RESEARCH ARTICLE

Chaotropic Nanoelectrocatalysis: Chemically Disrupting Water Intermolecular Network at the Point-of-Catalysis to Boost Green Hydrogen Electrosynthesis

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Abstract: Efficient green hydrogen production through electrocatalytic water splitting serves as a powerful catalyst for realizing a carbon-free hydrogen economy. However, current electrocatalytic designs face challenges such as poor hydrogen evolution reaction (HER) performance (Tafel slope, 100 - 140 mV dec^{-1}) because water molecules are thermodynamically trapped within their extensive hydrogen bonding network. Herein, we drive efficient HER by manipulating the local water microenvironment near the electrocatalyst. This is achieved by functionalizing the nanoelectrocatalyst's surface with a monolayer of chaotropic molecules to chemically weaken water-water interactions directly at the point-of-catalysis. Notably, our chaotropic design demonstrates a superior Tafel slope (77 mV dec^{-1}) and the lowest overpotential (0.3 V at 10 mA cm^{-2}_{ECSA}), surpassing its kosmotropic counterparts (which reinforces the water molecular network) and previously reported electrocatalytic designs by up to ~2-fold and ~3-fold, respectively. Comprehensive mechanistic investigations highlight the critical role of chaotropic surface chemistry in disrupting the water intermolecular network, thereby releasing free/weakly bound water molecules that strongly interact with the electrocatalyst to boost HER. Our study provides a unique molecular approach that can be readily integrated with emerging electrocatalytic materials to rapidly advance the electrosynthesis of green hydrogen, holding immense promise for sustainable chemical and energy applications.

Introduction

Achieving efficient electrocatalytic water splitting for green hydrogen production powers our transition towards a sustainable hydrogen economy and the deep decarbonization of our industries.[1] This approach offers the potential for ambient operation and facile integration with green electricity for large-scale implementation, effectively reducing the large carbon footprint and high energy demand associated with modern industrial H_2 production (e.g., steam-methane reforming).[2] Current electrocatalytic designs for improving water splitting primarily focus on reducing the kinetic overpotential in the electrochemical hydrogen evolution reaction (HER).[2c, 3] This typically involves combining metals, transition metals, and carbon-based materials to create functional nanocomposites that promote charge transfer processes and facilitate catalyst-reactant interactions.[4] For instance, the integration of gold nanoparticles with reduced graphene oxide (RGO/Au) sheets has significantly

enhanced the electron transfer process, resulting in higher HER catalytic activity compared to pristine RGO.[5] Despite the improvements in electrocatalytic activity, these nanocomposites still exhibit poor HER performance (Tafel slope, 100 - 140 mV dec^{-1}) and fall considerably short of the benchmark set by Pt electrocatalysts (Tafel slope, ~40 mV dec^{-1}). Furthermore, the fabrication of these electrocatalytic platforms is usually laborious and requires energy-intensive processes due to the use of elevated temperature and pressure conditions.[6]

The surface modification of electrocatalysts emerges as a straightforward solution to address these challenges by regulating a catalyst's surface wettability and electronic properties, thereby enhancing its interactions with protons or water molecules. Common techniques for modifying electrocatalyst's surface include atomic doping, surface defect engineering, and molecular functionalization.[7] For example, the functionalization of multi-aromatic ring porphyrin onto the electrocatalyst has demonstrated strong surface molecule-to-catalyst charge migration, leading to the formation of an electron-rich catalytic surface that enhances HER.[8] Another work reported the use of negatively charged alkynyl molecule to reduce the overpotential (0.5 V at 10 mA cm^{-2}_{ECSA}) for HER by facilitating rapid charge transfer to the reactant species.[9] However, it is worth noting that the alkynyl molecule exhibited a Tafel slope value akin to the control neutral molecules, indicating a slow rate of proton/water transfer to the electrocatalyst which poses a formidable performance bottleneck albeit the rapid charge transfer. This mass transfer limitation also affects other emerging electrocatalytic systems and is notably attributed to the thermodynamic trapping and stabilization of water molecules within their hydrogen bonding network.[10] Consequently, excess energy is needed to overcome these extensive intermolecular interactions and release free water molecules from the hydrogen bonding network for subsequent interactions with the electrocatalytic surfaces, a crucial pre-requisite for electrochemical HER. Moreover, while current research mainly focuses on the catalyst's electronic and/or surface properties, the local chemical microenvironment between the electrocatalytic surfaces and adjacent water molecular network and its effect on electrochemical HER remain elusive.[11]

Herein, we achieve efficient electrochemical HER by applying a self-assembled monolayer of functional molecules onto electrocatalyst's surface to effectively manipulate water hydrogen bonding network directly at the point-of-catalysis (Figure 1A). Our molecule-electrocatalyst strategy comprises two key components. (1) Utilizing nanoporous gold bowl (NPGB) as efficient electrocatalysts with large specific surface area to amplify the effects of surface chemistry and facilitate the charge transfer process. (2) Introducing a chaotropic molecular monolayer on NPGB surfaces to weaken water-water intermolecular interactions and disrupt the water molecular network near the electrocatalyst. This process is expected to enhance the accessibility of free/weakly-bound water molecules on electrocatalytic surfaces, thereby kinetically boosting water splitting for efficient green hydrogen generation. Additionally, we include kosmotropic chemistry for comparison because of its contrasting ability to strengthen the water hydrogen bonding network and retard HER. Our novelty thus lies in controlling water

