

# Decoupled Redox Catalytic Hydrogen Production with a Robust **Electrolyte-Borne Electron and Proton Carrier**

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the decoupling of both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) from the electrodes to two spatially separated catalyst bed reactors in alkaline solutions. Through a pair of close-loop electrochemicalchemical cycles, the system operates upon 7,8-dihydroxy-2-phenazinesulfonic acid (DHPS) and ferricyanide-mediated HER and OER, respectively, on Pt/  $Ni(OH)_2$  and  $NiFe(OH)_2$  catalysts. Near unity faradaic efficiency and sustained production of hydrogen has been demonstrated at a current density up to 100 mA/cm<sup>2</sup>. The superior reaction kinetics, particularly the HER reaction



mechanism of DHPS as a robust electrolyte-borne electron and proton carriers, were scrutinized both computationally and experimentally. We anticipate the system demonstrated here would provide an intriguing alternative to the conventional water electrolytic hydrogen production.

# INTRODUCTION

With the increasing concerns on energy and the environment, there has been an increasing demand for clean and renewable energy sources to replace fossil fuels.<sup>1,2</sup> Hydrogen, as an important feedstock for the chemical industry and energy carrier, is considered as one of most important clean fuels. However, a vast majority of hydrogen in the world is obtained by natural gas steam reforming, which produces  $CO_2$  with an inevitable carbon footprint.<sup>3-6</sup> Electrolytic water splitting by generating hydrogen and oxygen from water without additional emissions has attracted considerable attention due to its inherent advantages of producing relatively pure hydrogen, flexibility for small- and large-scale production, and sustainability when the electricity used in electrolysis comes from renewable sources.<sup>7–9</sup> In a conventional water splitting system where hydrogen and oxygen evolution occurred simultaneously at the two electrodes separated by a diaphragm or ionexchange membrane, a gas crossover issue is still faced especially at a low operating current density or elevated pressures, rendering further purification to be required for the collected hydrogen gas.<sup>10-12</sup> In addition, the formed OH· radicals deteriorate the membrane and other cell components.13

To mitigate the above issues, some novel systems have recently been devised to decouple the formation of H<sub>2</sub> and  $O_2$ .<sup>14–16</sup> One effective way is using a third redox system,

such as nickel hydroxide<sup>23</sup> or anthraquinone-2,7-disulfonic acid,<sup>24</sup> the redox potential of which is between the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) potentials, in order to divide the water electrolysis into two chronologically separated steps for H<sub>2</sub> and O<sub>2</sub> production at different times. Another way is employing an electroncoupled proton buffer that has a high proton-electron storage capacity, with which H<sub>2</sub> can be produced at a separate time on demand.<sup>12,25-27</sup> Nevertheless, despite improved separation of high-purity gases,  $H_2$  and  $O_2$  cannot be produced concurrently, which inevitably results in an extended time because of the intermittent operation. In addition, the formation of H<sub>2</sub> and/or O<sub>2</sub> mostly remains at the electrode/electrolyte interface, which results in an inflated overpotential due to the adsorption of the produced gaseous species on the electrodes.<sup>28</sup> The bubbles that evolved on the electrode may induce a blockage of the electrocatalyst surface and decrease ion conductivity in the electrolyte.<sup>29,30</sup> In an alternative approach, Girault and coworkers incorporated a redox-flow battery module, using  $\mathrm{V}^{2+/3+}$ 

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**Figure 1.** Illustration of the spatially decoupled  $O_2$  and  $H_2$  production. (a) Schematic illustration of the operation of a redox-flow electrolytic cell for spatially decoupled  $O_2$  and  $H_2$  production. In practice, the produced  $O_2$  could just be released to that surroundings while  $H_2$  is collected from the hydrogen production reactor. (b) Energy diagram of electrolyte-borne redox-assisted HER and OER reactions with DHPS and ferricyanide as the mediators, respectively. A regenerative electrochemical-chemical cycle is applied on anodic and cathodic compartments, respectively, for continuous and concurrent  $O_2$  and  $H_2$  production.

and Ce<sup>3+/4+</sup> as the redox mediators in strong acid media for both energy storage and task-specific H<sub>2</sub> production.<sup>31–33</sup> While it allows for concurrent off-electrode H<sub>2</sub>/O<sub>2</sub> generation, the concerns are the inherently large free energy loss and the use of corrosive electrolytes.

