*) co-determined the rate of alkaline HER (Fig. 5b), which sheds light on the long-standing puzzle about HER mechanism. Although a quantitative contribution of the water dissociation and hydrogen desorption in alkaline HER is beyond the scope of the current work, the structure–activity relationship bridges a previously unconsidered link between oxidation state and wide-pH-range HER activity. Owing to the limitation of the EMSI-induced TMDs support modulation in the current work, the oxidation state of single-atom Pt was mostly restricted to a record level of +1 or +2 H2. Further, more researches about the structure–activity relationship could be extended to the near-zero-valence single-atom metal or even negatively charged ultrasmall metal clusters. Apart from the oxidation state of single-atom metals, many complicated factors (e.g., coordination environment, reactive interface, interfacial water orientation)44,53,58–62 could also be considered for the development of structure–activity relationship and the rational design of high-performance HER catalysts.

In summary, the EMSI-induced variation in oxidation state of single-atom Pt catalyst effectively modulates the acidic and alkaline HER. The improved HER arises from optimized thermodynamics of HER for hydrogen adsorption and accelerated reaction kinetics for water dissociation. The oxidation state of single-atom Pt controls the catalytic activity towards HER by virtue of modulating the Pt–H/Pt–OH interactions. Such atomic-level understanding of the structure–activity relationship helps to shed more insights into other single-atom electrocatalytic reduction reactions, which also involve water dissociation or hydrogen adsorption/desorption steps in carbon dioxide reductions and nitrogen reduction reactions.

**Methods**

**Materials.** Molybdenum(iv) sulfide (MoS2) powder, molybdenum(iv) selenide (MoSe2) powder, tungsten(iv) sulfide (WS2) powder, n-butyllithium in cyclohexane (2.0 M), copper(II) sulfate pentahydrate (CuSO4·5H2O), potassium carbonate (K2CO3), hydrochloric acid (HCl), sulfuric acid (H2SO4), methanol (CH3OH), ethanol (C2H5OH), glacial acetic acid (CH3COOH), sodium hydroxide (NaOH), glycerol, sulfuric acid, potassium chlorate (KClO3), potassium hydroxide (KOH), perchloric acid (HClO4), tetrabutylammonium hydroxide (TBAB), sodium hydrogen carbonate (NaHCO3), hydrogen peroxide (H2O2), potassium hydroxide saturated 0.05 M H2SO4 solution containing 5 mM K2PtCl4. The electrode was kept at +1.0 +2 H2SO4. Further, more researches about the structure–activity relationship could be extended to the near-zero-valence single-atom metal or even negatively charged ultrasmall metal clusters. Apart from the oxidation state of single-atom metals, many complicated factors (e.g., coordination environment, reactive interface, interfacial water orientation)44,53,58–62 could also be considered for the development of structure–activity relationship and the rational design of high-performance HER catalysts.

**Synthesis of Pt-SAs/TMDs.** The single-atom Pt on different ce-TMDs nanosheets (Pt-SAs/TMDs) were synthesized via the site-specific electrodeposition method45. Details of the synthesis of ce-TMDs nanosheets are shown in Supplementary Methods. Briefly, a working electrode was made by drop-casting 5 μL of the well-dispersed ce-TMDs suspension (ce-MoS2, ce-WS2, c-MoSe2, or ce-WSe2) to cover a glassy carbon electrode (GCE, 3 mm diameter. A Cu UPD process was first performed on the ce-TMDs-modified GCE by controlling the potential at +0.10 V vs Ag/AgCl in an Ar-saturated 0.1 M H2SO4 solution containing 2 mM CuSO4. After the UPD process, the GCE was quickly transferred into an Ar-saturated 0.1 M H2SO4 solution containing 2 mM K2PtCl4. The electrode was kept in this solution for more than 20 min at an open circuit potential to ensure a complete galvanic replacement of Cu by Pt(II), forming atomically dispersed Pt decorated ce-TMDs nanohybrid (termed as Pt-SAs/TMDs). All the electrochemical measurements were carried out using a CHI 760E Instrument (Chenhua, China) at room temperature.