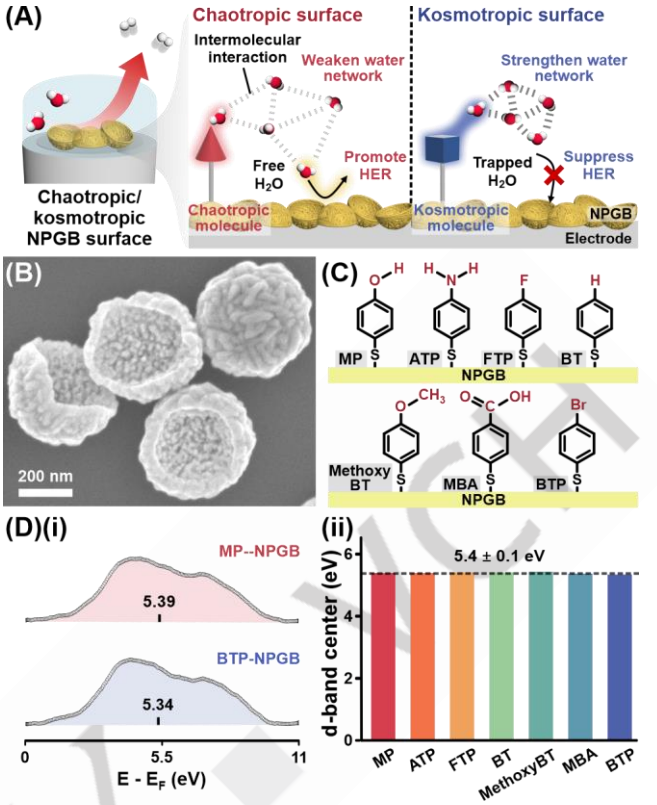

Figure 1. (A) Scheme illustrating the incorporation of chaotropic/kosmotropic surface chemistries onto nanoporous gold bowl (NPGB) nanocatalyst to promote or suppress electrocatalytic hydrogen evolution reaction (HER). (B) SEM image of the as-synthesized NPGBs. (C) Molecular structure of various para-substituted thiolated arenes used for NPGB surface modification. (D) d-band center of various surface-modified NPGBs. (i) XPS spectra of two representative thiol-functionalized NPGBs. (ii) Comparison of d-band center across various surface-modified NPGBs.

molecular network through surface molecular chemistries to boost electrochemical HER, which is distinct from conventional surface modifications that instead aim to promote water uptake but still require additional energy to overcome the strong hydrogen bonding in water.

Comprehensive investigations involving seven different surface chemistries reveal that mercaptophenol-functionalized NPGB exhibits the strongest chaotropic character, achieving a superior Tafel slope value of 77 mV dec^{-1} and the lowest overpotential of 0.3 V at 10 mA cm^{-2}_{ECSA}. This chaotropic electrocatalyst notably has electrocatalytic performance ~2-fold better than its kosmotropic counterpart and ~3-fold higher than other emerging electrocatalytic designs comprising carbon-based materials, transition metals, noble metals, and conventional surface modifications. Simulation study unveils that chaotropic surface chemistry plays a crucial role in disrupting the extensive hydrogen bonding network in water, thereby promoting catalyst-reactant interactions for effective reactant activation and enhanced electrochemical HER. By manipulating the local water microenvironment near an electrocatalyst, our work offers a unique approach to chemically enhance or suppress electrochemical HER. These valuable insights will expedite our

progress towards the efficient production of green hydrogen for sustainable energy and chemical applications.

Results and Discussion

The modification of nanoporous gold bowl (NPGB) surfaces with chaotropic/kosmotropic chemistries plays a vital role in controlling the local water microenvironment near the electrocatalyst to enhance electrochemical hydrogen evolution reaction (HER; Figure 1A). We employ NPGBs as the model electrocatalyst because of their large specific surface area and high catalytic activity. These nanoparticles are prepared through a two-step seed-mediated synthesis using polyvinylpyrrolidone (PVP) surfactant as a capping agent, whereby NPGB is initially deposited on AgCl nanocube template via in-situ reduction of Au^{3+} ions, followed by the chemical etching of AgCl template to yield the NPGB (Figure S1).[12] The as-synthesized NPGB displays a hollow bowl-like structure (diameter, 432 ± 42 nm) consisting of uniform and interdigitated ligaments (thickness, 21 ± 4 nm; Figure 1B, Figure S2). The chemical identity of NPGB is affirmed as Au^0 metal by its distinct diffraction patterns and spectral features in X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and surface-enhanced Raman spectroscopy (SERS) characterizations (Figure S3-7), respectively.

