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Ultralow-voltage hydrogen production and simultaneous pollutant recycling in neutral media

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Abstract:

Electrocatalytic water splitting for hydrogen production is hampered by the sluggish oxygen evolution reaction (OER) and large power consumption and replacing the OER with thermodynamically favorable reactions can improve the energy conversion efficiency. Since metal atoms reconstruct and generate oxidation currents before OER on transition metal-based electrocatalysts, a novel strategy to integrate the hydrogen evolution reaction (HER) with waste Fe upgrading reaction (FUR) is proposed and demonstrated for energy-efficient hydrogen production in neutral media. The heterostructured MoSe₂/MoO₂ on carbon cloth (MSM/CC) shows superior HER performance to that of commercial Pt/C at high current densities. By replacing conventional OER with FUR, the potential required to afford 10 mA cm⁻² decreases by 95%. The HER/FUR overall reaction shows an ultralow voltage of 0.68 V for 10 mA cm^{-2} with a power equivalent of 2.69 kWh per m³ H₂. In addition to energy-saving hydrogen production, the Fe species formed at the anode extract the Rhodamine B (RhB) pollutant by flocculation and also produce nanosized magnetic powder and beneficiated RhB for valueadding applications. This work demonstrates both energy-saving hydrogen production and pollutant recycling by a single system and reveals a new direction to integrate hydrogen production with environmental recovery to achieve carbon neutrality.

Keywords: energy-saving hydrogen production, hydrogen evolution reaction, neutral water splitting, zero-carbon emission, environmental recovery

1. Introduction

Electrochemical water splitting driven by sustainable energy is one of the promising techniques to produce high-purity hydrogen in the global efforts to replace fossil fuels and achieve carbon neutrality [1-4]. The efficiency of hydrogen production depends on the physicochemical and electrochemical properties of the electrocatalytic couples and electrocatalysts [5, 6]. Electrochemical water splitting consists of the hydrogen evolution reaction (HER) on the cathode and oxygen evolution reaction (OER) on the anode. OER is considered the ratedetermining step due to the large theoretical potential barrier ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$, 1.23 V vs. RHE) in addition to a big overpotential, thus entailing high electricity consumption [7]. Therefore, developing a thermodynamically easier and less energy-demanding reaction to replace OER is critical.

Recently, thermodynamically favorable oxidation of small molecules and organic species electro-oxidative reactions have been integrated to produce hydrogen by HER [8-13]. For instance, Qian et al. have utilized hydrazine oxidation to replace OER and the two-electrode electrolyzer requires cell voltages of 0.071 and 0.76 V for 10 and 400 mA cm⁻², respectively [14]. The combination of electrooxidation of organic pollutants and HER in a single system is a promising solution for the simultaneous treatment of wastewater and renewable energy generation [15-17]. Sun et al. have demonstrated hydrogen production by hybrid seawater splitting coupled with hydrazine degradation, which presents a low electricity equivalent of 2.75 kWh per m³ H₂, thus enabling hydrogen production and removal of harmful pollutants at the same time [18]. These strategies have been shown to improve the energy efficiency of hydrogen production but nevertheless, the gaseous products either need purification or contribute to carbon emission. Moreover, the kinetics of HER and anodic reactions must match in order to improve the Faradaic efficiency in overall water splitting.

To attain zero carbon emission and energy-saving hydrogen production, it is desirable to develop an anodic oxidation reaction which is thermodynamically easier than OER and has high synergism. Transition metal-based electrocatalysts undergo reconstruction before OER, during which, metal atoms with a low valance state are oxidized to a higher valancy to produce an oxidation current with thermodynamic favorability [19-21]. Hence, it is possible that the reconstruction process in the metal oxidation reaction can replace OER and be coupled with HER to enhance overall water splitting. However, this strategy has seldom been reported so far, perhaps because metal oxidation consumes the anode, consequently raising the operating and materials costs. Electrochemical flocculation has been used in environmental fields to remove pollutants including heavy metal ions and organic species in pH-neutral wastewater. It proceeds at a positive potential *via* the Fe oxidation reaction to form the flocculant (hydroxy complex, polynuclear hydroxy complex, and hydroxide) [22]. In addition, Fe tends to self-corrode and forms magnetic oxide species (Fe upgrading reaction, FUR), even though applying a very small positive potential can facilitate FUR [23, 24]. Therefore, integrating HER at the cathode and FUR at the anode may result in highly efficient hydrogen production. However, the design and construction of high-performance HER electrocatalysts for neutral water splitting are still challenging.