**Physical characterization.** Transmission electron microscopy (JEOL JEM-2100, Japan) and field emission electron microscopy (JEOL JEM-2800, Japan) were utilized to characterize the morphologies and elemental maps of catalysts. The atomic force microscopy (AFM) measurements were carried out using a commercial AFM (Bruker, Dimension FastScan, Icon Scanner, USA). High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) characterizations were carried out on a FEI Titan3 G2 60-300 equipped with double aberration correctors, which was operated at 200 kV. X-ray diffraction patterns (XRD, XTRA, Switzerland) were collected to characterize the crystal structures of samples. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the loading of single-atom Pt in Pt-SAs/TMDs on a CHN-O-Rapid (Germany). The samples were each dispersed in a Teflon-lined autoclave at 230 °C for 12 h. The X-ray absorption spectroscopy at the Pt L2,3-edge was observed at the 14W1 beam line of the Shanghai Synchrotron Radiation Facility, using a Si(111) double-crystal monochromator operated at 3.5 GeV in fluorescence mode. The oxidation states/formal d-band hole counts of different single-atom Pt catalysts can be determined quantitatively by integrating the white-line area34. Specifically, the differential XANES (ΔXANES) spectra were obtained by subtracting the spectra of Pt-SAs/TMDs from that of Pt foil reference (Supplementary Fig. 12). Owing to the linear relationship between the white-line area and the oxidation states/formal d-band hole counts, these two parameters of single-atom Pt can be fitted by correlation. All the samples were first exposed to H2 for 2 h before their XPS spectra were collected. The core-level spectra of W 4f, Mo 3d, S 2p, Se 3d, Pt 4f were measured by using the Al Ka source with the kinetic energies at around 1450 eV, 1258 eV, 1324 eV, 1432 eV, and 1414 eV, respectively. The UPS measurements were carried out by using the UVS 10/35 UV source (SuperUPS) in He (21.2 eV). The UPS valence-band spectra of single-atom Pt were obtained by subtraction of the normalized ce-TMDs spectra from the Pt-SAs/TMDs spectra (Supplementary Fig. 19). The pass energy was set at 40 eV for XPS measurements and 2 eV for UPS measurements.

**Electrochemical measurements for HER.** Linear sweep voltammetry (using CHI 760E instrument, Chenhua, China) with scan rate of 20 mV s−1 was conducted in either 0.5 M H2SO4 or 1.0 M KOH solution using an Ag/AgCl electrode (saturated KCl) as the reference, a graphite rod as the counter electrode, and a glassy carbon electrode (GCE) as the working electrode. The Ag/AgCl (saturated KCl) electrode was calibrated with respect to the reversible hydrogen electrode (RHE). In 1.0 M KOH solution, the loading amount of Pt-SAs/MoS2, Pt-SAs/MoSe2, Pt-SAs/WS2, and Pt-SAs/WSe2 on the GCE were 5 μg, 4.35 μg, 5.65 μg and 5.90 μg, respectively, (E(RHE) = E(Ag/AgCl) +1.012 V; in 0.5 M H2SO4 solution, the loading amount of Pt-SAs/MoS2, Pt-SAs/MoSe2, Pt-SAs/WS2, and Pt-SAs/WSe2 on the GCE were 0.625 μg, 0.55 μg, 0.715 μg and 0.85 μg, respectively, (E(RHE) = E(Ag/AgCl) +0.098 V). The commercial Pt/C catalyst ink was prepared by ultrasonically mixing 2 mg of the 12 μL 5% Nafion and 1 mL water/ethanol (v/v, 19) suspension for 1 h. Geometric area of GCE is 0.07065 cm2. Then, 5 μL of the ink was drop-cast onto the GCE and dried naturally in air. The loading amount of Pt was about 28.3 μg cm−2. Before each HER LSV measurement, the catalyst on the electrode was first activated by cyclic voltammetry scanning between 0.05 V and 1.3 V (vs RHE) for 20 cycles at a scan rate of 50 mV s−1 in Ar-saturated electrolyte (1.0 M KOH/0.5 M H2SO4). For CO stripping measurement, pure CO gas was first adsorbed on the working electrode at a fixed potential of 0.1 V Ag/AgCl in a CO-saturated 1.0 M KOH electrolyte for 10 min. All the cyclic voltammograms (CVs) of CO stripping were collected after purging with Ar gas at a scan rate of 20 mV s−1.

The reaction product of hydrogen was measured using a gas chromatograph (GC-2014, SHIMADZU) equipped with a separation column (MS-13X, 80/100 mesh, 3.2 × 2.1 mm × 2.0 m) and a thermal conductivity detector (TCD). Nitrogen was used as the carrier gas in the chromatograph. The parameters were set as follows: column temperature, for ICP TCD temperature, 100 °C; He, bridge current, 60 mA. The TOF of the catalysts was calculated according to the following equation:

\[
\text{TOF} = \frac{1}{(2F \times n)}
\]  

where \(J\) represents the measured current during linear sweep measurement, \(F\) is the Faraday constant (96,500 C mol−1) and \(n\) is the mole amount of active Pt site. The factor 1/2 represents that two electrons in this reaction form one hydrogen molecule (2H* + 2e− → H2).
References

