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RGO induced one-dimensional bimetallic carbide nanorods: An efficient and pH-universal hydrogen evolution reaction electrocatalyst

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ABSTRACT

It is an urgent mission to develop efficient and stable non-precious metal electrocatalyst toward hydrogen evolution reaction (HER) for the implementation of hydrogen energy. Here, we demonstrate a novel RGO (reduced graphene oxide) induced one-dimensional bimetallic carbide nanorods (Fe₃W₃C NRs/RGO), which exhibits extraordinary HER performance with almost zero onset potential, small Tafel slope and extreme high electrochemical durability in wide pH range. Experimental results in combination with density functional theory calculations reveal that the chemical and electronic coupling between the Fe₃W₃C and RGO synergistically promotes the charge-transfer, proton adsorption and reduction, giving rise to excellent HER performance.

1. Introduction

With the increasing global energy shortage and climate change caused by greenhouse gases, human beings have projected the strategy of sustained development depends on clean renewable energy sources. As a definite clean chemical fuel with high gravimetric specific energy density, hydrogen (H₂) has been considered as one of the most promising alternative energy source candidates that may replace carbon based fossil fuels in the future. Being an environment-friendly hydrogen generation strategy, electrochemical water splitting has recently been emerging as a carbon-free approach to produce H₂, which has attracted increasing attentions on the high efficient electrocatalysts toward hydrogen evolution reaction (HER). Pt-based electrocatalysts exhibit excellent activity toward HER. However, because the scarcity and high cost of Pt, it is impossible for the Pt-based electrocatalysts to be deployed in large-scale commercial applications. Hence, many scientists devoted themself to investigate the possibility of using earth abundant and inexpensive materials to replace Pt, and some remarkable achievements have been made, such as transition metal carbide [1–4], transitional metal nitrides [5–7], transitional metal chalcogenides [8–10], transitional metal phosphides [11–13], transitional metal borides [14,15], g-C₃N₄ [16,17], carbon-based metal-free catalysts [18], and so on.

Due to its excellent electrical conductivity, high corrosion resistance, high stability, high melting point, the similarity of the electronic states with noble Pt at the Fermi level, etc., WC has been considered as one of the promising non-precious metal catalyst toward HER. As a result of increasing research interest, great efforts have been made to synthesize nanostructured WC, such as WC nanotubes [19], WC nanorods [20], WC nanowalls [21], truncated hexagonal pyramid (THP) WC [22], 2D WC crystals embedded in graphene [4], which aimed to optimized the physical and chemical properties of the WC. However, the application of WC is still restricted by its mediocre HER activity.

Usually, introduce another element to the catalysts is a practical way to tailor its electronic structure, improve its physical and chemical properties, and facilitate its practical applications [16,23,24]. Bimetallic carbides, formed after the second transition metal (such as Fe and Co) incorporated into the transitional metal carbide (such as WC and Mo₂C), has been reported as co-catalyst to noble metal catalysts [25–27]. And recently, we have successfully synthesized Co₆Mo₆C nanoframes [1], Co₆Mo₆C nanosheets [28] and Co₆W₆C nanosheets [29], which exhibit higher HER performance than the monometallic carbide. Usually, in these bimetallic carbides, the electron-negativity of second metal (Co/Fe) is slightly lower than the first metal (Mo/W), which would lead a partial charge transform from Co/Fe to Mo/W, and this charge redistribution would weak the binding strength of hydrogen, leading to better HER activity [28–30].