Despite the excellent HER capability of Pt- and Ru-based noble catalysts[25-27], more cost-effective candidates such as metal carbides [28-30], metal phosphides [31, 32], metal sulfides [33, 34], metal nitrides [35-37], and metal selenides [38, 39] are being explored as replacements. In particular, two-dimensional layered molybdenum selenides (MoSe₂) have attracted much attention due to the favorable hydrogen adsorption free energy ($\Delta G_{\rm H}$) and tunable active sites [40, 41]. MoSe₂ normally exists in the 1*T* and 2*H* phases. 2*H*-MoSe₂ is an indirect bandgap semiconductor with low electrical conductivity, whereas 1*T*-MoSe₂ has metallic behavior and better HER capability, albeit poorer stability [42]. Qu et al. have prepared the Mo/(1*T*-2*H*)-MoSe₂ composite, which shows a small Tafel slope of 35 mV dec⁻¹ and good stability [43]. Deng et al. have constructed the bi-phase (1*T*-2*H*)-MoSe₂ on a conductive substrate and shown a small overpotential of 126 mV to achieve 10 mA cm⁻² [44]. Therefore,

2H-MoSe₂ as the substrate can facilitate modification of the electronic structure of 1T-MoSe₂, which serves as the main active center in the (1T-2H)-MoSe₂ electrocatalyst. However, MoSe₂ is oxidized quite easily, consequently compromising the long-term stability. Nevertheless, combining electrochemically active 1T-MoSe₂ with highly conductive and stable Mo-based oxides may be a good strategy to produce highly active and stable composite electrocatalysts.

Herein, we propose to realize energy-saving and efficient hydrogen production by a combined water splitting and pollutant extracting strategy in a neutral electrolyte. In the process, electrolysis of neutral water on the cathode produces high-purity hydrogen *via* HER, while Fe is converted into Fe^{2+} at the anode *via* FUR instead of OER. HER is catalyzed by the heterostructured MoSe₂/MoO₂ composite prepared on carbon cloth (MSM/CC) produced by *in situ* phase separation. Fe^{2+} generated on the anode forms the Fe(OH)₂ to adsorb Rhodamine B (RhB, a typical and soluble dye molecule applied in a variety of industries) by flocculation to facilitate wastewater treatment. Meanwhile, magnetic Fe₃O₄ nanoparticles are produced. All in all, the dual process produces hydrogen and remove RhB pollutant at the same time without carbon emission, as schematically illustrated in **Scheme 1**. The HER/FUR couple requires 0.68 V to generate a current density of 10 mA cm⁻² and can be powered by solar cells with an electricity equivalent of 2.69 kWh per m³ H₂. The results reveal a new direction to realize energy-efficient hydrogen production in neutral media with zero-carbon emission and environmental recovery at the same time.



Scheme 1. Schematically illustration of the concept of HER/FUR couple for ultralow-voltage hydrogen production and simultaneous magnetic Fe₃O₄ nanoparticles production, wastewater purification as well as RhB beneficiation in neutral media.

2. Experimental Section/Methods

*Synthesis of MoO*₃/CC: The MoO₃ nanowire arrays were grown on carbon cloth (CC) by a solution method. In detail, 0.9 g of $(NH_4)_2MoO_4$ were added to a solution (50 mL) of HNO₃ and deionized water (DW) with a volume ratio of 4:1. A piece of clean CC (2 × 3 cm²) was immersed in the solution and then heated to 70 °C for 1 h in a water bath. The product was CC covered by MoO₃ nanowires (MoO₃/CC).

Synthesis of MSM/CC: The MoSe₂/MoO₂ core-shell structure was prepared by CVD. MoO₃/CC and 1 g of Se powder were put on two separate porcelain plates with the Se powder upstream in the tube furnace. MoO₃/CC was heated to 400 °C for 1 h at a ramping rate of 5 °C min⁻¹ under N₂/H₂ (containing H₂ of 8%) and then cooled to room temperature. The product was designated as MSM/CC.