To incorporate the designed surface chemistries on the electrocatalyst, we chemisorb a self-assembled monolayer of thiolated molecules onto NPGB surface by utilizing the strong affinity of the sulfhydryl functional group (-SH) for gold. Our study involves seven different para-substituted thiolated arenes to provide crucial insights into the relationships between surface molecules-water interactions, the water hydrogen bonding network, and the resulting electrochemical HER performance (Figure 1C, S7). The model thiols include 4-mercaptophenol (MP), 4-aminothiophenol (ATP), 4-fluorothiophenol (FTP), benzenethiol (BT), 4-methoxybenzenethiol (MethoxyBT), 4-mercaptobenzoic acid (MBA), and 4-bromothiophenol (BTP). These para-substituted chemical groups are expected to interact differently with water molecules through various intermolecular interactions, such as hydrogen bonding and dipole interactions. We observe that the NPGBs retain their structural integrity even after the surface modification. Surface-sensitive XPS and SERS measurements jointly ascertain the successful modification of NPGB surfaces with various thiolated molecules. This is evident from the appearance of characteristic Au 4f and S 2p XPS features of Au-S chemical bond, as well as from the presence of the vibrational fingerprints of respective thiolated molecules (Figure S8, S9).[13] For instance, MP-functionalized NPGB (MP-NPGB) exhibits a unique C-O stretching at 1251 cm^{-1}, while BTP-grafted NPGB (BTP-NPGB) displays the distinct C-Br stretching mode at 1073 cm^{-1}.[14] These results provide concrete evidence that the functional molecules are indeed chemically attached to the NPGB via the thiol moiety, with the para-substituent readily exposed to the water molecular network to facilitate their intermolecular interactions. We also note consistent SERS intensity (<10% deviation) even after an additional cycle of surface modification (Figure S10). This observation underscores the full and uniform coverage of the self-assembled molecular monolayer on NPGB surface, thereby eliminating potential experimental deviations due to incomplete/partial molecular coverage. From this point forward, we will refer to these molecule-electrocatalyst hybrids as “XX-NPGB”, with “XX” representing the surface molecule attached to the NPGB.

Notably, electrocatalytic activity is commonly reported to be influenced by the surface, electronic, and structural properties of the electrocatalyst. To accurately assess the effect of chaotropic/kosmotropic surface chemistry on electrochemical HER, we first investigate and eliminate potential complications that could arise from variations in NPGB’s (1) crystallite sizes, (2) chemical states and d-band centers, and (3) surface wettability. It is noteworthy that d-band center is a critical catalytic descriptor as the position of a metal’s d-band center strongly affects its adsorption capacity with active reactants and the associated HER initiation step (Figure 1D-i). Comprehensive characterizations of the surface-modified NPGBs highlight three crucial findings. First, XRD analyses of NPGB before and after surface modification reveal similar diffraction patterns and crystallite size (~10 nm; Figure S11, Supplementary information 1), indicating that the chemisorption process does not affect NPGB’s intrinsic structural/crystal property. Second, XPS measurements show consistent binding energies of Au^+ and Au^0 chemical species and similar d-band center values of ~5.4 eV across all seven surface-modified NPGBs (Figure 1D-ii, S12). This is concrete evidence that the para-substituent on the thiolated molecules does not have significant effect on NPGB’s surface electron density and electronic structure. Third, our model thiolated molecules confer similar hydrophilic properties to the NPGB surfaces (contact angle, θ <90°, Figure S13). Given the similar intrinsic structural, electronic, and wettability characteristics of these surface-modified NPGBs, we effectively exclude their potential contribution to any subsequent changes in electrocatalytic activity. This demonstration ensures a representative examination of chaotropic/kosmotropic effects on electrochemical HER.

As a proof-of-concept demonstration, we employ these thiol-modified NPGBs as electrocatalysts and begin by tuning their mass loadings and structural configurations to optimize electrochemical HER (Figure 2A). The former affects the electrochemical surface area (ECSA) available for electrocatalysis, while the latter influences intrinsic catalytic activity of the material. Our electrocatalytic setup consists of a three-electrode system; the working electrode is prepared by depositing NPGB onto glassy carbon, with Pt wire serving as the counter electrode, Ag/AgCl (3M KCl) as the reference electrode, and 0.5 M aqueous H_2SO_4 solution as the electrolyte solution. We choose glassy carbon as a current collector for NPGB because it is electrocatalytic inactive and does not interfere with current measurements within the target potential window (0 to -0.6 V vs NHE) during water electrolysis (Figure S14). Cyclic voltammetry measurements reveal an initial increase in ECSA as the NPGB mass loading increases from 0.04 to 0.16 mg (Figure S15A). Further increments in NPGB mass loading beyond 0.16 mg do not improve ECSA but result in a plateau due to the saturation of NPGB coverage on the glassy carbon electrode (Figure S15B).

