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Integrating Hydrogen Production with Aqueous Selective Semi-Dehydrogenation of Tetrahydroisoquinolines over a Ni₂P Bifunctional Electrode

Chenqi Huang[†], Yi Huang[†], Cuibo Liu, Yifu Yu, and Bin Zhang^{*}

Abstract: Exploring an alternative anodic reaction with accelerating kinetics to produce value-added chemicals with high selectivity, especially integrated with promoted hydrogen (H₂) generation, is highly desirable. Here, a selective semi-dehydrogenation of tetrahydroisoquinolines (THIQs) is demonstrated to replace oxygen evolution reaction (OER) for boosting H₂ evolution reaction (HER) in water over a Ni₂P nanosheet electrode. The value-added semidehydrogenation products, dihydroisoquinolines (DHIQs), can be selectively obtained with high yields at anode. The controllable semidehydrogenation is attributed to the in situ formed Ni^{II}/Ni^{III} redox active species. Such strategy can deliver a variety of DHIQs bearing electron-withdrawing/donating groups in good yields and excellent selectivities, and can be facilely applied to gram-scale synthesis. Furthermore, a two-electrode Ni₂P bifunctional electrolyzer can produce both H₂ and DHIQs with robust stability and high Faradaic efficiencies at a much lower cell voltage than that of overall water splitting.

Electrocatalytic water splitting represents a promising way to produce clean hydrogen (H₂).^[1] The sluggish kinetics of oxygen evolution reaction (OER), however, often limits the overall water efficiency.^[2] well-designed splitting Although some electrocatalysts have been developed to promote the kinetic of OER,^[3] a large potential is still required to match hydrogen evolution reaction (HER), leading to low energy conversion efficiency. An alternative strategy that replacing the anodic OER with the electrooxidation of thermodynamically more favorable species is of increasing importance to boost HER.^[4] A myriad of value-added chemicals, rather than O₂, are produced at anode. Nevertheless, in most cases, the fully electrooxidized products are obtained.^[4a] Thus, using electrooxidative power to drive controllable transformations of chemicals into corresponding semi-oxidized products with high selectivity and industrial practicability is highly challenging but more significant.

Dihydroisoquinolines (DHIQs) display a wide range of bioactivities on anti-tumor, anti-fungal, vasodilation and nonoamine oxidase inhibition, which demonstrate highly potential applications in pharmaceutical industry.^[5] The dehydrogenation of tetrahydroisoquinolines (THIQs) is a potential way to synthesize the DHIQs, but the typical thermal-

and photocatalytic strategies usually lead to the complete dehydrogenation products, isoquinolines (IQs).^[6] The semidehydrogenation products (DHIQs) are more difficult to be obtained, especially via a sustainable route, such as a very popular electrochemical dehydrogenation.^[7] Therefore, the controllable electrooxidation from THIQs to DHIQs with high selectivity at low potential over a low cost electrocatalysts, especially coupled with efficient HER, will be economically attractive, but remains highly challenging.

Herein, we demonstrate an efficient strategy to promote H₂ replacing OER with production by selective semidehydrogenation of THIQs over a Ni₂P anode (Figure 1). The in situ formed Ni"/Ni" redox active species in water are found to be key factors for the controllable semi-dehydrogenation of THIQs into DHIQs. Such anodic semi-dehydrogenation process can selectively produce gram-scale DHIQs with electron-withdrawing or donating groups in good yields. Additionally, the bifunctional Ni₂P electrodes can be assembled into a two-electrode electrolyzer for boosting HER by coupling with the semidehydrogenation of THIQs at a smaller voltage than that of overall water splitting.



Figure 1. (a) Electrocatalytic semi-dehydrogenation of THIQs 1 coupled with HER in water. (b) Dehydrogenation reaction of 1 to form DHIQs 2 and IQs 3. (c) Scanning electron microscopy (SEM) image of Ni₂P nanosheet electrode.

The Ni₂P porous nanosheet electrode was synthesized by a facile phosphidation of porous nickel oxide precursors (Figure S1). The scanning electron microscopy (SEM) images (Figure 1c and Figure S2) show that porous nanosheet arrays with open network like structure are grown on nickel foam (Figure S3), which can be further observed from transmission electron microscopy (TEM) image (Figure S4a). The high-resolution TEM (HRTEM) image (Figure S4b) displays well-resolved lattice fringes with interplanar distances of 0.170 and 0.292 nm, which are attributed to the (300) and (110) planes of Ni₂P, respectively. The X-ray diffraction (XRD) pattern (Figure S5) reveals that all the diffraction peaks are indexed to Ni₂P (JCPDS No. 03-0953) and Ni. The X-ray photoelectron spectroscopy (XPS) spectra further show the characteristic Ni^{δ +} of Ni₂P in as-prepared

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electrode (Figure S6). These results suggest the successful synthesis of Ni₂P nanosheet electrode.