Synthesis of $MoSe_2/CC$ and MoO_2/CC : Pure MoSe_2 was prepared by CVD similar to that for MSM/CC except that the temperature was 500 °C. The product was designated as $MoSe_2/CC$. Pure MoO_2 was prepared by hydrogen reduction, in which MoO_3/CC was put in a tube furnace, heated to 550 °C for 3 h under N_2/H_2 (containing H_2 of 8%), and cooled to room temperature. The product was designated as MoO_2/CC .

Materials characterization: The morphology and composition of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, TESCAN MIRA LMS), transmission electron microscopy (TEM, FEI F200), high-resolution TEM (HR-TEM) equipped with energy dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD, LabX XRD-6100, Shimadzu) with a Cu K_a source, and Raman scattering (HR RamLab). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, Thermo Fisher) with monochromatic Al K_a X-rays was performed to determine the chemical state of the samples and the binding energy of 284.6 eV of C 1*s* was the reference. The electrical conductivity was evaluated by a four-point probe using the Keithley 2450. The magnetic properties were investigated on the vibrating sample magnetometer (Lakeshore 7404). The total organic carbon (TOC) in the electrolyte was measured by a carbon analyzer (Elementar Vario TOC) and the UV-vis spectra were acquired from the PerkinElmer Lambda 35.

Electrochemical characterization: The electrochemical measurements were carried out based on the three-electrode configuration on the CHI 760E (Shanghai CH Instrument, China). The reference and counter electrodes were the saturated calomel electrode (SCE) and graphite rod, respectively. The CC modified with the nanostructures served as the working electrodes. A typical waste steel rod used for construction was used as the working electrode (anode) in FUR (overall reaction). All the potentials in HER were *iR* corrected and calibrated to the reversible hydrogen electrode (RHE) by the Nernst equation $E(RHE) = E(SCE) + 0.242 + 0.059 \times pH$, where the pH values of 0.5 M H₂SO₄, 1.0 M KOH, and 0.5 M Na₂SO₄ were 0.48, 13.58, and 5.80 (FE28, Mettler Toledo), respectively. Linear sweep voltammetry (LSV) was conducted at a scanning rate of 5 mV s⁻¹ and the Tafel slope was calculated from the linear portion of the Tafel plot. Electrochemical impedance spectroscopy (EIS) was performed with an amplitude of 5 mV in the frequency range of 100 kHz ~ 0.1 Hz. The electrochemically active surface area (ECSA) was determined by cyclic voltammetry (CV) in the potential range between –0.5 and –0.6 V *vs*. SCE. The HER stability was determined at a potential of –1.4 V *vs*. SCE and the amount of H₂ produced was measured by the water displacement method.

3. Result and discussions

Figure S1 illustrates the preparation of the core-shell MoSe₂/MoO₂ composite. The MoO₃ nanowires are grown on the carbon cloth (MoO₃/CC) by a solution method and then phase-separated to form the core-shell MoSe₂/MoO₂ on CC (MSM/CC). The surface morphological evolution during phase separation is schematically presented in **Figure 1a** and confirmed by morphological characterization. The field-emission scanning electron microscopy (FE-SEM) images in **Figures S2a-b** show that the uniform nanowire array with a smooth surface covers the carbon fibers. After CVD for selenation, the nanowire array structure remains, but the surface becomes rough and sheet-like (**Figures 1b-c**). In addition, the diameter of the nanowires increases distinctly. By increasing the CVD temperature to 500 °C, similarly rough nanowire arrays are still obtained as shown in **Figure S3**. Hence, nanosheets are formed on the surface of the nanowires after selenation. After annealing the MoO₃/CC in the same atmosphere but without the Se precursor, the nanowire structure can still be observed as shown in **Figure**

The transmission electron microscopy (TEM) images in **Figure S5** and **Figure 1d** confirm the nanosheet-nanowire core-shell structure of the CVD product with a core diameter of ~200 nm and a shell diameter of ~400 nm, in line with SEM analysis. The nanosheet structure is beneficial for active site exposure for fast catalysis. **Figure 1e** indicates firm integration between the nanowire core and nanosheet shell without sharp boundaries. Furthermore, the high-resolution TEM (HR-TEM) image in **Figure 1f** shows two sets of distinct lattice fringes with a neighboring distance of 0.24 nm of the nanowire core ascribed to the MoO₂ (–211) plane (JCPDS card No. 32-0671), whereas the lattice of 0.65 nm of the nanosheet shell belongs to the MoSe₂ (002) plane (JCPDS card No. 77-1715). The elemental maps in **Figure 1g** disclose the Mo-O core and Mo-Se shell in the as-prepared MSM.