1. Dumesic, J. A. Sustainable hydrogen production. Science 305, 972–974 (2004).
2. Xiao, S. et al. Micro-wave-induced metal dissolution synthesis of core-shell copper nanowires/ZnS for visible light photocatalytic H2 evolution. Adv. Energy Mater. 9, 1900775 (2019).
3. Liu, G. et al. Combining theory and experiment in electrocatalysis: Insights into materials design. Science 355, eaad4998 (2017).
4. Shi, Y. et al. Hot electron of Au nanorods activates the electrocatalysis of hydrogen evolution on MoS2 nanosheets. J. Am. Chem. Soc. 137, 7365–7370 (2015).
5. Shi, Y. et al. Energy level engineering of MoS2 by transition-metal doping for accelerating hydrogen evolution reaction. J. Am. Chem. Soc. 139, 15479–15485 (2017).
6. Luo, M. et al. Strain-controlled electrocatalysis on multilayered nanosheets. Nat. Rev. Mater. 2, 17059 (2017).
7. Wang, X. et al. Strategies for design of electrocatalysts for hydrogen evolution under alkaline conditions. Mater. Today 36, 125–138 (2020).
8. Chen, G. et al. Interfacial electronic effects control the reaction selectivity of platinum catalysts. Nat. Mater. 15, 564–569 (2016).
9. van Deelen, T. W. et al. Control of metal-support interactions in heterogeneous electrocatalysts to enhance activity and selectivity. Nat. Catal. 2, 955–970 (2019).
10. Langkamp, Y. et al. Counting electrons on supported nanoparticles. Nat. Mater. 15, 284–288 (2016).
11. Vayssilov, G. N. et al. Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles. Nat. Mater. 10, 310–315 (2011).
12. Shi, Y. et al. Electronic metal-support interaction to modulate MoS2-supported Pd nanoparticles for the degradation of organic dyes. ACS Appl. Nano Mater. 2, 3385–3393 (2019).
13. Liu, P. et al. Surface coordination chemistry of metal nanomaterials. J. Am. Chem. Soc. 139, 2122–2131 (2017).
14. Wang, X. et al. A heterogeneous single-atom catalyst. Nat. Rev. Chem. 2, 65–81 (2018).
15. Hu, H. et al. Electronic metal-support interactions in single-atom catalysts. Angew. Chem. Int. Ed. 53, 3418–3421 (2014).
16. Chen, Y. et al. Discovering partially charged single-atom Pt for enhanced anti-Markovnikov alkene hydrosilylation. J. Am. Chem. Soc. 140, 7407–7410 (2018).
17. Xue, Z. et al. Efficient and robust carbon dioxide electroreduction enabled by atomically dispersed Sn2+ sites. Adv. Mater. 31, 1808135 (2019).
18. Jiang, K. et al. Single platinum atoms embedded in nanoporous cobalt selenide as electrocatalyst for accelerating hydrogen evolution reaction. Nat. Commun. 10, 1743 (2019).
19. Yang, J. et al. Electronic metal–support interaction of single-atom catalysts and applications in electrocatalysis. Adv. Mater. 32, e2003300 (2020).
20. Kwon, H. C. et al. Carbon monoxide as a promoter of atomically dispersed platinum catalyst in electrochemical hydrogen evolution reaction. J. Am. Chem. Soc. 140, 16198–16205 (2018).
21. Qiao, B. et al. Single-atom catalysis of CO oxidation using Pt2+/Fe3+. Nat. Chem. 3, 634–641 (2011).
22. Li, J. et al. Highly active and stable metal single-atom catalysts achieved by strong metal electronic–support interactions. J. Am. Chem. Soc. 141, 14515–14519 (2019).
23. Navrojk, J. K. et al. Density functional theory in surface chemistry and catalysis. Proc. Natl Acad. Sci. USA 108, 937–943 (2011).
24. Fang, S. et al. Uncovering near-flat platinum single-atom dynamics during electrochemical hydrogen evolution reaction. Nat. Commun. 11, 1029 (2020).
25. Iwasita, T. et al. Adsorption of water at Pt(111) electrode in HClO4 solutions. The potential of zero charge. J. Electroanal. Chem. 411, 95–102 (1996).
26. Makarik-Jirkovsky, J. et al. Design of active and stable Co–Mo–S2 chalcogels as pH-universal catalysts for the hydrogen evolution reaction. Nat. Mater. 15, 197–203 (2016).
Acknowledgements
The authors acknowledge the financial support from Singapore National Research Foundation under the grant of NRF2017NRF-NSFC001-007, NUS Flagship Green Energy Programme, the National Key Research and Development Program of China (2017YFA0206500), the National Natural Science Foundation of China (21902076, 21635004), and the Natural Science Foundation of the Jiangsu Province (BK20190289). The authors thank Prof. Li. Song, Prof. Shuang-Ming Chen, Dr. Yu Wang, and Wen-Jie Xu for assistance in structural analysis. The authors thank Dr. Xiao-Kun Huang and Dr. Yu Wang for his useful discussion on DFT simulations. The authors thank Dr. Zhang-Liu Tian, Dr. Da-Feng Yan, Dr. Wen-Rui Dai, Ms. Yu-Min Da, and Ms. Meng Wang for assistance in the research work. The authors also gratefully thank the Shanghai Synchrotron Radiation Facility (14W1, SSRF).

Author contributions
Y.S., X.X. and W.C. conceived the project. Y.S., Z.M. and Y.X. carried out the synthesis of the catalysts, physical and electrochemical characterizations. Y.Y., W.H. and G.S. assisted in the data analysis. Z.H. and Y.-Y.S. performed the DFT calculations. Y.Z., F.M. and R.H. carried out and assisted in the morphology characterization. Y.S., X.X. and W.C. wrote the manuscript. All authors commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-23306-6.

Correspondence and requests for materials should be addressed to Y.S., X.-H.X. or W.C.

Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2021