In this paper, we reported the RGO induced growth of Fe₃W₃C nanorods, which involves a two-step approach: hydrothermal reaction of
Fe(WO$_4$) nanorods and subsequent pseudomorphic transformation of Fe(WO$_4$) nanorods to Fe$_3$W$_3$C nanorods. The Fe$_3$W$_3$C NRs/RGO exhibits outstanding catalytic activity and robust electrochemical durability toward HER in a wide pH range. The HER activity of Fe$_3$W$_3$C NRs/RGO is very close to the benchmarked Pt/C catalyst, and exhibit much better HER activity than WC nanorods on RGO support (WC NRs/RGO). The first principle density functional theoretical (DFT) calculations suggest that the excellent electrocatalytic properties of Fe$_3$W$_3$C NRs/RGO originate from the chemical and electronic coupling synergistic effect between Fe$_3$W$_3$C and RGO. After coupling Fe$_3$W$_3$C with RGO, the charge density in Fe$_3$W$_3$C NRs/RGO hybrid's interlayer was redistributed in the form of an apparent charge transfer from C (from graphone), Fe and W to the interface between Fe$_3$W$_3$C and RGO, giving rise to an electron-rich region at the interface between Fe$_3$W$_3$C and RGO. And this electron interaction leads to excellent HER performance. These findings prove that the well-designed Fe$_3$W$_3$C NRs/RGO shows similar HER performance to Pt/C, and open a new avenue towards replacing Pt by non-precious metal catalysts in water splitting and a wide variety of applications.

2. Experimental section

2.1. Chemicals and reagents

Concentrated sulfuric acid (H$_2$SO$_4$, 98 wt%), hydrogen peroxide (H$_2$O$_2$) solution (30 wt%), sodium nitrate (NaNO$_3$), potassium permanganate (KMnO$_4$), graphite powders (325 mesh, XFNANO Material Technologic Co. Ltd., Nanjing, China), Potassium hydroxide (KOH), manganate (KMnO$_4$), graphite powders (325 mesh, XFNANO Material Technologic Co. Ltd., Nanjing, China), Potassium hydroxide (KOH), potassium sulphate (K$_2$SO$_4$), ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_12$O$_4$nH$_2$O) and potassium ferrocyanide (K$_4$Fe(CN)$_6$·3H$_2$O). Platinum on an XC-72 support (Pt/C, 20 wt%, TKK, Japan) was purchased as reference.

2.2. Synthesis of graphite oxide

Modified Hummers’ method was applied to synthesize the graphite oxide. Firstly, 46 mL concentrated H$_2$SO$_4$ (98 wt%) was put in a beaker (500 mL), placed the beaker in an ice bath. When the temperature of the concentrated H$_2$SO$_4$ was cooled to about 0°C, 2.0 g natural graphite powder was gradually added into concentrated H$_2$SO$_4$ under strong agitation. After mixing was reacted for 15 min, then a mixture of 50 g KMnO$_4$ and 5.0 g NaNO$_3$ was also added into the suspension gradually, kept the temperature lower than 20°C. Secondly, increased the suspension temperature to 40°C. After 35 min, 50 mL deionized water was added into the suspension slowly, kept the suspension temperature at about 95°C. After 35 min, the suspension color turn to yellow from dark brown, then 50 mL H$_2$O$_2$ (30 wt%) solution was add to the suspension. Finally, the suspension was filtered, and the product was washed by 1 M HCl aqueous solution (250 mL) and plenty of deionized water, respectively.

2.3. Synthesis of RGO induced one-dimensional Fe$_3$W$_3$C nanorods

Firstly, 30 mg graphite oxide powder was dissolved in 30 mL deionized water, mechanical agitation and ultrasonic dispersing are applied simultaneously for 2 h to exfoliated the graphite oxide to graphene oxide (GO). Then an mixture of 10 mL (NH$_4$)$_6$H$_2$W$_12$O$_4$nH$_2$O (2.58 mL) and 20 mL K$_4$Fe(CN)$_6$·3H$_2$O (9 mL) was added into the GO dispersion. After mechanical agitation and ultrasonic dispersing for 2 h, the mixture was transformed to a 50 mL Teflon vessel, and the Teflon vessel was strictly sealed in a stainless steel autoclave and heated at 230 °C for 2 h. Secondly, the product was filtered and washed by deionized water, after freeze-dried, the precursor was transferred to tube furnace, and was annealed at 900°C (labeled as Fe$_3$W$_3$C NRs/RGO) and 1000°C (labeled as Fe$_3$W$_3$C NRs/RGO_1000) for 2 h under argon atmosphere.