Figure 1. (a) Schematic of the conversion of the MoO₃ nanowire into MSM core-shell structure; (b-c) FE-SEM and (d-e) TEM images of MSM/CC; (f) HR-TEM image and (g) Elemental maps

of MSM/CC; (h) XRD spectra, (i) Raman scattering spectra, and (j) Electrical conductivity of the electrocatalysts.

The X-ray diffraction (XRD) pattern in Figure S6 shows that the product formed by the solution process is MoO₃ (JCPDS card No. 21-0569). After CVD for selenation at 400 °C, Figure 1h indicates that the diffraction patterns (red line) of the product belong to the composite of MoSe₂ (JCPDS card No. 77-1715) and MoO₂ (JCPDS card No. 32-0671). The results confirm that MoO₃ is phase-separated into the composite of MoSe₂ and MoO₂ during selenation. By increasing the selenation temperature to 500 °C, the pure phase of MoSe₂ (JCPDS card No. 77-1715) appears as shown in Figure 1h (black line). By annealing MoO₃/CC at 550 °C for 3 h without the Se powder precursor, the pure phase of MoO₂/CC (JCPDS card No. 32-0671) is formed as shown by the blue line in Figure 1h. Pure MoO₂ cannot be obtained at a lower annealing temperature (450 °C, 6 h) or in a shorter time duration (550 °C, 2 h) as shown in Figure S7, suggesting that the Se powder precursor is important to the conversion of MoO₃ into MoO₂. The products are investigated by Raman scattering as shown in Figure 1i, which confirms the composite of MoO₂ and 1*T*-MoSe₂ [45]. Figure 1j indicates that conversion from MoO₃/CC to MoO₂/CC improves the electrical conductivity, but the pure selenide MoSe₂/CC product shows lower electrical conductivity. It has been reported that 1T-MoSe₂ shows excellent electrocatalytic activity in HER [42] and therefore, combining the highly active 1T-MoSe₂ with a highly conductive skeleton may enhance the catalytic capability. The electrical conductivity of the core-shell structure of MSM/CC is about six times larger than that of the pure phase MoSe₂/CC as well as superior to the MoO₃/CC precursor, as indicated in Figure 1j. The synergetic effects of high active site exposure and electrical conductivity of the MSM/CC composite are expected to benefit HER.

The chemical composition of the electrocatalysts was investigated by X-ray photoelectron spectroscopy (XPS). The selenide products including MSM/CC and MoSe₂/CC show the presence of Se in the surface survey in **Figure S8**. The high-resolution XPS spectra of Se 3*d*

in **Figures S9a-b** show similar spectra for the selenide samples and the peaks at 55.7/54.8 eV is Se²⁻ $3d_{3/2}/3d_{5/2}$. However, the Mo 3*d* spectra of MSM/CC, MoO₂/CC and MoSe₂/CC are different as shown in **Figures S10a-c**. MoO₂/CC is composed of Mo⁴⁺ (233.2 and 230.0 eV) and Mo⁶⁺ (235.6 and 232.1 eV) as shown by the Mo 3*d* spectra (**Figure S10a**). The presence of Mo⁶⁺ in MoO₂/CC stems from surface oxidation in air as reported before [46]. **Figures S10b-c** show that the Mo 3*d* peak in MSM/CC and MoSe₂/CC is composed of Mo⁴⁺ 3*d*_{3/2} and 3*d*_{5/2}. The Mo⁴⁺ peaks in MSM/CC are shifted ~0.56 eV lower compared to MoO₂/CC, but ~0.20 eV higher than MoSe₂/CC. The peak shifts reveal the electronic interactions between the MoO₂ and MoSe₂ phases at the MSM heterointerface.