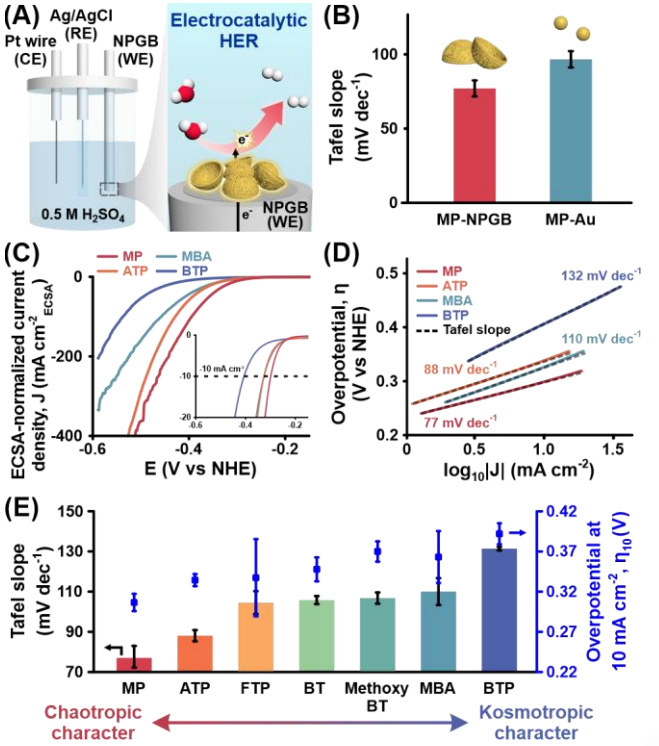

Figure 2. (A) Electrocatalytic setup for hydrogen evolution reaction (HER) using NPGB-deposited glassy carbon electrode as working electrode. (B) Tafel slope of Au-based electrocatalysts with similar MP surface modification. (C) ECSA normalized linear sweep voltammograms (LSV) and (D) the corresponding Tafel plots of various surface-modified NPGB electrocatalysts. Inset: magnified LSV to illustrate the overpotential at 10 mA cm^{-2}_{ECSA}. (E) Comparison of Tafel slope values and overpotentials at 10 mA cm^{-2}_{ECSA} (η_{10}) across various surface chemistries.

Moreover, we also compare our MP-NPGB with control electrocatalytic platform composed of Au nanoparticles (MP-Au) of similar size to that of NPGB's ligament. MP-NPGB clearly demonstrates ~1.3-fold superior electrocatalytic activity (Tafel slope, 77 mV dec^{-1}) compared to control MP-Au (Tafel slope, 97 mV dec^{-1}; Figure. 2B, Figure S16), even though both electrocatalytic platforms are constructed from Au and share the same surface chemistry. This finding underscores the importance of NPGB's open structure and nanoporosity in improving electrochemical HER through its large specific surface area which enhances the charge transfer process and facilitates extensive surface molecule-water interactions. Hereon, we standardize the use of NPGB as an efficient electrocatalyst with an optimized mass loading at 0.175 mg for subsequent evaluations of electrochemical HER performance (Table S1).

Having established the optimal electrocatalyst parameters, we compare the electrochemical HER performance across various NPGB platforms to uncover the effects of chaotropic/kosmotropic surface chemistries on the electrocatalytic water splitting process. We assess electrocatalytic performance using common metrices, such as current density, overpotential (at 10 mA cm^{-2}_{ECSA}), and Tafel slope value, to facilitate direct comparisons with previously reported electrocatalytic designs. It is worth noting that an efficient electrocatalyst is typically associated with high current density (indicating increased electrochemical reactions), low overpotential (reflecting a reduced kinetic activation barrier), and a lower Tafel slope value (a kinetic parameter influenced by proton transfer to the electrocatalyst; to be discussed in detail in next paragraph).[10, 15] Among the seven distinct surface chemistries, MP-NPGB notably demonstrates the best electrochemical HER performance by having the highest current density of -360 mA cm^{-2}_{ECSA} at 0.5 V and lowest overpotential of 0.3 V at 10 mA cm^{-2}_{ECSA} (Figure 2C, Figure S17A). Following MP-NPGB are ATP-, FTP-, BT-, MethoxyBT-, MBA-, and BTP-NPGB, showing a diminishing trend in current density and an increasing trend in overpotential, both of which indicate declining electrocatalytic activity. We also observe that MP-NPGB exhibits 7-fold and 1.3-fold more superior current density and overpotential compared to BTP-NPGB (current density, -50 mA cm^{-2}_{ECSA} at 0.5 V; 0.4 V at 10 mA cm^{-2}_{ECSA}) despite having similar surface hydrophilicity. This observation implies that differences in electrochemical HER performance among these surface chemistries arise from the variation of surface molecule-water chemical interactions rather than an increase in water uptake due to higher hydrophilicity.