2.4. Synthesis of RGO induced one-dimensional WC nanorods

The one-dimensional WC nanorods on RGO (WC NRs/RGO) was synthesized by the similar method with Fe$_3$W$_3$C NRs/RGO. Firstly, 30 mg graphite oxide powder was dissolved in 30 mL deionized water, mechanical agitation and ultrasonic dispersing are applied simultaneously for 2 h to exfoliated the graphite oxide to graphene oxide (GO). Then 10 mL (NH$_4$)$_6$H$_2$W$_12$O$_4$nH$_2$O (2.58 mL) was add into the GO dispersion. After mechanical agitation and ultrasonic dispersing for 2 h, the mixture was transformed to a 50 mL Teflon vessel, and the Teflon vessel was strictly sealed in a stainless steel autoclave and heated at 230 °C for 2 h. Secondly, the product was filtered and washed by deionized water, after freeze-dried, the precursor was transferred to tube furnace, the sample was annealed at 1000°C for 2 h under argon atmosphere.

2.5. Characterizations

Powder X-ray diffraction (XRD) test was performed on a Rigaku D/MAX-III using Cu Kα radiation operating at 30 kV and 30 mA. The Raman spectroscopic measurements were carried out on a Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser with a wave length of 514.5 nm. The transmission electron microscopy (TEM), high resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and STEM – energy dispersive X-ray spectroscopy (STEM-EDX) elemental mapping were performed on a field emission transmission electron microscope (FETEM, FEI Tecnai G2 F30), which was operated at 300 kV. Scanning electron microscope (SEM) images were carried out on a field emission scanning electron microscope (FESEM,JEOL Ltd.) X-ray photoelectron spectroscopy (XPS) measurement was performed on a ESCALAB 250 (Thermo-VG Scientific Ltd.).

2.6. Electrode preparation

The GCE (glassy carbon electrode, area = 0.2826 cm$^2$) was polished with 0.05 μm alumina slurry, and sonicated in ethanol and deionized water to give a clean surface. Homogeneous ink solution was prepared by sonicating a suspension consisting of 10 mg catalyst, 0.5 mL Nafion solution (0.05 wt %, DuPont, USA) and 0.5 mL ethanol, then a certain amount of the ink was dropped on the GCE surface and dried to form a catalyst thin film.

2.7. Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (Autolab PGSTAT 302, ECO Chemie, Netherlands) with a standard three-electrode system. The working electrode was the sample modified GCE, the reference electrode was a homemade reversible hydrogen (RHE) electrode, and the counter electrode was a piece of graphite (10 × 1 cm$^{-2}$) electrode.

Polarization curves were obtained using linear sweep voltammetry (LSV) curves conducted with a scan rate of 2 mV s$^{-1}$ at 25°C in acid (0.5 M H$_2$SO$_4$) solution. Electrochemical impedance spectroscopies (EIS) were performed at different overpotentials, in the frequency range from 100 kHz to 0.1 Hz with the modulation amplitude of 10 mV. The current density was calculated against geometric area of the glassy carbon electrode and presented after IR correction. The electrochemical durability of the catalysts was investigated through accelerate durability test (ADT) by potential cycling between −0.25 and 0.15 V (vs. RHE) at a sweep rate of 50 mV s$^{-1}$ for 10,000 cycles at 25°C. The HER performance of the Fe$_3$W$_3$C NRs/RGO was also investigated in neutral (0.5 M K$_2$SO$_4$) and alkaline (1 M KOH) solutions. For non-Pt catalysts the catalyst loading is 0.82 mg cm$^{-2}$.

For comparison, 20 wt% Pt/C was measured under the same conditions, the Pt metal loading is 12.5 μg Pt cm$^{-2}$.
2.8. Computational methods

On the basis of the density functional theory (DFT), all the calculations were performed using the projector augmented wave (PAW) method [31] as implemented in the Vienna ab initio simulation package (VASP) [32]. The slab model of Fe₃W₃C@RGO was built by stacking the unit cell of Fe₃W₃C (001) surface and the RGO with a vacuum of 15Å along the slab normal direction. The optimized lattice constants of this heterostructure are \( a = 12.81 \) and \( b = 9.86 \AA \). Brillouin zone integration was calculated using \( 1 \times 1 \times 1 \) k-point meshes and the energy cutoff was set as 500 eV. The convergence tolerance of force on all the atoms was set to be 0.02 eV Å⁻¹. Spin polarization effect was considered in all the calculations.