The electrocatalytic semi-dehydrogenation of THIQs was carried out in 1.0 M KOH aqueous solution. The 1,2,3,4tetrahydroisoquinoline 1a is selected as a model substrate. Figure 2a displays the linear sweep voltammetry (LSV) curves in the presence and absence of 1a over a Ni₂P anode. In the absence of 1a, the onset potential is about 1.48 V vs. RHE (reversible hydrogen electrode) and the obvious O2 bubbles appeared after this potential. The oxidation peak centered at about 1.40 V is attributed to Ni^{II}/Ni^{III}.^[8] After adding 1a, the current density increases dramatically from about 1.32 V and O₂ bubbles start to appear when the potential reaches to about 1.48 V. The products obtained at different reaction times are collected at the constant potential of 1.35 V. The product 2a increases with the time and no fully dehydrogenated product, isoquinoline, is generated (Figure 2b). The reaction can be completed within 1 h. To investigate the effect of potential on the selectivity of oxidative dehvdrogenation. series of а long-term chronoamperometry at various potentials from 1.30 to 1.70 V were carried out with 0.5 mmol 1a (Figure 2c). At 1.30 V, no product can be collected. At the potentials from 1.35 to 1.45 V, the products were collected after passing charge of about 96 C (the theoretical charge for the semi-dehydrogenation of 1a to 2a). 2a with Faradaic efficiencies (FEs) of about 96% and selectivities of about 99% are achieved. O2 bubbles can be observed obviously after 1.50 V. When the potential is increased to 1.70 V, the FEs and yields for 2a reduce to about 50% due to OER, while the selectivity of 2a is still about 96%.



Figure 2. (a) LSV curves of a Ni₂P anode at a scan rate of 5 mV s⁻¹ in 40 mL of 1.0 M KOH with and without 0.5 mmol 1a. (b) Time-dependent evolution of 1a and its semi-dehydrogenation product 2a. (c) FEs and selectivities of 2a at different potentials. (d) Cycle-dependent yields and FEs of 2a.

The durability of electrocatalytic semi-dehydrogenation over a Ni_2P anode was also investigated. After six cycle runs, no apparent decrease of activity is observed and the yields and FEs of **2a** is ~96% (Figure 2d), reflecting the good stability of the Ni_2P anode for this electrocatalytic reaction. The Ni_2P electrode after stability test was characterized. The maintained nanosheet arrays morphology can be observed from SEM images (Figure

S7). The high-resolution XPS spectra show the partial surface oxidation of Ni_2P after semi-dehydrogenation test (Figure S8), which suggests that the oxidized Ni species on the surface of Ni_2P may be the actual active sites for electrocatalytic semi-dehydrogenation.



Figure 3. (a) CV curves of a Ni₂P anode in 0.1 M KOH with and without **1a.** (b, c) Potential-dependent *in situ* Raman spectra of a Ni₂P anode collected without **1a** (b) and with **1a** (c). (d) *In situ* Raman spectra collected under chronoamperometry (*I*-t) test at 0.5 V vs. Ag/AgCl in 0.1 M KOH solution without **1a** (initial) and after the addition of **1a.** (e) Proposed conversion process of semi-dehydrogenation over a Ni₂P anode. (f) CV curves (anodic parts) in acetonitrile with glassy carbon (GC) as the working electrode.

To further get insight into the mechanism for electrocatalytic semi-dehydrogenation of THIQs over a Ni₂P anode, in situ potential-dependent Raman spectroscopy was first measured. The cyclic voltammetry (CV) was performed with and without 1a (Figure 3a), and Raman spectra at different potentials were collected (Figure 3b, c). The oxidation peak (0.4-0.5 V vs. Ag/AgCl) of Ni^{II}/Ni^{III} can be clearly observed in the CV curve without 1a, and at the same time, two peaks, attributed to the Ni-O vibrations of NiOOH, [3b] start to appear at 472 and 553 cm⁻¹, and their intensity increase gradually with the potentials (Figure 3b). After the addition of 1a, the current is obviously enhanced, as observed from CV curve (Figure 3a). But, the NiOOH peaks do not appear until the potential reaches to 0.6 V (Figure 3c). In addition, the NiOOH peaks without 1a can be weakened gradually and disappear in about 20 s after adding 1a (Figure 3d). Considering the formation of NiOOH on the surface of Nibased electrocatalysts toward OER in an alkaline electrolyte,^[1a,8,9] it is reasonable to conclude that with **1a**, Ni^{III}-OOH is firstly formed on the surface of Ni₂P, and then quickly captures the electrons from 1a to go back to Ni^{ll}, meanwhile, the 1a is oxidized to 2a, so that the peaks of NiOOH are not observed from in situ Raman spectra during the process of organic transformation (Figure 3e). Therefore, Ni^{II}/Ni^{III}, on the surface of electrode, works as an efficient redox active species