More importantly, the Tafel slope values derived from the current-voltage polarization curves again ascertain MP-NPGB as the best-performing electrocatalyst and provide valuable insights into the origin of its superior HER performance. Tafel slope value -highligreflects the HER reaction kinetics, whereby a lower Tafel slope (less steep) value indicates the need for less overpotential to reach the same current density.[16] Furthermore, it sheds light on HER reaction mechanism which generally involves two elementary steps, including (i) adsorption and discharge of proton onto the active site (Volmer reaction) and (ii) desorption of H_2 gas from active site (Tafel or Heyrovsky reactions). Specifically, Tafel slope values >40 mV dec^{-1} indicate that the rate-determining step involves proton adsorption and discharge, whereas values <40 mV dec^{-1} suggest a slow hydrogen gas desorption step. The observed trend in electrocatalytic activity derived from Tafel slope values closely aligns with those obtained from current density and overpotential. That is, MP-NPGB again outperforms other thiolated molecules by achieving the lowest Tafel slope value of 77 mV dec^{-1}, followed by ATP- (88 mV dec^{-1}), FTP- ~ BT- ~ MethoxyBT- (105-107 mV dec^{-1}), MBA- (110 mV dec^{-1}), and BTP-NPGB (132 mV dec^{-1}; Figure 2D-E, Figure S17B). We also note that all these Tafel slope values exceed 40 mV dec^{-1}, signifying that the rate-determining step involves the transfer of proton/water to the electrocatalyst surface for adsorption and discharging. These results evidently highlight that the MP-NPGB is the most effective surface chemistry in accelerating the proton adsorption process on the electrocatalytic site, achieving HER kinetics up to 1.7-fold better than other surface chemistries.

Our findings collectively suggest that MP-NPGB's superior electrochemical HER performance stems from its chaotropic character, which effectively perturbs the water hydrogen bonding network to improve water/proton accessibility to the electrocatalyst surface. We further employ density functional theory (DFT) simulations to understand the molecular origins of the enhanced water electrolysis process facilitated by MP-NPGB (Figure 3A). This investigation focuses on three crucial

parameters, including (i) the entropy of water molecule (S_{water}), (ii) the bond order of H_2O-Au interactions, and (iii) the intramolecular

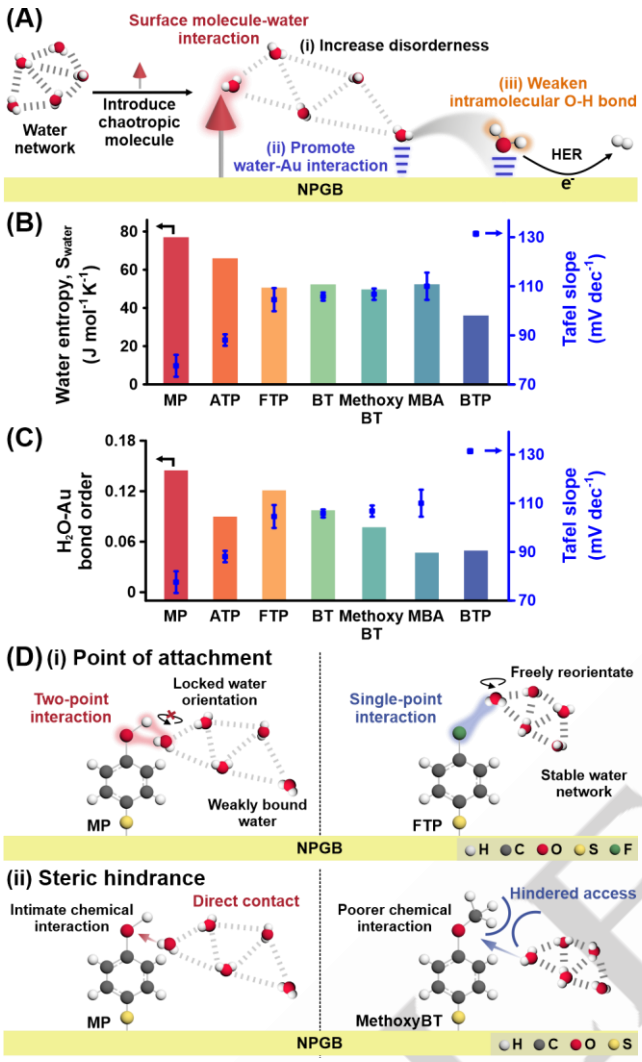

Figure 3. (A) Schematic illustration on the effects of chaotropic surface chemistry on the water hydrogen bonding network and the resulting surface molecule-water-catalyst interactions during electrochemical HER. DFT-simulated (B) entropy of water molecule (S_{water}) and (C) the cumulative water-Au bond order of various surface-modified NPGBs. These simulated parameters are also compared with the experimental Tafel slope values. (D) Scheme depicting the effects of (i) point of attachment and (ii) steric hindrance rendered by the para-substituent on the water hydrogen bonding network.