The electrochemical properties of the electrocatalysts were studied systematically based on the three-electrode configuration. **Figure 2a** depicts the polarization curves of the electrocatalysts in the alkaline electrolyte (1.0 M KOH) for HER. The MSM/CC electrocatalyst requires only 181 mV for a current density of 10 mA cm⁻², which is a common criterion to evaluate the activity of water splitting. The overpotential of the MSM/CC electrocatalyst is smaller than those of the pure phase of MoSe₂/CC (216 mV), MoO₂/CC (358 mV) and MoO₃/CC (363 mV), as listed in **Table S1**. Moreover, the MSM/CC electrocatalyst exhibits a rapid rise in the current density and an overpotential of 449 mV is needed to generate a large current density of 500 mA cm⁻². **Figure 2b** shows the Tafel slope of the electrocatalysts. The smallest Tafel slope of 110.4 mV dev⁻¹ is observed from the MSM/CC electrocatalyst compared to the pure phase of MoSe₂/CC (133.6 mV dev⁻¹), MoO₂/CC (117.6 mV dev⁻¹), and MoO₃/CC (385.8 mV dev⁻¹). A smaller Tafel slope normally implies accelerated mass transport and charge transfer, which can be confirmed by electrochemical impedance spectroscopy (EIS) in **Figure 2c**. The smaller charge transfer resistance of MSM/CC suggests fast charge transfer in HER due to the tight combination of the MoSe₂ shell and highly conductive MoO₂ core.

Density-functional theory calculation (**Supporting Note 1**) was performed to elucidate the mechanism of the MSM/CC heterostructure. The simulated model for the MSM composed of

MoSe₂(002) and MoO₂(-211) heterointerface is depicted in **Figure S11a**. The calculated $\Delta G_{\rm H}$ of MoSe₂, MoO₂, and MSM heterointerface was adopted to estimate the hydrogen evolution activity, as shown in **Figure S11b**. MSM shows a $\Delta G_{\rm H}$ of -0.18 eV, which is closer to zero compared to pure MoSe₂ (-0.24 eV) and MoO₂ (0.54 eV), indicating that the interaction between MoSe₂ and MoO₂ at the heterointerface regulates the electronic structure of the active center to accelerate HER.

The electrochemically active surface area (ECSA) was derived to evaluate active site exposure based on cyclic voltammetry (**Figure S12**). The larger the ECSA, the greater is the active site exposure. As shown in **Figure 2d**, the MSM/CC electrocatalyst has the largest ECSA of 80.6 mF cm⁻², which is about 10 times that of the MoO₃/CC precursor, suggesting more active site exposure after phase separation. The results are supported by the SEM images after selenation showing that the surface of the nanowire becomes rough and sheet-like so that more active sites are exposed. The smaller overpotential, Tafel slope, and charge transfer resistance, as well as the larger ECSA of the MSM/CC electrocatalyst confirm the promotional effect of the MoSe₂ and MoO₂ heterostructure. The outstanding HER performance should be ascribed to the modulated electronic structure of the heterointerface between the two phases and the synergistic effects of highly active MoSe₂ and conductive MoO₂.

The HER capability of the MSM/CC electrocatalyst in electrolytes with a universal pH range was investigated and shown in **Figures 2e-f** and the overpotentials and Tafel slopes are listed in **Table S2**. The MSM/CC electrocatalyst needs both smaller overpotentials and Tafel slope in the acidic electrolyte (0.5 M H₂SO₄) than in the alkaline medium. The HER performance of the MSM/CC electrocatalyst in a neutral electrolyte (0.5 M Na₂SO₄) was studied and an overpotential of 568 mV was required for 10 mA cm⁻², together with a Tafel slope of 174.6 mV dec⁻¹. Generally, the HER characteristics in neutral media are inferior to those in acidic and alkaline media, but it is more practical to produce hydrogen in neutral electrolytes due to less electrode damage and equipment corrosion. The MSM/CC

electrocatalyst shows a more rapid rise in the current density throughout the applied potential range than the commercial Pt/C catalyst, as indicated in **Figure 2g**. The overpotentials required to produce a current density beyond 45 mA cm⁻² are even smaller compared to the commercial catalyst. The HER characteristics of the MSM/CC electrocatalyst and other typical transition metal-based electrocatalysts in neutral electrolytes are compared in **Figure 2h** and the former indeed delivers outstanding performance.