To address these issues, here, we report an alkaline redoxflow electrolytic cell integrated with separate gas production reactors to spatially decouple the concurrently generated H<sub>2</sub> and  $O_2$  (Figure 1). A pair of redox mediators was employed as electrolyte-borne charge carriers circulating between the central electrode compartment and separate catalyst bed. Upon operation, the mediators are electrochemically charged on the electrode and then chemically discharged through catalytic HER and OER reactions in the respective reactor tank. For alkaline water electrolysis, despite the advantage of better durability and feasibility for large-scale production,<sup>8,34</sup> a major challenge is that an additional energy barrier stemming from the sluggish water dissociation step needs to be overcome to generate the essential H\* intermediates for hydrogen evolution.<sup>5,35-37</sup> Herein, 7,8-dihydroxy-2-phenazinesulfonic acid (DHPS) is employed as a HER redox mediator, which acts as both proton and electron carriers to circumvent the above rate-limiting step. As shown in Figure 1b, the reduction (or hydrogenation) of DHPS on the cathode generates DHPS-2H (step 1), which is kinetically faster than the direct  $H_2O$ reduction, and then initiates the HER reaction while it flows through a catalyst bed in the reactor. The dehydrogenation (or

oxidation) of DHPS-2H on the Pt catalyst in the gas production reactor spontaneously releases H<sub>2</sub> (step 2), with which DHPS is regenerated for a second round of reactions upon circulating back to the anodic compartment. For the OER side,  $[Fe(CN)_6]^{3-/4-}$  serves as an energetic charge carrier and instigates the OER reaction when it flows through a NiFe(OH)<sub>2</sub> catalyst bed in a separate reactor (steps 3 and 4). With such a flow cell setup, DHPS and  $[Fe(CN)_6]^{4-}$  are instantaneously regenerated as the electrolyte circulates through the cell while H<sub>2</sub> and O<sub>2</sub> are uninterruptedly produced in the tank, thus obviating a complex gas electrode design and gas mixing. The mechanistic process underlying the DHPSmediated HER reaction was collectively scrutinized with operando ultraviolet-visible (UV-vis), nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR) spectroscopy and computational studies.

# RESULTS AND DISCUSSION

**Electrochemical–Chemical Characterizations.** The phenazine derivative DHPS has been reported as a robust anodic redox mediator for alkaline flow battery.<sup>38</sup> It was synthesized with the procedures described in the Supporting Information, with its structure confirmed by NMR (Figure S1). The electrochemical properties of DHPS and  $[Fe(CN)_6]^{3-/4-}$  were scrutinized with voltammetric measurements. DHPS exhibits exemplary robustness in alkaline solution at a potential of -0.05 V (vs RHE), which nearly coincides with that of

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HER, while  $[Fe(CN)_6]^{3-/4-}$  has a potential of 1.37 V (vs RHE), slightly higher than that of the OER reaction (Figure 2a). In this study, hierarchical Pt-decorated Ni(OH)<sub>2</sub> and



Figure 2. Electrochemical-chemical characterizations between the mediator and catalyst. (a) CV curves of 5 mM DHPS and  $[Fe(CN)_6]^{3-/4-}$  in a 4 M NaOH solution at different scan rates on a glassy carbon electrode. (b) LSV curves of the two catalyst electrodes in a 4 M NaOH solution, and LSV curves of 1 M DHPS/ NaOH and 0.6 M K<sub>4</sub>Fe(CN)<sub>6</sub>/NaOH performed on a glassy carbon rotating disc electrode at a rotation speed of 1600 rpm, respectively. The scan rate was 10 mV/s. (c) LSV curves of a DLE in a 4 M NaOH solution with/without 5 mM DHPS, and that of a CC electrode in DHPS/NaOH solution. As the reduced DHPS is prone to being oxidized in air, all the LSV measurements were conducted under N2 protection using a H-cell setup. The two electrode compartments were separated by an anion-exchange membrane to avoid the interference of O2 generated on the counter electrode. (d) LSV curves of a DLE in 4 M NaOH solution with/without 5 mM  $[Fe(CN)_6]^{3-/4-}\!\!\!\!$  , and that of a CC electrode in  $[Fe(CN)_6]^{3-/4-}\!\!\!/$ NaOH solution. The scan rate was 0.1 mV/s to avoid the mass transport effect. The inset is an illustration of the DLE structure and associated electrochemical-chemical reactions. All the above measurements were conducted with a three-electrode system.

 $NiFe(OH)_2$  nanosheets were synthesized as the HER and OER catalysts, respectively. Considering that the powdery materials are susceptible to flowing with the electrolyte, the materials were thus deposited on a Ni foam substrate. The detailed morphological, structural, and compositional characterizations of the two catalysts can be found in the Supporting Information (Figures S4–S8).

One essential prerequisite for the decoupled water splitting on the basis of a regenerative electrochemical-chemical cycle is that the electrochemical process of the pair of redox mediators should inherently be faster than that of the electrolytic HER and OER reactions, so that the overall kinetics particularly here that are in tandem with an additional catalytic chemical process will not be impaired. Controlled linear sweep voltammetry (LSV) was thus conducted to compare the reaction kinetics of both OER and HER reactions with those of the above two redox mediators (Figure 2b). With the same set of catalysts, direct overall electrolytic water splitting in alkaline solution requires 1.57 V at a current of 20 mA/cm<sup>2</sup>, which is considerably higher than the thermodynamic limit, 1.23 V. In contrast, only 1.39 V is required to complete the redox reactions of DHPS and  $[Fe(CN)_6]^{4-}$  at the same current. Note that the first oxidation peak at ~1.38 V (vs RHE) is due to the oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup> in NiFe(OH)<sub>2</sub>.