It is now well-accepted that the hydrogen evolution activity is strongly correlated with the Gibbs free energy of hydrogen bonding (\( \Delta G_{H_2} \), * denotes an adsorption site) to the catalyst surface [33,34]. The free energy change for \( H^* \) adsorption on Fe₃W₃C (001) surfaces (\( \Delta G_{H^*} \)) was calculated as follows [35]:

\[
\Delta G_{H^*} = E_{\text{total}} - E_{\text{surf}} - E_{H_2}/2 + \Delta E_{\text{ZPE}} \cdot \text{TAS}
\]

Where \( E_{\text{total}} \) is the total energy for the adsorption state, \( E_{\text{surf}} \) is the energy of pure surface, \( E_{H_2} \) is the energy of \( H_2 \) in gas phase, \( \Delta E_{\text{ZPE}} \) is the zero-point energy change and \( \Delta S \) is the entropy change. \( \Delta E_{\text{ZPE}} \) is calculated by \( E_{\text{ZPE}} = E_{\text{total}} - E_{\text{calc}} \), where \( E_{\text{calc}} \) denotes the zero-point energy of \( n \) adsorbed \( H \) on Fe₃W₃C@RGO, and \( E_{\text{ZPE}} \) represents the zero-point energy of gas phase \( H_2 \). \( \Delta S_{\text{H}} \) is obtained by \( \Delta S_{\text{H}} = -\frac{\Delta G_{\text{H^*}}}{T} \), where \( \Delta S_{\text{H}} = \text{entropy of } H_2 \) in the gas phase at the standard conditions (\( \Delta S_{\text{H}} \approx 130 \text{ J mol}^{-1} \text{ K}^{-1} \)) [36]. Thus, the minimum energy pathways for \( H_2 \) evolution is calculated by the climbing-image nudged elastic band (CI-NEB) method [37].

3. Results and discussion

The morphology and structure of Fe₃W₃C NRs/RGO were investigated by SEM and HAADF-STEM. From the SEM images, the Fe₃W₃C nanorods grown on RGO surface tightly on both upper and lower surfaces, forming a sandwich-like structure, and the Fe₃W₃C nanorods scaffold was cross-linked with each other with high uniformity and fineness of nanorod diameter (∼10 nm) (Fig. 1a and b). The HAADF-STEM image of Fe₃W₃C NRs/RGO shows the one-dimensional structure of Fe₃W₃C nanorods with ∼10 nm in diameter (Fig. 1c). The high resolution HAADF-STEM image clearly reveals the lattice fringe of 0.34 nm, which is ascribed to the Fe₃W₃C (311) facet (Fig. 1d). Fig. 1e and i shows the STEM-EDX (energy-dispersive X-ray spectroscopy) mapping images of C–K, Fe–K, Fe–L, W–M and W–L that collected from the red dashed box in Fig. 1c. The uniform distribution of the C–K, Fe–K, Fe–L, W–M and W–L reveals the C–Fe–W chemical composition of Fe₃W₃C nanorods, which is also confirmed by the EDX pattern (Fig. S1). The XRD pattern of the Fe₃W₃C NRs/RGO suggests that Fe₃W₃C (Cubic, Fd3m(227)) was formed, which is indexed by the red perpendicular lines (PDF#41–1351), as shown in Fig. 2. The broad diffraction peak at 26.2° is ascribed to graphite (002) facet (000) of the RGO support. The morphology and structure of WC nanorods were also confirmed by TEM, and the HRTEM image clearly reveals the lattice fringe of 0.25 nm, which is ascribed to the WC (100) facet (Fig. S7).