O-H bond order of the water molecule nearest to the NPGB. On the one hand, the simulated entropy assesses changes in the disorderness/randomness of the water network near the electrocatalyst surface that arise from surface molecule-water interactions, an important parameter for identifying potential chaotropic or kosmotropic effects. Chaotropic molecules are expected to disrupt water hydrogen bonding network, consequently increasing the entropy of water molecule. On the other hand, bond order reveals the strength of chemical interactions between two chemical species resulting from changes in the water molecular network (i.e., alterations in water system entropy) due to surface molecule interactions. For instance, a higher H_2O-Au bond signifies stronger water-electrocatalyst interaction, while a lower intramolecular O-H bond order of a water molecule indicates a weaker bond that can easily break to enhance proton adsorption on the electrocatalyst surface. Our simulation model comprises a thiolated molecule attached to a gold cluster via Au-S bonds whereby its para-substituent is exposed for interaction with the water molecular network.

Notably, the corroboration of simulation and experimental studies unveil three key observations. First, we find an inverse relationship between the simulated S_{water} and the experimentally measured Tafel slope values (Figure 3B, Supplementary information 2). This correlation indicates that increasing the randomness of the water molecular network enhances electrochemical HER, leading to lower Tafel slope value. For example, MP-NPGB featuring the highest electrochemical HER activity (Tafel slope, 77 mV dec^{-1}) showcases the most pronounced chaotropicity, as evident from the highest degree of disorder in the water molecule (e.g., largest S_{water} of 77 J $mol^{-1}K^{-1}$). In contrast, BTP-NPGB with the poorest electrocatalytic performance (Tafel slope, 132 mV dec^{-1}) possesses the strongest kosmotropic character (i.e., least chaotropic) by having the lowest S_{water} of 36 J $mol^{-1}K^{-1}$. Second, MP-NPGB exhibits 3-fold increase in H_2O-Au bond order when compared to BTP-NPGB. This observation implies that increasing disorderness in the disrupted water hydrogen bonding network compels water molecules towards the Au surface, resulting in stronger interactions between the reactant and the electrocatalyst (Figure 3C). Third, we observe that the intramolecular O-H bond of the interacting water molecule has the lowest bond order when in the presence of chaotropic MP-NPGB (bond order, 1.63; Figure S18). The bond order gradually increases across the different surface chemistries in similar trend, reaching the highest value of 1.67 for kosmotropic BTP-NPGB. The weakening of the intramolecular O-H bond by MP-NPGB enhances the tendency of proton adsorption and discharge on the electrocatalytic surface during HER. This observation aligns well with our results from Tafel plots and overpotential, which also indicate a faster proton transfer process and a reduced kinetic activation barrier, respectively.

Interestingly, we also note that the hydrophilic BTP-NPGB yields similar Tafel slope (132 mV dec^{-1}) values to those of the hydrophobic dodecanethiol-functionalized NPGB (DDT-NPGB; 133 mV dec^{-1}). It is worth mentioning that DDT-NPGB (long-alkyl thiolated molecule) lacks functional groups that can interact with water, thereby allowing water molecules to still form an extensive hydrogen bonding network around the hydrophobe, akin to a cavity effect (Figure S19, S20). Based on these comparisons, we infer that the strong kosmotropic effect of BTP-NPGB facilitates the formation of a highly ordered water molecular network similar to that observed with hydrophobic DDT-NPGB. These finding highlight that manipulating surface chemistry to regulate the local water microenvironment near the electrocatalyst surface may have a more significant impact on enhancing electrocatalysis compared to simply improving surface wettability.

Our thermodynamic and chemical bond analyses jointly reveal vital mechanistic insights into the effects of chaotropic/kosmotropic surface chemistries on the electrochemical HER process. In the presence of chaotropic MP-

NPGB, surface molecule-water interactions disrupt water-water interactions which hinder the optimal positioning and orientation of water molecules for extensive intermolecular hydrogen bonding. This disruption process leads to the formation of a highly disorganized and destabilized water network (e.g., higher S_{water}), where water molecules exist as free or weakly-bound entities. Consequently, the enhanced availability of free water molecules near the electrocatalytic surfaces promotes stronger reactant-electrocatalyst chemical interactions through the H_2O-Au linkage (e.g., higher H_2O-Au bond order), favoring the water adsorption process. The intimate H_2O-Au interaction weakens the intramolecular O-H bond of water molecule (e.g., reduced O-H bond order of water molecule), possibly due to the stronger steric repulsion arising from the close contact between Au surface and the reactant. As a result, the water's O-H bond is activated which facilitates the discharge of protons and their adsorption on the electrocatalyst surface for subsequent electrochemical HER. By facilitating water adsorption and proton discharge processes, these two phenomena notably promote the Volmer process to kinetically boost the HER (e.g., low Tafel slope and low overpotential). In contrast, the presence of a more kosmotropic molecule (e.g., BTP) strengthens water-water interactions to induce an organized water hydrogen bonding network (e.g., lower S_{water}). The stabilized water network thermodynamically traps water molecules, reducing the availability of free or weakly-bound water molecule for adsorption on the Au electrocatalytic surfaces (e.g., lower H_2O-Au bond order). This phenomenon results in a less effective activation of water's intramolecular O-H bond (e.g., higher intramolecular O-H bond order of water), thereby hindering the proton transfer processes and suppressing electrochemical HER. Therefore, it is evident that chaotropic and kosmotropic chemistries can influence the water hydrogen bonding network and the corresponding electrocatalytic water splitting process.