The reversible off-electrode redox-mediated HER reaction of DHPS on the  $Pt-Ni(OH)_2$  catalyst was investigated with a double-layer electrode (DLE), which was made of a carbon cloth (CC) sandwiched with  $Pt-Ni(OH)_2$  and separated by an insulating glass fiber spacer (inset of Figure 2c). DHPS, which serves both as the electron and proton carriers, can shuttle between the CC electrode and  $Pt-Ni(OH)_2$  through the porous spacer layer. When the electrode is negatively biased, DHPS is reduced on the CC electrode:

$$DHPS + 2H_2O + 2e^- \rightarrow DHPS - 2H + 2OH^-$$
(1)

The hydrogenated DHPS-2H then diffuses through the porous separator and undergoes a catalytic dehydrogenation reaction on the  $Pt-Ni(OH)_2$  catalyst, releasing  $H_2$ :

DHPS-2H 
$$\xrightarrow{\text{Pt-Ni(OH)}_2}$$
 DHPS + H<sub>2</sub> $\uparrow$  (2)

Such a catalytic process is distinct from the conventional electrocatalysis where the Pt catalyst, as part of the electrode, receives electrons directly from the current collector. In comparison, here, the electrolyte-borne redox mediator acts as both the electron and proton carriers and transfers them to  $Pt-Ni(OH)_2$  while it reaches the catalyst layer. The regenerated DHPS then diffuses back to the CC electrode for a second round of reaction.

As depicted in Figure 2c, the DLE electrode was first tested in a 4 M NaOH electrolyte free of redox mediator, for which the LSV curve (black curve) shows a sluggish HER reaction that only occurred on carbon cloth. Interestingly, when 5 mM DHPS is present in the electrolyte, the current density is drastically increased (orange curve)-a nearly 5 times enhancement was observed at -0.40 V (vs RHE). To verify the contribution of Pt-Ni(OH)<sub>2</sub>, LSV was conducted with a bare CC electrode in the same DHPS-containing electrolyte (blue curve), which reveals a larger current density than that of the HER while staying far lower than that with the DLE electrode. The former suggests that the kinetics of DHPS reduction on carbon felt is superior to the HER reaction, while the latter indicates a "synergy" between DHPS and Pt- $Ni(OH)_2$  despite the fact that it is not in electrical contact with the electrode. The green curve in Figure 2c depicts the current difference curve between the DLE and bare CC electrode in DHPS electrolyte, from which the contribution of the catalytic off-electrode HER (or dehydrogenation of DHPS-2H) reaction on Pt-Ni(OH)<sub>2</sub> could be estimated. The steadystate behavior is indicative of an electrochemical-chemical process of DHPS confined in between the CC electrode and  $Pt-Ni(OH)_2$  through the thin spacer layer.

The off-electrode catalytic OER reaction was similarly examined with a DLE electrode when the catalyst layer was replaced with NiFe(OH)<sub>2</sub> (see the inset of Figure 2d) in  $[Fe(CN)_6]^{3-/4-}$ -containing electrolyte. Upon anodic polarization,  $[Fe(CN)_6]^{4-}$  is first electrochemically oxidized on the electrode,

$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$$
 (3)

With the increase of  $[Fe(CN)_6]^{4-}$  concentration and meanwhile decrease of  $[Fe(CN)_6]^{4-}$  concentration (or more accurately activity), the equilibrium potential of the redox species increases gradually. When it reaches the OER reaction onset potential, oxygen evolution is then triggered on the NiFe(OH)<sub>2</sub> surface by the holes carried by  $[Fe(CN)_6]^{3-}$  in the solution; despite that, the catalyst stays away from the electrode,

$$4[\operatorname{Fe}(\operatorname{CN})_{6}]^{3-} + 4\operatorname{OH}^{-} \xrightarrow{\operatorname{NiFe}(\operatorname{OH})_{2}} 4[\operatorname{Fe}(\operatorname{CN})_{6}]^{4-} + \operatorname{O}_{2} \uparrow + 2\operatorname{H}_{2}\operatorname{O}$$