Raman spectrum of the Fe₃W₃C NRs/RGO was measured to investigate the bonding state of carbon atoms in RGO support. The peak at 1350 cm⁻¹ represents a zone-edge A₁g mode due to the disorder. The G peak at 1577 cm⁻¹ reflects the zone center E₂g mode of perfect graphite. The Raman intensity of the I_D/I_G values of WC NRs/RGO is much smaller than that of GO, which indicates that the RGO supports disorder decrease considerably and restore to the pristine graphene structure, which give rise to high electric conductivity of the Fe₃W₃C NRs/RGO, thus facilitating the electron transfer during the HER process [41].

The catalytic activity of Fe₃W₃C NRs/RGO toward HER was investigated by using a typical three-electrode system. The HER performance of benchmarked commercial Pt catalyst (TCK, 20 wt% Pt on Vulcan XC-72R carbon black, Pt/C) was also measured as reference. The Pt/C exhibits the highest HER activity with zero onset overpotential (Fig. 4a). The overpotential at current density of 10 mA cm⁻² of Pt/C is just 37 mV (η₀ = 37 mV). The onset overpotential of Fe₃W₃C NRs/RGO is also almost zero. The η₀ of the Fe₃W₃C NRs/RGO is 57 mV, only 20 mV higher than Pt/C, which is compare favorably to most of the previous reports for VB/VIB group TMCS, including MoC₃ nano-octahedrons [42], np-MoC₂NWs [43], WₓC@GL [44], Mo/C-CNT-GR [45], 2D-WC–G [46] and 2D TaC–RGO [2]. It is worth to note that the η₀ of Fe₃W₃C NRs/RGO is smaller than those of previously reported...
bimetallic carbides, such as nw-W₄MoC [46], C–CoWC [47] and Co₆Mo₆C/G [1]. Table S1 shows the performance comparison of various non-precious metal catalysts for HER. The $\eta_{10}$ of WC NRs/RGO is 151 mV, much higher than that of Fe₃W₃CNRs/RGO. Fig. S9 shows the HER performance comparison of Fe₃W₃C NRs/RGO, Fe₃W₃C NRs/RGO₄₀₀₀, WC NRs/RGO and Pt/C. The $\eta_{10}$ of the Fe₃W₃CNRs/RGO₄₀₀₀ is 64 mV, only 7 mV higher than Fe₃W₃CNRs/RGO (57 mV), and much smaller than WC NRs/RGO (151 mV).

The catalytic mechanism of the catalysts were investigated by fitting the polarization curve by Tafel equation ($\eta = b \log |j/j_0|$), where j is the

![Fig. 1. (a–b) The representative SEM images of Fe₃W₃C NRs/RGO, (c) HAADF-STEM image of Fe₃W₃C NRs/RGO, (d) high resolution HAADF-STEM image of Fe₃W₃C NRs/RGO, (e–i) STEM-EDX elemental mapping images of C–K, Fe–K, Fe-L-M and W-L in Fe₃W₃C NRs/RGO.](image)

![Fig. 2. XRD pattern of Fe₃W₃C NRs/RGO.](image)
current density, $b$ is the Tafel slope and $j_0$ is exchange current density ($j_0$) [48,49]. An ideal catalyst has low Tafel slope and high exchange current density. The Tafel slope of Pt/C is 30 mV dec$^{-1}$ (Fig. 4b), which suggests that the hydrogen evolution on Pt/C is dominated by Volmer–Tafel reaction mechanism ($\text{H}_3\text{O}^++\text{e}^-\rightarrow\text{H}_{\text{abs}}+\text{H}_2\text{O};\text{H}_{\text{abs}}+\text{H}_{\text{abs}}\rightarrow\text{H}_2$), in which the discharge reaction (Volmer step) is fast and $\text{H}_2$ is evolved by a rate-determining combination reaction (Tafel step) [50]. The Tafel slope of Fe$_3$W$_3$C NRs/RGO is 50 mV dec$^{-1}$ (Fig. 4b), which suggest the hydrogen evolution Fe$_3$W$_3$C NRs/RGO probably proceed via Volmer-Heyrovsky reaction mechanism ($\text{H}_3\text{O}^++\text{e}^-\rightarrow\text{H}_{\text{abs}}+\text{H}_2\text{O};\text{H}_3\text{O}^++\text{e}^-+\text{H}_{\text{abs}}\rightarrow\text{H}_2+\text{H}_2\text{O}$), in which the discharge reaction is fast and $\text{H}_2$ is evolved by a rate determining