To understand the molecular origin of the chaotropic and kosmotropic properties in various surface chemistries, we further study the energy-optimized molecular configurations between surface-modified NPGBs and the water system. Interestingly, we identify three key factors governing the chaotropicity or kosmotropicity of a functional molecule. (1) The surface molecules must possess the ability to interact with water molecule(s) through intermolecular forces like hydrogen bonding or dipole-dipole interaction. Moreover, the strength of the surface molecule-water interaction should be strong to exert effective control over both the orientation and position of adjacent water molecule, allowing them to either constructively or destructively interfere with the water hydrogen bonding network. Taking BTP and MP as examples, MP's hydroxyl (-OH) group interacts strongly with water molecule via hydrogen bonding, whereas BTP can bind water molecule only through weaker dipole-dipole interactions with the bromine atom. The loose BTP-water interaction permits a higher degree of water molecule movement, facilitating its re-orientation to maximize water-water interactions for the formation of a stable, organized water network. (2) The presence of neighbouring electron donor and acceptor atoms on the thiolated molecule is essential to enhance the chaotropicity of a surface molecule, as evident when comparing MP-NPGB and FTP-NPGB which contain electron-rich O-atom and F-atom, respectively. However, MP leans towards chaotropicity while FTP has more kosmotropic character. The disparity in chemical properties arises from MP's additional ability to bind water

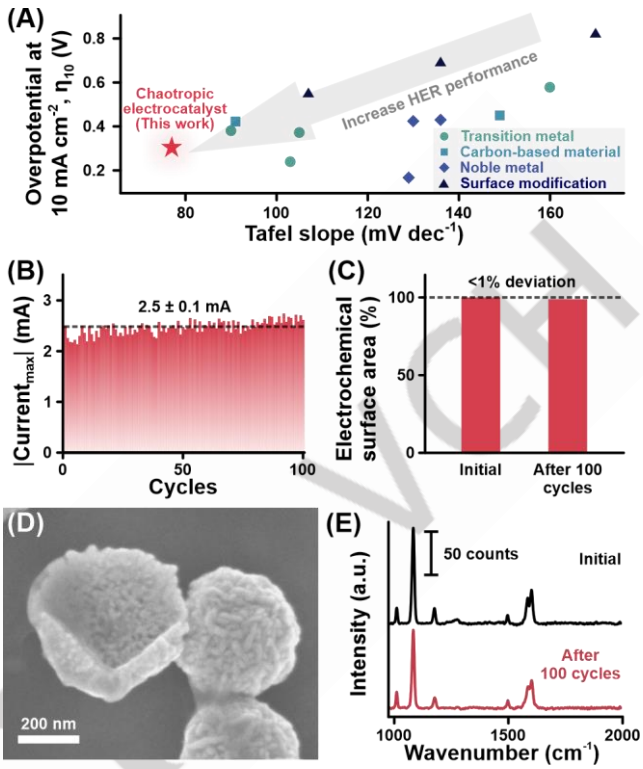

Figure 4. (A) Comparison of our chaotropic electrocatalyst (MP-NPGB) with other reported electrocatalytic platforms involving transition metals, carbon-based materials, noble metals, and conventional surface modifications. (B) Maximum current responses of electrocatalytic HER recorded from MP-NPGB over 100 cycles. (C) MP-NPGB's electrochemical surface area before and after the cyclability test in (B). (D) SEM image and (E) SERS spectra of MP-NPGB after electrocatalysis.

molecule via a two-point chemical attachment involving the H-atom and O-atom of the hydroxyl (-OH) group (Figure 3D-i). This bidentate-like interaction plays a vital role in locking the orientation of water molecule in three-dimensional space, as well as blocking two out of the four hydrogen bonding sites on the water molecule to prevent its extensive interactions with nearby water molecules. This chemical effect consequently creates disorder in the water network near the electrocatalytic surfaces. (3) Steric hindrance in the para-substituent can obscure effective surface molecules-water interaction, leading to lower chaotropicity. To illustrate this point, we first compare MP's -OH group with MethoxyBT's -OCH_3 group. While both MP and MethoxyBT contains an oxygen donor atom, the presence of a bulky methyl group on the donor atom in the latter induces steric repulsion and drastically increase its oxygen-water bond length to 2.09Å. In contrast, MP exhibits a shorter oxygen-water bond length of 1.98Å (Figure 3D-ii). The weakening of Methoxy-water interaction results in less control over the water molecule mobility, allowing it to easily reorient itself to maximize hydrogen bonding with neighbouring water molecules. It is noteworthy that these rules of thumb provide valuable insights for designing functional

surface chemistry to address the additional thermodynamic penalty arising from the extensive hydrogen bonding in the water network during electrocatalytic water splitting.