$$\tag{4}$$

Different from DHPS, which acts both as the electron and proton carriers,  $[Fe(CN)_6]^{3-/4-}$  only serves as a hole carrier, with which the OER reaction shares a greater similarity to the electrolytic process on NiFe(OH)<sub>2</sub> except for the electrolyteborne charge transfer. The DLE electrode was first tested in 4 M NaOH electrolyte, for which the LSV curve shows a sluggish OER reaction that only occurred on bare CC at relatively high potentials. Despite the fact that NiFe(OH)<sub>2</sub> is not in electrical contact with the electrode, the presence of  $[Fe(CN)_6]^{3-}$  in the electrolyte substantially promotes the OER reaction, as reflected by the reduced onset potential and markedly enhanced current density at higher potentials (e.g., the current is boosted by a factor of  $\sim$ 7 at 1.60 V, Figure 2d). To verify the contribution of redox-assisted catalytic OER reaction, which may occur on the carbon cloth, LSV was also conducted with a bare CC electrode in the same  $[Fe(CN)_6]^{3-}$ -containing electrolyte. The current density arising from the OER reaction (blue curve) is considerably lower than that with the DLE electrode, albeit greater than that with the  $[Fe(CN)_6]^{3-}$ -free electrolyte, corroborating a similar "synergy" between [Fe- $(CN)_6$ <sup>3-</sup> and NiFe(OH)<sub>2</sub> to that of the HER process.

Spatially Decoupled Water Splitting. On the basis of the above, an electrolytic flow cell integrated with two catalyst packed-bed reactors (see Figure 3 and Video S1) was assembled to demonstrate continuous off-electrode productions of H<sub>2</sub> and O<sub>2</sub>. An anion-exchange membrane (Sustainion X37-50 membrane) was employed to separate the two electrode compartments, through which OH<sup>-</sup> migrates from the cathodic to anodic side during the electrolytic process. Aqueous solutions of 10 mL of 0.6 M DHPS in 4 M NaOH and 50 mL of 0.6 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 4 M NaOH were, respectively, used as the negolyte and posolyte circulating between the corresponding electrode compartment and reactor. Here, the posolyte was in excess, ensuring that the HER reaction was not limited by the more sluggish OER reaction, and thus, the following discussion is based on the cathodic reaction unless otherwise stated.

Figure 3a depicts the voltage profile of the flow cell at different current densities from 20 to 100 mA/cm<sup>2</sup>. At the initial short period of electrolysis, the cell voltage went up quickly with the reduction of DHPS on the electrode (Reaction 1). The formed DHPS-2H was then dehydrogenated, which releases H<sub>2</sub> in the reactor, while the negolyte flowed through the Pt–Ni(OH)<sub>2</sub> catalyst bed. When the rate of catalytic DHPS-2H dehydrogenation in the reactor equals the reduction rate of DHPS on the electrode, the cell voltage becomes stabilized and H<sub>2</sub> is constantly generated in the hydrogen production reactor. Similar electrochemical–chemical processes of  $[Fe(CN)_6]^{3-/4-}$  take place at the anodic side, involving constant O<sub>2</sub> evolution on the NiFe(OH)<sub>2</sub> catalyst bed. A voltage plateau at 1.53 V and a faradaic efficiency nearly 100% were attained at 20 mA/cm<sup>2</sup> after the cell reached steady



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**Figure 3.** Characterization of spatially decoupled water splitting system. (a) Voltage profile and faradic efficiency of an electrolytic flow cell at different current densities. (b) GC curves of the gas samples collected from the electrolytic flow cell and a conventional electrocatalytic cell. See experimental details in the Methods section. (c) Voltage profile of the flow cell upon continuous H<sub>2</sub> production for 82 h at 20 mA/cm<sup>2</sup>. The inset is a photo of the setup, including an electrolytic flow cell, two reactor tanks, and two gas collectors. (d and e) UV–vis spectra of DHPS in negolyte (d) and  $[Fe(CN)_6]^{3-}$  in posolyte (e) recorded at different durations of charging of the flow cell without and with the addition of a respective catalyst in the reactor tank. The current density was 10 mA/cm<sup>2</sup>.

state. Such a high faradaic efficiency is well retained for prolonged testing, as revealed in Figure S9. The plateau voltage increases with the current density, considering that a higher concentration of DHPS-2H is required for enhanced H<sub>2</sub> production in the reactor besides other overpotentials. Upon increasing the current density, the average cell voltage increased to 1.64 V at 40 mA/cm<sup>2</sup>, 1.70 V at 60 mA/cm<sup>2</sup>, 1.83 V at 80 mA/cm<sup>2</sup>, and 1.91 V at 100 mA/cm<sup>2</sup>. For each increment of current density, the faradaic efficiency of the cell initially attenuates and then gradually ramps up before a new steady state is established (Figure 3a). This is due to the fact that, despite the instantaneous increase of DHPS reduction on the electrode, it takes a short while to generate sufficient DHPS-2H in the electrolyte before the H<sub>2</sub> production rate in the reactor catches up and becomes balanced. The electrolytic flow cell was further studied by a galvanostatic intermittent titration technique (GITT), which determined the IR drop accounts for around 19 mV of the voltage increase for every 10 mA/cm<sup>2</sup> of current density increment (Figure S10). The produced H<sub>2</sub> gas was analyzed by gas chromatography (GC), and nearly no O2 was detected compared with those collected from a conventional electrolyzer (Figure 3b), showing the superiority of the electrolytic flow cell in producing pure H<sub>2</sub>.