Figure 2i shows the stability of the MSM/CC electrocatalyst in the neutral electrolyte and the catalyst worked stably for more than 75 h without obvious decay in the current density. Moreover, the morphology of the MSM/CC electrocatalyst remains the same and the nanosheets cover the nanowire arrays (**Figure S13**). **Figure S14** shows similar diffraction patterns from the MSM/CC electrocatalyst after a long-term test, compared to the fresh one, implying high stability. The amount of H₂ produced by the MSM/CC electrocatalyst in HER under the neutral condition is measured by the water displacement configuration as schematically illustrated in **Figure 2j**. The volume of hydrogen collected is determined by a measuring cylinder (100 mL) and 60.5 mL of hydrogen is produced after HER for 80 min at a constant current density of 100 mA cm⁻². High-purity hydrogen is emitted from the neutral electrolyte at a fast rate of 1.85 mmol h⁻¹ (**Figure 2k**). In addition, the Faradaic efficiency is calculated to be as high as 99.58% (**Supporting Note 2**) corroborating the high efficiency in the neutral medium.



Figure 2. (a) Polarization curves, (b) Tafel slopes, (c) EIS, and (d) ECSA of the electrocatalysts measured in 1.0 M KOH electrolyte; (e) Polarization curves and (f) Tafel slopes of the MSM/CC electrocatalyst in different electrolytes; (g) Polarization curves of MSM/CC and commercial Pt/C electrocatalysts in 0.5 M Na₂SO₄; (h) Comparison of the overpotentials of MSM/CC with those of previously reported electrocatalysts in neutral electrolytes, including Fe@N-CNT [22], CuNiTCA [47], Co-NRCNTs [48], CZTS NPs [49], Pd@VNU1 [50], Pd@Zr-AzoBDC [51]; (i) Stability of MSM/CC in 0.5 M Na₂SO₄; (j) Photograph of the HER system with the MSM/CC electrocatalyst and H₂ gas generation determined by the water

displacement method; (k) Experimental and theoretical amounts of H_2 produced by the MSM/CC electrocatalyst and Faradaic efficiency at 100 mA cm⁻².

Since Fe corrodes easily and even self-corrodes in the electrolyte, during which both the anodic and cathodic reactions will occur spontaneously at the electrode surface, and as a result the electrode potential will be different from the reversible or equilibrium potential of each reaction occurring at the surface. In this case, the corrosion potential of Fe is intermediate between the equilibrium potential of the two half-reactions, as indicated by the open circuit potential (also called corrosion potential) measurement in Figure S15. Iron-based species have been investigated as OER electrocatalysts and reconstruction by oxidizing to higher valance states occurs before OER. That is, the FUR is more thermodynamic favorable than the OER. More importantly, waste steel in the construction industry can be recycled to be used as Fe electrodes instead of fresh smelting to reduce the cost, energy consumption, and carbon emission. Here, a waste steel rod (Figure S16) is used as the Fe electrode to determine the FOR properties. The polarization curve in Figure 3a shows that merely 0.11 V vs. RHE is required to generate a current density of 10 mA cm⁻² in FUR in the neutral electrolyte (0.5 M Na₂SO₄), which is 2.01 V smaller than that in OER and even 1.71 V smaller than that of the commercial IrO_2 electrocatalyst (Figure 3a and Figure S17). The results show that by replacing OER with FUR, the energy consumption by the anodic reaction can decrease by 95%. During FUR, white flocculent precipitates are formed as shown in Figure S18a. To analyze the product of FUR, the final electrolyte after FUR was put in a KMnO₄ aqueous solution. The purple KMnO₄ solution turns to clay-bank as shown in Figures S18b-c, suggesting that Fe(II) is produced in FUR due to electrochemical oxidation of the Fe electrode, which is consistent with the literature [22]. The results predict that combining HER and FUR can give rise to energy-saving hydrogen production with hydrogen being the only gaseous product together with other value-adding by-products.