More importantly, the chaotropic electrocatalyst (MP-NPGB) outperforms other emerging electrocatalytic designs based on carbon-based materials, transition metals, and/or noble metal electrocatalysts, achieving up to 2-fold better Tafel slope value and ~2-fold reduction in the overpotential required for HER (Figure 4A, Table S2).[4a, 5, 17] Our unique approach for manipulating local water microenvironment also demonstrates up to ~2-fold and ~3-fold superior performance in terms of proton transfer kinetics and HER overpotential, respectively, when compared to conventional surface modification methods. [7a, 9] The improvements in both parameters clearly emphasize MP-NPGB's ability to boost both charge transfer and proton transfer processes, thereby accelerating the water electrolysis process. Our chaotropic electrocatalyst also exhibits high electrochemical and physical robustness, as evident from the consistent current density (<5% deviation) and ECSA (<1% deviation) even after 100 repeated electrocatalytic cycles (Figure 4B-C, Figure S21). Moreover, the surface-modified electrocatalytic platform maintains its structural stability and crystallinity after electrocatalysis (Figure 4D). We also affirm that the surface molecular layer remains chemically intact on NPGB surfaces throughout the electrochemical HER through SERS characterization (Figure 4E).

Conclusion

In conclusion, we have achieved efficient electrochemical hydrogen evolution reaction (HER) by introducing a novel surface molecular tool based on chaotropic/kosmotropic chemistry to manipulate water intermolecular network directly at the point-of-catalysis. This molecule-electrocatalyst design plays a crucial role in overcoming the extensive hydrogen bonding network between water molecules, thereby facilitating the electrocatalytic water splitting process. Our systematic investigations across seven different surface chemistries reveal that the chaotropic electrocatalyst delivers a superior Tafel slope of 77 mV dec^{-1} and the lowest overpotential of 0.3 V at 10 mA cm^{-2}_{ECSA}. More importantly, the chaotropic electrocatalyst outperforms its kosmotropic counterparts by ~2-fold and demonstrates up to a ~2-fold and ~3-fold enhancements in proton transfer kinetics and HER overpotential, respectively, when compared to other emerging electrocatalytic designs comprising carbon-based materials, transition metals, noble metals, and conventional surface modifications. Both experimental and simulation studies confirm the vital role of chaotropic surface chemistry in disrupting water-water intermolecular interactions. This disruption of the hydrogen bonding network promotes intimate catalyst-reactant interactions and the corresponding weakening of water's intramolecular O-H bond, thereby kinetically promoting the proton discharge processes for enhanced HER.

By enabling the effective control over the local water microenvironment, our unprecedented work on chaotropic/kosmotropic chemistries offers a unique perspective for chemically enhancing or suppressing electrochemical HER. These valuable insights can also be integrated with other emerging HER electrocatalysts, as well as extended to diverse water-related reactions and various energy/environmental catalysis where water molecules interfere, such as the carbon dioxide reduction reaction and nitrogen reduction reaction. Future work can also be directed towards further experimental validation of water molecules entropy and specific changes to hydrogen bond to unravel the molecular effects of chaotropic/kosmotropic chemistry during electrochemical HER. We envision that advancements in both (1) functional surface chemistry and the (2) development of efficient electrocatalytic materials will work in parallel, jointly accelerating our progress towards efficient green hydrogen production and the realization of an ideal, sustainable hydrogen economy.

Acknowledgements

H.K.L. thanks the funding supports from the Singapore Ministry of Education (AcRF Tier 1 RS13/20 and RG4/21), A*STAR Singapore (AME YIRG A2084c0158), the National University of Singapore Center of Hydrogen Innovation (CHI-P2022-05), and the Nanyang Technological University start-up grants. The research was conducted as a part of NICES (NTU-IMRE Chemistry Lab for Eco Sustainability; REQ0275931), a joint research initiative between Nanyang Technological University (NTU) and Institute of Materials Research and Engineering (IMRE) from Agency for Science, Technology, and Research (A*STAR).

Keywords: Chaotropic • Kosmotropic • Hydrogen Evolution Reaction • Electrocatalysis • Nanomaterials

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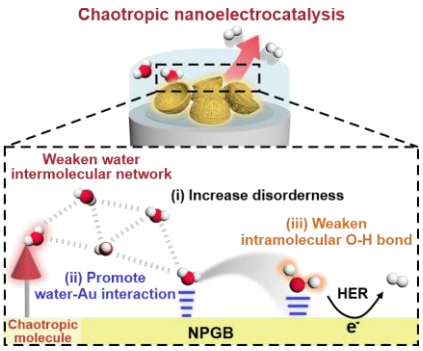

Chaotropic electrocatalyst chemically disrupts water intermolecular networks at the point-of-catalysis to release free/weakly bound water, promoting intimate catalyst-reactant interactions and proton discharge processes for efficient green hydrogen production. Our molecule-electrocatalyst design demonstrates 2-fold and 3-fold better Tafel slope and overpotential when compared to its kosmotropic counterparts and emerging electrocatalytic designs.