The stability of the decoupled water electrolyzer system was assessed at a constant current density of 20 mA/cm<sup>2</sup>, and the cell voltage retained at around 1.53 V for more than 80 h without obvious degradation (Figure 3c).

To monitor the HER/OER reactions of the mediators on the respective catalyst in the redox-flow cell, operando UV-vis spectroscopic measurement was conducted. A spectroelectrochemical flow cell (Figure S12) was connected to the outlet cathodic or anodic flow channel of a flow cell to track the concentration changes of DHPS or  $[Fe(CN)_6]^{3-}$  in the respective electrolyte upon electrolysis. In the absence of a catalyst, the concentration of DHPS monotonously decreased over the charging process (Figure 3d and Figure S13a). In comparison, the cell loaded with Pt-Ni(OH)<sub>2</sub> showed extended time series spectra of DHPS with its concentration nearly stabilized while the reactions proceeded, implying the balance of consumption and generation of DHPS on the electrode and in the reactor. Similarly, the concentration of  $[Fe(CN)_6]^{3-}$  in the posolyte increased constantly without loading NiFe(OH)<sub>2</sub>, which however reached a steady state in the presence of a catalyst (Figure 3e and Figure S13b), suggesting a balanced electrochemical-chemical reaction cycle upon redox-mediated OER in the anodic compartment.

Computational and Experimental Investigations on HER Activity. The redox potential of DHPS is marginally lower than that of HER of water in alkaline solution. The Gibbs free energy change ( $\Delta G$ ) of the HER process through dehydrogenation of DHPS-2H was determined to be -0.10 eV, which makes H<sub>2</sub> formation thermodynamically favorable. First-principles density functional theory (DFT) calculations were first performed to explore the reaction mechanism of the dehydrogenation process of DHPS-2H on Pt (111) for H<sub>2</sub> generation. Figure 4a depicts the conceivable reaction intermediates and the calculated reaction free energies. In the initial dehydrogenation step, the reaction may involve the activation of DHPS-2H at the phenolic hydroxyl groups (DHPS-H-O<sub>1</sub> and DHPS-H-O<sub>2</sub>) or at amidogen groups (DHPS-H-N<sub>1</sub> and DHPS-H-N<sub>2</sub>), among which the formation of DHPS-H-O<sub>1</sub>· radical presents the lowest free energy (Figures S15 and S16, Table S1). It suggests that the phenolic hydroxyl group O1 of DHPS-2H loses a hydrogen atom first and forms DHPS-H-O<sub>1</sub>· and H\*. The second dehydrogenation step was treated in a similar way (Figures S17 and S18, Table S2). It was found that the removal of a hydrogen atom from the amidogen group N<sub>4</sub> of DHPS-H-O<sub>1</sub>• presents a relatively possible step entailing the formation of DHPS- $N_4$  (or DHPS') and H\*. However, given that the calculated reaction free energy of the second dehydrogenation step is considerably higher than that of the first step, it would not be predominant in the reaction. For HER in alkaline solution, the dissociation of a water molecule is considered as a key rate-determining step. Figure 4b compares the energy barriers for water dissociation and DHPS-2H dehydrogenation. The energy barrier for breaking the H-OH bond in water is 0.96 eV, which increases to 1.87 eV when taking the pH effect into account. In comparison, the energy barriers of dehydrogenation of DHPS-2H and DHPS-H are 0.95 and 1.48 eV, respectively. Therefore, the dehydrogenation of DHPS-2H (even DHPS-H) is energetically more favorable than the direct dissociation of a water molecule on the same Pt surface, implying a faster kinetics of HER reaction mediated by DHPS-2H.



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Figure 4. Computational and experimental investigations on HER activity. (a) Calculated reaction free energies of the sequential dehydrogenations of DHPS-2H on the Pt (111) surface. The red, white, gray, blue, and yellow spheres represent O, H, C, N, and S atoms, respectively. (b) Reaction energy diagram of water dissociation and sequential dehydrogenations of DHPS-2H on the Pt (111) surface. (c) EPR spectra of DHPS-2H measured before and after the immediate addition of different amounts of commercial Pt/C catalyst. (d) <sup>1</sup>H NMR spectra of pristine DHPS, DHPS-2H, and fully regenerated DHPS' in 2 M NaOH. Ten volume percent deuterium oxide (D<sub>2</sub>O) was added for sufficient lock signal and suppressed water resonance.