To assess the practicability of the HER/FUR strategy for hydrogen production, the overall reaction of HER and FUR using the MSM/CC electrocatalyst and waste steel rod as electrodes was carried out, as shown in Figure 3b. The polarization curve acquired in the neutral electrolyte (0.5 M Na₂SO₄) is presented in Figure 3c. The voltage required by the MSM/CC-Fe couple is smaller than that of the commercial Pt/C-IrO₂ couple. In detail, a voltage of 0.68 V is needed to generate a current density of 10 mA cm⁻² for the MSM/CC-Fe couple in the neutral electrolyte and it is superior to those of the HER/OER couple in acidic and basic electrolytes, as listed in Table S3. The faraday efficiency of the HER/FUR overall configuration for H₂ production was calculated to be 99.5% in an electrolyzer without a separator as shown in Figure S19a-b, which suggested that the reactants and products of the redox reactions occurring on the cathode and anode do not interact with each other. The evaluation of the stability and feasibility of the HER/FUR integrated system in Figure S20 shows a slight decay of the current density after continuous testing for 24 h, which can be ascribed to the consumption of the Fe anode since the current density returns to the initial state after Fe electrode replacement. The precipitated floccule (after washing and drying) formed in HER/FUR was studied by FE-SEM and XRD revealing nanosized Fe₃O₄ (JCPDS card No. 75-0033) particles (Figure 3d and Figure S21), resulting from partial oxidation of Fe(II) since it is generally unstable and prefers to be oxidized. Moreover, the magnetic properties of the asobtained Fe₃O₄ nanoparticles and commercial Fe₃O₄ were investigated and shown in Figure 3e. The magnetic hysteresis loop shows no remanence or coercivity at room temperature, thus indicating that the nanosized particles have superparamagnetic characteristics. The as-obtained Fe₃O₄ nanoparticles and commercial Fe₃O₄ particles have magnetic saturation (MS) values of approximately 52.0 and 2.6 emu g⁻¹, respectively, suggesting superior magnetic properties for the as-obtained Fe₃O₄ nanoparticles. In addition, the final Fe product can be picked up by a magnet as shown in the inset in Figure 3e, suggesting promising magnetic applications. Generally, the nanosized magnetic powder is more valuable than the waste steel rod at the anode

and therefore, the anodic reaction is value-adding and should further reduce the cost of hydrogen production. Furthermore, the electricity requirement for the HER/FUR couple in the neutral electrolyte is calculated to be 2.69 kWh per m³ H₂ (**Supporting Note 3**). More importantly, high-purity hydrogen and value-adding Fe₃O₄ nanoparticles are produced in conjunction with zero carbon emission. It is lower than that of common overall water splitting systems and even less than the theoretical limit of conventional overall water splitting (2.94 kWh per m³ H₂), as shown in **Figure 3f**.



Figure 3. (a) LSV curves of FUR with a waste steel rod as the working electrode; (b) Model of the HER/FUR couple; (c) LSV curves of MSM/CC-Fe and Pt/C-IrO₂ couples; (d) SEM images and (e) Magnetic properties of the as-obtained Fe₃O₄; (f) Comparison of the energy requirement of the HER/FUR overall reaction system in this work with those of theoretical overall water splitting and reported works, including Ni-P-B/Ni foam [52], CDs/CoP/NF [53], CoSAs-MoS₂/TiN NRs [54], CoS_x||Co₉S₈ [55], FeMn-MOF/NF(1:1) [56], HP-TiO₂/Ni foam [57], LIA-Ni-BDC||LIA-MIL-101(Fe) [58], Ni₃S₂/NF||Ni₃S₂/NF [59], and N-Ni₃S₂/NF [60].

Coupling FUR and HER enables energy-saving hydrogen production but FUR consumes Fe. To further increase the economic benefits of HER/FUR, the product can be used to extract RhB from polluted water via flocculation, a process commonly used in environmental fields to remove pollutants including heavy metal ions and organic species from neutral wastewater. After adding RhB into the neutral electrolyte, the polarization curves for the HER and HER/FUR overall reaction remain the same, as shown in Figure S22. During the HER/FUR overall reaction, the color of the electrolyte changes from rose red to garnet accompanied by floccule formation. The electrolyte then turns colorless and precipitates are formed as shown in Figure 4a. The precipitation process is shown in the Supporting Video which shows that bubbles are emitted from the cathode and floccule precipitates in the electrolyte in HER/FUR. Figure 4b shows the schematic of recovery of polluted water and formation of value-adding products in the process. RhB-containing wastewater can be purified by the HER/FUR overall reaction, as indicated by the fact that the total organic carbon (TOC) decreases from 167.9 to 19.5 mg L⁻¹ (Figure S23). At the same time, RhB can be recovered from the electrolyte by coagulation of the floccule. The UV-vis spectra of the electrolyte during the overall reaction are shown in Figure 4c, which indicates that RhB can be removed completely after the reaction in ~30 min. The UV-vis spectra of coagulated electrolyte indicate the same peak location to the initial one but the absorbance increases by 80% as shown in Figure 4d, suggesting the RhB is beneficiated to a higher concentration. The results reveal that the chemistry of RhB remains unchanged through floccule precipitation, during which RhB can be beneficiated. Furthermore, the HER/FUR overall reaction can be powered by a solar cell with an output voltage of 1.5 V as illustrated in Figure 4e. Bubbles are generated from the MSM/CC electrode only as shown in Figures 4f-g. The results indicate that energy-saving hydrogen production can be realized in conjunction with RhB recovery from polluted water in one system powered by sustainable energy.