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to promote the conversion of **1a** into **2a**, similar to the reported organic electrooxidation processes driven by TEMPO mediator.^[10] In addition, the radical process is possibly involved in the electrocatalytic selective semi-dehydrogenation of **1a** to **2a** (Figure 3e and Figure S9).^[6a, 11]

The CV was also carried out in acetonitrile with glassy carbon (GC) as the working electrode to analyze the electrooxidative behaviour of organic substrate (for details see the Supporting Information). As shown in Figure 3f, two main peaks at 1.29 and 2.47 V vs. Ag/AgCl, associated with the first and secondary oxidation of 1a, respectively, are observed from CV curve recorded in the solution of 1a (magenta line) compared to that of in the solution of 2a (blue line). Upon the addition of a small amount of water, the first peak remains, while the current density sharply increases from the potential of 1.69 V because OER starts to proceed at this potential, suggesting that the secondary dehydrogenation of **1a** would be more difficult than OER. That is to say, combining with the results above of in situ Raman spectra, the in situ formed Ni^{II}/Ni^{III} can boost the conversion of 1a into 2a and the OER can happen to inhibit the generation of full dehydrogenation products at high potentials, so that the high selectivity of semi-dehydrogenation can be achieved (Figure 2c). Furthermore, such electrocatalytic semi-dehydrogenation strategy shows good compatibility with various THIQs with electron-withdrawing or donating groups, and the corresponding semi-dehydrogenation products can be obtained in high yields (Table 1 and Figure S10). Besides, the developed method was also applied to the dehydrogenation of tetrahydroguinoline (THQ) (Figure S11), which also shows more thermodynamically favourable than OER to boost the HER at cathode. Unfortunately, only complete dehydrogenation product, quinoline, was obtained.

Table 1. Substrate scope of the selective semi-dehydrogenation of THIQs over a Ni_2P anode. $^{\rm a}$



^aReaction conditions: THIQs (0.5 mmol), Ni₂P anode (working area: 1 cm²), Pt cathode, 1.0 M KOH (40 mL), room temperature (RT, 25 °C), 0.35 V vs. Ag/AgCl, 1-3 h (passing charge of about 96 C). Yields are determined by gas chromatograph. The products are indentified by NMR.

Impressively, the as-prepared Ni₂P electrode is also highly active for HER (Figure S12)^[4h, 12] and can be assembled into a two-electrode electrolyzer for both HER and semidehydrogenation of THIQs, which show much better energy efficiency compared to overall water splitting (Figure 4a). For example, achieving the current density of 20 mA cm⁻² requires a 300 mV smaller voltage than that of overall water splitting (inset of Figure 4a). A long-term electrolysis at 1.50 V vs. counter electrode (CE) was also carried out. The FEs of generated H₂ and 2a reach to about 100% and 96%, respectively (Figure 4b). The high selectivity of 2a can also be retained after the longterm test. Additionally, no apparent decrease of FEs is observed after six cycle runs, indicating the excellent durability. Note that such assembled two-electrode electrolyzer for semidehydrogenation reaction coupled with HER can be also driven by a 1.5 V single-cell battery (Figure S13, 14) and conducted to a gram scale synthesis of DHIQs with excellent yields (Figure S15), suggesting a great potential for practical application.



Figure 4. (a and inset) LSV curves and potential comparison for achieving benchmark current densities (10 and 20 mA cm⁻²) over a Ni₂P II Ni₂P electrolyzer in 1.0 M KOH with and without 0.5 mmol **1a**. (b) Cycle-dependent FEs of a Ni₂P II Ni₂P electrolyzer for both H₂ and **2a** production in 1.0 M KOH solution with 0.5 mmol **1a**.

In summary, we have developed a facile but efficient strategy to boost H₂ production coupled with selective semidehydrogenation of THIQs instead of OER in water over a Ni₂P anode. The controllable semi-dehydrogenation conversion of THIQs into DHIQs is attributed to the *in situ* formed Ni^{II}/Ni^{III} redox active species to boost semi-dehydrogenation reaction. Impressively, the bifunctional Ni₂P electrodes can be assembled into a two-electrode electrolyzer for both HER and semidehydrogenation of THIQs, which requires a smaller voltage than that of overall water splitting. This work opens an economical and highly efficient route for the electrochemical production of both hydrogen and DHIQs.

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A selective semi-dehydrogenation of tetrahydroisoquinolines (THIQs) instead of oxygen evolution reaction is reported to boost H₂ evolution reaction in water over a Ni₂P nanosheet electrode. Both value-added semi-

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