To unravel the transformations of DHPS intermediates during the redox-mediated H<sub>2</sub> generation on Pt, EPR studies of DHPS-2H in 4 M NaOH aqueous solution were carried out under different conditions (Figure 4c). The freshly prepared DHPS-2H sample, however, revealed a weak signal of a suit of characteristic 3-peak with an intensity ratio of 1:2:1, presumably attributed to the oxidation of the molecule by a trace amount of O2 in the surroundings, forming radical species. After injecting commercial Pt/C powder into the solution, numerous small gas bubbles evolved from the catalyst surface and the three characteristic peaks become considerably enhanced, which continually rose in the presence of an excess amount of catalyst, suggesting that the Pt catalyst favorably accelerates radical formation. The radical signal was confirmed through the simulated spectrum with hyperfine coupling constants  $A_{1,2}^{H} = 0.8$  G at a g value of 2.0046 (Figure S21). The comparison of the experimental and simulated results indicates that the radical center of the new species exists in the phenolic hydroxyl group of a catechol structure, consistent with the first dehydrogenation intermediate DHPS-H-O1. predicted by the DFT calculations.

Proton NMR analysis was carried out to substantiate the structure of the DHPS intermediates upon H<sub>2</sub> formation on Pt. The NMR data in Figure 4d (see also Figures S22–S24) clearly show that there was a significant difference in the chemical shift, peak splitting, and peak shape of the pristine, reduced, and reoxidized DHPS. The proton signals 5 and 6 in the pristine DHPS appeared as two singlets at  $\delta$  5.47 and 5.40, respectively, whereas both appeared as a singlet at  $\delta$  5.63 in its reduced form (DHPS-2H, Figure 4d and Figure S23). This was due to the symmetrical attachment of the hydroxyl and amine groups to the aromatic ring. In addition, the proton signals 7, 8, and 9 of DHPS-2H were broadened and shifted slightly

upfield due to the shielding effect of -NH functional groups. During the dehydrogenation process, the removal of hydrogen atoms from the phenolic hydroxyl (O1) and amidogen (N4) groups leads to a significant change in the electronic properties and structures of the molecule. As a result, in the formed tautomer (DHPS', Figure 4d and Figure S24), protons 5 and 6 appeared again as two singlets due to the change in adjoining functional groups. Furthermore, the chemical shifts for all the protons were shifted downfield when compared to those of the pristine DHPS and its reduced form. This was due to the electron withdrawing nature of the carbonyl group (C= $O_1$  in DHPS') and the attainment of sp<sup>2</sup> hybridization of one of the nitrogen atoms (N4 in DHPS').

The above computational and magnetic resonance spectroscopic studies provide compelling information on the dehydrogenation process of the reduced DHPS on Pt for  $H_2$ formation. As shown in the panoramic reaction pathway depicted in Figure 5, the redox-mediated HER reactions



**Figure 5.** Schematic diagram of electrochemical–chemical reaction process. Proposed reaction mechanism of the stepwise chemical dehydrogenation process of DHPS-2H on Pt for  $H_2$  formation and regenerative electrochemical hydrogenation process of DHPS on electrode. These form a close-loop electrochemical–chemical cycle for sustained and spatially decoupled  $H_2$  generation.

proceed with the electrochemically generated DHPS-2H, which acts as an electrolyte-borne electron and proton carrier and generates H\* through a dehydrogenation process on Pt. While the overall catalytic HER reaction of DHPS-2H is energetically downhill, the formation of DHPS-H-O<sub>1</sub> as a critical reaction intermediate requires an activation process on Pt, as identified by the EPR measurements. Given that the energy barrier is significantly lower than that of water dissociation, the DHPS-mediated HER reaction would proceed with a faster kinetics than the conventional water electrolysis. The H\* could be dominantly generated from the first dehydrogenation step of DHPS-2H, dependent on the energy barrier of the second step under actual operating conditions. The DFT calculations show the subsequent H<sub>2</sub> molecule formation process, a Tafel mechanism involving two surfaceadsorbed H\* on Pt that is energetically more favorable than the reaction route between one H\* and one DHPS-2H or other intermediates (see details in the Supporting Information).

Such a redox-mediated process through a close-loop electrochemical-chemical cycle endows the electrolytic

redox-flow cell with several salient features over the conventional electrolyzers. Besides the continuous production of H<sub>2</sub> of enhanced purity, a notable advantage for the redox-mediated approach is that the cell could be made more compact than the conventional electrolyzer for reduced cost. This could be rationalized with the fact that the redox species (i.e., DHPS and  $[Fe(CN)_6]^{4-}$  possess faster reaction kinetics than the respective HER/OER on the same electrode. In addition, the cell stack shares the same configuration as the redox flow batteries, with multiple single cells made of bipolar electrodes packed in series and thus with excellent scalability and operation flexibility.<sup>39,40</sup> In contrast, the design would be somewhat more sophisticated for the conventional electrolyzer in order for balanced electrolyte feeding and gas bubbles removal at the three-phase interfaces. Moreover, the distinct reaction pathway of the redox-assisted HER/OER may create interesting opportunities for the development of low-cost and robust catalysts. This would be plausible considering that the redox-mediated reactions involve different reactants and intermediates that may behave differently from water molecules, as those demonstrated in this study, and break the subtle scaling relations in the conventional electrocatalytic processes. Lastly, the approach reported here also has implications in the context of solar-driven water electrolysis.<sup>41</sup> Considering that solar energy could be converted into chemical energy and stored in large scale in the electrolyte tanks, the decoupled feature of redox-flow electrolytic cell is particularly adaptive to the intermittent solar irradiance without having additional energy storage system, applicable to the on-demand and task-specific H<sub>2</sub> production.