Figure 4. (a) Pictures of the HER/FUR electrolyte in different states; (b) Schematic of polluted water recovery and formation of value-adding products; (c) UV-vis spectra of the electrolyte (6 times dilution) during the HER/FUR overall reaction; (d) UV-vis spectra of the fresh electrolyte and beneficiated RhB with 6 times dilution; (e) Photograph showing the solar cell-powered HER/FUR overall reaction system; Photographs of (f) Anode and (g) Cathode in the HER/FUR reaction.

The RhB beneficiation process and mechanism are described in the Supporting Note. Firstly, the Fe rod is oxidized into Fe^{2+} on the anode in the reaction. Owing to the small Ksp (solubility product constant) of Fe(OH)₂, Fe²⁺ prefers to form a nanosized Fe(OH)₂ precipitate in the neutral electrolyte (0.5 M Na₂SO₄, pH = 5.80) as described in the Supporting Note 4. Secondly, the RhB molecules adsorb onto the Fe(OH)₂ and precipitate with it. As a result, RhB is extracted from the polluted electrolyte and the resulting concentration diminishes. Generally, Fe(II) is unstable and prefers to be oxidized. Thirdly, by means of separation of the Fe(OH)₂ and RhB by coagulation, the adsorbed RhB is released into the solution to form the beneficiated solution. At the same time, $Fe(OH)_2$ is precipitated and sinks to the bottom. In the full cycle of absorption and release of the RhB, only electrostatic adsorption works and therefore, RhB can be beneficiated without chemical evolution. Therefore, the FUR coupled HER overall reaction not only decreases the energy consumption of hydrogen production intrinsically but also beneficiates RhB from polluted water for recycling. Moreover, magnetic Fe₃O₄ nanoparticles are produced from the waste steel rod, as analyzed in Supporting Note 5. The process accomplishes clean energy production and environmental recovery at the same time while emitting zero carbon.

4. Conclusion

A novel strategy to integrate HER and FUR is demonstrated for simultaneous energy-saving hydrogen production and organic pollutant removal/recovery in neutral media. High-purity hydrogen is produced on the cathode electrocatalyzed by a heterostructured MSM/CC electrocatalyst, which requires 568 mV to generate a current density of 10 mA cm⁻² and shows a Tafel slope of 174.6 mV dec⁻¹ in 0.5 M Na₂SO₄. The outstanding HER capability in the neutral electrolyte originates from the synergetic effects of high active site exposure and electrical conductivity of the MSM/CC heterostructure. Owing to the favorable thermodynamics of FUR compared to OER, the potential required to achieve an anodic current

density of 10 mA cm⁻² decreases by 95%. Additionally, the HER/FUR couple requires 0.68 V to achieve 10 mA cm⁻² and can thus be powered by solar cells. The electricity equivalent of the HER/FUR couple in the neutral electrolyte is calculated to be 2.69 kWh per m³ H₂ for the production of high-purity hydrogen with zero carbon emission. The waste steel rod used as the anode is oxidized into Fe²⁺, which can be used to extract RhB from wastewater. As a result, purified water with extremely low TOC has been obtained. The beneficiated RhB has been separated from the electrolyte by the following coagulation of Fe species. In addition, value-adding Fe₃O₄ magnetic powder with superparamagnetic characteristics and high magnetic saturation value is also formed. Our work reveals a new way to realize energy-efficient hydrogen production and environmental recovery and the strategy is promising for carbon-neutral energy and ecological systems.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Zhitian Liu, Biao Gao, and Paul K Chu supervised and conceived this project. Xiang Peng, Song Xie, Shijian Xiong, Rong Li, and Peng Wang carried out materials fabrication, materials characterizations, electrochemical measurements, and DFT calculations. Xiang Peng, Xuming Zhang, and Liangsheng Hu analyzed the results and wrote the paper. Xiang Peng, Zhitian Liu, Biao Gao, and Paul K Chu revised the manuscript and triggered helpful discussion. All authors discussed the results and commended the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at

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