![Fig. 3. (a) XPS spectra of Fe$_3$W$_3$C NRs/RGO, high-resolution scan of W 4f (b), Fe 2p (c) and C 1s (d) of Fe$_3$W$_3$C NRs/RGO.](image_url)

![Scheme 1. Schematic illustration of the synthesis of Fe$_3$W$_3$C NRs/RGO.](image_url)
ion + atom reaction. The Tafel slope of WC NRs/RGO is 101 mV dec$^{-1}$ (Fig. 4b), which suggests that the discharge reaction is slow. The Tafel slope of Fe$_3$W$_3$C NRs/RGO,1000 is 56 mV dec$^{-1}$ (Fig. 5a), which is very close to Fe$_3$W$_3$C NRs/RGO (50 mV dec$^{-1}$), suggesting the similar reaction mechanism (Volmer-Heyrovsky reaction mechanism). The exchange current density ($j_0$) is another important kinetic parameter that correlate to the rate of electron transfer under reversible conditions (that is, at zero overpotential) [50]. The $j_0$ of Fe$_3$W$_3$C NRs/RGO is 0.225 mA cm$^{-2}$, which is almost as high as Pt/C (0.279 mA cm$^{-2}$), which suggests that Pt-like activity of Fe$_3$W$_3$C NRs/RGO toward HER. While the WC NRs/RGO exhibits much lower $j_0$ of 0.067 mA cm$^{-2}$, which indicate sluggish reaction kinetics.

Electrochemical impedance spectroscopy (EIS) was used to investigate the as-constructed electrode/solution interface reaction properties and electron transfer kinetics of Fe$_3$W$_3$C NRs/RGO during the HER process. Fig. 4c shows the Nyquist plots of Fe$_3$W$_3$C NRs/RGO and WC NRs/RGO at the overpotential of 100 mV. The Nyquist plots of Fe$_3$W$_3$C NRs/RGO and WC NRs/RGO were fitted by a facile Randle equivalent circuit (inset in Fig. 4c). A two-time-constant phase element was used for this fitting procedure [48,51]. In this model, $R_s$ represents the electric resistance of the solution, wires and the contact resistance between the glassy carbon electrode and the catalyst layer, and the $R_s$ connects in series with two additional branches: one is related to the charge-transfer process ($CPE1$-$R_{ct}$), the other to the surface porosity ($CPE2$-$R_p$). The charge-transfer resistance ($R_{ct}$) determined from the semicircle registered at low frequencies, reflects the HER kinetics, a smaller $R_{ct}$ value corresponds to faster kinetics. The charge-transfer resistance ($R_{ct}$) of Fe$_3$W$_3$C NRs/RGO is 36.7 Ω (at $\eta = 100$ mV), which is much smaller than that of WC NRs/RGO (187.4 Ω at $\eta = 100$ mV), suggesting much faster electron transfer from active sites of Fe$_3$W$_3$C NRs/RGO to protons during HER. The $R_{ct}$ of Fe$_3$W$_3$C NRs/RGO was reduced when the overpotential was increased from 68.9 Ω (at 50 mV) to 24.6 Ω (at 150 mV), which was confirmed by the decrease of the diameter of the semicircles (Fig. 4d). In order to gain insight into the intrinsic activities of the electrocatalysts, the turnover frequency (TOF) was studied. The TOF of WC NRs/RGO and Fe$_3$W$_3$C NRs/RGO are 0.02 and 0.23 s$^{-1}$ (−100 mV vs RHE), respectively, which suggest the Fe$_3$W$_3$C NRs/RGO is a more efficient HER catalyst than WC NRs/RGO.