The practical application of electrolytic water splitting requires a greater operational current density and durability. It is encouraging that the DHPS/ $[Fe(CN)_6]^{4-}$  flow cell (involves electrochemical reactions of redox mediators) has revealed impressive power performance. It could operate at 100 mA/cm<sup>2</sup> with an average charging voltage as low as 1.60 V and excellent cycling stability in alkaline media.<sup>38,42</sup> Hence, there is ample room to improve the current of the water electrolytic flow cell at relatively low overpotentials. For instance, by leveraging the decoupled feature, the overall power performance could be enhanced by loading more catalysts (particularly for OER) in the reactor tanks without altering the electrochemical cell. In addition, the electrolyte could be introduced into the reactor in the form of a spray to avoid flooding of the catalyst bed and facilitate the removal of the formed gas.

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In summary, we have demonstrated a spatially decoupled approach with reduced overpotentials for the uninterrupted production of high-purity hydrogen from alkaline solutions. The approach was realized on the basis of redox-mediated HER and OER reactions through a pair of electrochemical– chemical cycles. The two redox couples DHPS/DHPS-2H and  $[Fe(CN)_6]^{3-/4-}$ , which work as electrolyte-borne charge carriers circulating between the catalyst bed and electrode compartment, undergo swift catalytic HER and OER reactions in the respective reactor tank and electrochemical regeneration reactions on the electrode. Enabled by the robustness and superior reaction kinetics of the two redox species as well as the decoupled feature of the flow cell, the system presented a near unity steady-state faradaic efficiency and fast and sustained production of hydrogen. The computational and

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spectroscopic studies of the DHPS-mediated HER reaction unveil a distinct hydrogen formation mechanism involving sitespecific dehydrogenation reactions of DHPS-2H on Pt, accounting for the fast hydrogen generation as compared to the conventional electrocatalytic HER reaction. With these encouraging results, we anticipate that the redox-mediated approach would provide an intriguing alternative for hydrogen production and should adequately engineer studies especially those on the reactor design to be conducted in future.

# EXPERIMENTAL SECTION

**Electrochemical Measurements of Electrocatalysts.** Cyclic voltammetry (CV) and linear scan voltammetry (LSV) were conducted on an Autolab electrochemical workstation (Metrohm, PSTA30). A three-electrode cell system was used to test the CV of DHPS and  $[Fe(CN)_6]^{4-/3-}$ . Graphite rod and Hg/HgO were used as the counter and reference electrodes, respectively. The electrolyte was 4 M NaOH aqueous solution bubbled with N<sub>2</sub> for 1 h prior to use. For the CV test of DHPS, the cells were sealed with N<sub>2</sub> protection. The potentials were presented versus the reversible hydrogen electrode on the basis of the following equation:

 $E (V vs RHE) = E_{Hg/HgO} + 0.098V + 0.0591V \times pH$ 

The LSV curves in Figure 2c were carried out by using a H-cell system. Both the working and reference electrodes were placed on one side and sealed with N<sub>2</sub> protection, while the counter electrode (graphite rod) was placed on the other side without sealing. The membrane was a Sustainion X37-50 membrane. The structure of the double-layer electrode (DLE) is shown in the inset of Figure 2c,d. Considering that the redox mediator should diffuse fast from one side to the other, thin carbon cloth was used as the working electrode here. A piece of carbon cloth (CC,  $1.0 \times 1.0 \text{ cm}^2$ ), glass fiber separator (GF,  $1.2 \times 1.2 \text{ cm}^2$ ), and catalyst@Ni foam ( $1.0 \times 1.0 \text{ cm}^2$ ) were clamped together. All the LSV measurements in Figure 2c,d were carried out at a scan rate of 0.1 mV/s.

Electrolytic Flow Cell Test and Hydrogen Evolution Reaction. The cell was assembled by sandwiching two pieces of carbon felt as the cathode and anode. The active area of the electrode was 5 cm<sup>2</sup>. Each half-cell had a graphite plate as the current collector connected to the external electrical circuit. An anion-exchange membrane (Sustainion X37-50 membrane) was used as the separator. The posolyte consisted of 50 mL of 0.6 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 4 M NaOH, while the negolyte consisted of 12 mL of 0.6 M DHPS in 4 M NaOH. The electrolytes were circulated through the cell stack and tanks using peristaltic pumps. The Pt-Ni(OH)2 catalyst was loaded in the cathodic tank, while the NiFe(OH)<sub>2</sub> catalyst was in the anodic tank. Pt-Ni(OH)<sub>2</sub> catalyst (10 cm<sup>2</sup>) and 15 cm<sup>2</sup> NiFe(OH)<sub>2</sub> catalyst were used in the test (Figure 4a,c). The voltage profiles of the flow cell were recorded in galvanostatic mode with an Arbin battery tester. The negolyte was purged with N<sub>2</sub> before charging. Gases that are produced in the tank were collected by water displacement. A measuring cylinder filled with water was placed upside-down in a water bath. The gas produced in the tank was fed into the water-filled measuring cylinder through a silicone tube. The gas production was then determined by the volume of displaced water.