The HER activity of Fe$_3$W$_3$C NRs/RGO in neutral (0.5 M H$_2$SO$_4$) and alkaline (1 M KOH) electrolytes was also investigated since an ideal HER catalyst should exhibit outstanding performance in wide pH range [52]. Fig. 5a compares the polarization curves of Fe$_3$W$_3$C NRs/RGO in 0.5 M H$_2$SO$_4$, 0.5 M K$_2$SO$_4$ and 1 M KOH solutions. The $\eta_{10}$ of Fe$_3$W$_3$C NRs/RGO in 0.5 M H$_2$SO$_4$ and 1 M KOH solutions are 103 mV and 77 mV, respectively, which is a litter higher than that in 0.5 M H$_2$SO$_4$ solution (57 mV). The Tafel plots of Fe$_3$W$_3$C NRs/RGO in 0.5 M H$_2$SO$_4$, 0.5 M K$_2$SO$_4$ and 1 M KOH solutions are 50 mV dec$^{-1}$, 77 mV dec$^{-1}$ and 80 mV dec$^{-1}$ (Fig. 5b). Generally speaking, the HER activities of Fe$_3$W$_3$C NRs/RGO are in this order: 0.5 M H$_2$SO$_4$ > 1 M KOH > 0.5 M K$_2$SO$_4$.

The electrochemical durability of Fe$_3$W$_3$C NRs/RGO in 0.5 M H$_2$SO$_4$, 0.5 M K$_2$SO$_4$ and 1 M KOH solutions was investigated by using continuous cyclic voltammetry technology. As shown in Fig. 5c and d, the polarization curves of Fe$_3$W$_3$C NRs/RGO after 10,000 cycles were
almost overlapped with their own initial ones in 0.5 M H₂SO₄, 0.5 M K₂SO₄ and 1 M KOH solutions, which suggest that the Fe₃W₃C NRs/RGO are extremely stable in wide pH range.

We conducted density functional theory (DFT) calculations to show the interlayer electronic-coupling effect between Fe₃W₃C and RGO. Fig. S10 presents the total density of states (DOS) and orbital-resolved partial DOS of the bulk Fe₃W₃C, RGO, Fe₃W₃C surface, and Fe₃W₃C@RGO heterostructure. For the bulk Fe₃W₃C, the Fe-3d orbitals are strongly hybridized with the W-5d orbitals between approximate −8.6 eV and 2.9 eV (see Fig. S10a). When cleaved into Fe₃W₃C surface, the DOS changes little (see Fig. S10c), indicating the Fe₃W₃C surface retains most of the electronic properties of the bulk Fe₃W₃C. As shown in Fig. S10b, the C-2p orbitals of RGO distribute in a very wide range of energy. After the stacking of Fe₃W₃C surface and RGO, the C-2p orbitals of RGO are hybridized with the W-5d orbitals between −6.8 eV and 4.0 eV and with the Fe-3d orbitals between approximate −5.2 and 4.0 eV (see Fig. S10d). The strong orbital hybridization contributes to the stability of Fe₃W₃C@RGO heterostructure. To better understand the bonding mechanism of the Fe₃W₃C@RGO heterostructure, the charge density difference Δρ of this heterostructure is calculated based on the following equation:

\[ Δρ = ρ_{Fe₃W₃C@RGO} - ρ_{Fe₃W₃C} - ρ_{RGO} \]

where \( ρ_{Fe₃W₃C@RGO} \), \( ρ_{Fe₃W₃C} \) and \( ρ_{RGO} \) are the total charge of the Fe₃W₃C@RGO heterostructure, the Fe₃W₃C surface, and the RGO, respectively. As shown in Fig. 6, we find that the electron losses mainly come from the C atoms (from RGO), Fe and W atoms (from Fe₃W₃C), indicating Fe-C and W-C bonds are formed, and the electrons tend to accumulate at the interface between Fe₃W₃C and RGO, thus resulting in strong interlayer coupling. This redistribution of charge and the formation of Fe–C and W–C bonds contribute to stabilize the Fe₃W₃C@RGO heterostructure and facilitate the electrocatalytic HER.