**Gas Chromatography Headspace Measurement.** GC headspace analysis was performed using a Shimadzu GC-2010 Plus system by direct autoinjection of gas from the headspace of the negolyte holding into the GC through a silicone tube. For the decoupled water splitting system, the flow battery and electrolyte were prepared as described above. For the conventional water splitting system, the cell was assembled by sandwiching NiFe(OH)<sub>2</sub> and Pt–Ni(OH)<sub>2</sub> as anode and cathode, respectively. Fifty milliliters of 4 M NaOH and 12 mL of 4 M NaOH were used as the posolyte and negolyte, respectively. Each negolyte was purged with  $N_2$  before charging. The electrolysis process was operated at a constant current of 40 mA/cm<sup>2</sup>.

**EPR Test.** The EPR spectra were obtained with an EMX-plus 10/ 12 spectrometer from Bruker at room temperature operating at a frequency of 9.84 GHz (X-band) and a 2 mW microwave power with a 0.2 G modulation amplitude at 100 kHz. The three EPR samples were collected from the fully charged negolyte (DHPS-2H) of the flow cell, and two of them were subsequently added with different amounts of commercial Pt/C catalyst (1 and 10 mg) prior to the test. The solutions were sealed in high-purity quartz capillary tubes with vacuum grease at two ends of the tubes. Continuous small bubbles were generated in the quartz capillary tubes of samples added with Pt/ C catalyst during the EPR test.

Computational Details. The spin-polarized DFT computations were performed using the VASPsol, a software package that incorporates solvation into the Vienna Ab-initio Simulation Package (VASP) within a self-consistent continuum model. Core electrons were treated using a projector augmented wave (PAW) method with generalized gradient approximation (GGA) designed by Perdew, Burke, and Ernzerhof (PBE) with a plane wave kinetic energy cutoff of 350 eV. The atomic positions were fully relaxed with an energy convergence of  $10^{-4}$  eV per cell between two consecutive selfconsistent steps and a force convergence of  $10^{-2}$  eV Å<sup>-1</sup> to obtain the equilibrium configuration. To guarantee that the supercell size of surface model was sufficiently large enough to avoid the effect of DHPS between their mirror images, the calculations were performed with a 3  $\times$  3 Pt (111) surface with four layers. A *k*-mesh grid of 2  $\times$  2  $\times$  1 was set to sample the Brillouin zone during the structural optimization. The vacuum layer thickness was adopted to be more than 20 Å in order to avoid the artificial interaction between the layers and their periodic images. The zero-point vibration energy (ZPE) corrections were made over the frequencies at  $\Gamma$  point, on the basis of the harmonic approximation on the most energetically favorable structure. The energy of DHPS at different intermediate states was calculated by the Gaussian 09 program suite, with B3LYP hybrid exchange-correlation functional. A solvation model based on density (SMD) was used with water as a solvent.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c09510.

Discussions of materials, syntheses, and characterization methods, cyclic voltammetry tests of redox mediators, hydrogen and oxygen production during decoupled water splitting, comparison of two different anionexchange membranes, operando UV-vis spectroscopic measurement, comparison of decoupled and direct water splitting, DFT calculations of DHPS-mediated HER reaction, EPR measurement of DHPS-2H upon dehydrogenation, NMR measurement of DHPS-2H upon dehydrogenation, and comparison of different decoupled water splitting methods, figures of <sup>1</sup>H and <sup>13</sup>C NMR spectra, peak current vs. the square root of scan rate, CV curves, SEM and TEM images, EDS mapping and EDX spectrum, XPS spectra, LSV curves, voltage profiles, GITT curve, EIS analysis, configuration of the spectroelectrochemical setup for operando UV-vis spectroscopic measurements, absorbance changes, comparison of overall energy efficiency, H<sub>2</sub> yield, and collection rate, possible reaction pathways, models of the adsorption configuration, reactant, intermediate, and product structures, initial state and final state structures, and EPR experimental and simulated spectra, and tables of values used for the free energy, entropy, zero-point energy corrections, and Gibbs reaction free energy and comparison of the spatially decoupled water electrolyzer reported here with other decoupled water splitting systems reported in the literature (PDF)

Video of electrolytic flow cell integrated with two catalyst packed-bed reactors (MP4)

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## Author Contributions

<sup>II</sup>F.Z. and H.Z. contributed equally.

#### Notes

An invention disclosure based on the reported system has been submitted.

The authors declare no competing financial interest.

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