The Gibbs free energies of hydrogen bonding (ΔG_H*) is highly related to the HER activity of the catalyst [33, 34], and the ΔG_H* should be zero for an ideal HER catalyst, which means the adsorption and desorption of H_ads species on the catalyst surface is in a perfect equilibrium. The DFT-calculated free-energy diagram of HER at the equilibrium potential for the catalysts and Pt reference is shown in Fig. 7, in which a three-state diagram, comprising an initial state H⁺ + e⁻, an intermediate adsorbed H*, and a final product \( \frac{1}{2}\)H₂, was used to describe the overall HER [16]. The ΔG_H* of Pt is −0.09 eV, which is very close to zero, suggesting that Pt is almost the ideal HER catalyst. The negative value of ΔG_H* indicates that the chemical adsorption of H* on the Pt surface is fast and the overall HER rate is determined by the H₂ evolution step, which is consistent with Tafel analyses. A large positive ΔG_H* = 1.93 eV on RGO indicates a very weak chemical adsorption of H*, which make electrocatalytic HER on RGO rarely occur [53]. While a large negative ΔG_H* = −0.49 eV on Fe₃W₃C indicates that the chemical adsorption of H* is strong, which is also unfavorable for the electrocatalytic HER. After coupling with RGO, the hybrid exhibits a mediated adsorption–desorption behavior (|ΔG_H*|→0), which is favorable for the electrocatalytic HER. Such improvement originates from the redistribution of charge and the electrons accumulation at the interface between Fe₃W₃C and RGO, which can reduce the adsorbed H* species to the final molecular hydrogen. Furthermore, to understand the role of Fe and W components in the Fe₃W₃C NRs/RGO, we also investigated the ΔG_H* of WC and WC/RGO. As shown in Fig. 7, the ΔG_H* of WC is −1.21 eV, which is much lower than Fe₃W₃C (−0.49 eV), suggesting weaker but more reasonable hydrogen adsorption strength of Fe₃W₃C. This likely because electron-
negativity of Fe is slightly lower than W, which would lead to a partial charge transform from Fe to W [30], and this charge redistribution would weak the binding strength of hydrogen. After coupling with RGO, the Δ\(\text{G}^{\text{H*}}\) of WC/RGO (−0.62 eV) is also much lower than Fe\(_3\)W\(_3\)C/RGO (−0.20 eV). These results reveal that after Fe was incorporated into the WC, formed bimetallic carbide (Fe\(_3\)W\(_3\)C), the Δ\(\text{G}^{\text{H*}}\) become more close to zero, leading to better HER activity.

4. Conclusion

In summary, we developed a feasible two-step strategy for the synthesis of Fe\(_3\)W\(_3\)C nanorods on RGO support (Fe\(_3\)W\(_3\)C NRs/RGO). The Fe\(_3\)W\(_3\)C NRs/RGO exhibits Pt-like activity toward HER with zero onset potential, small overpotential at 10 mA cm\(^{-2}\), small Tafel slope and extreme high electrochemical durability in wide pH range, which is highly competitive among the non-precious metal catalysts toward HER, making it one of the most candidates for replacing Pt-based catalyst toward HER. The DFT calculations reveals that the remarkable HER performance of Fe\(_3\)W\(_3\)C NRs/RGO mainly stem from the synergistic effect of chemical and electronic couplings between Fe\(_3\)W\(_3\)C NRs and RGO.

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Appendix A. Supplementary data

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References


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Fig. 6. Top and side views of the charge density difference of the Fe\(_3\)W\(_3\)C@RGO heterostructure. (a) Electron gains and losses, (b) electron gains, and (c) electron losses. The yellow and cyan areas represent electron gains and losses, respectively.

Fig. 7. DFT-calculated free energy diagrams for the electrochemical reduction of H\(^+\) at the equilibrium potential for Pt, RGO, Fe\(_3\)W\(_3\)C, WC, Fe\(_3\)W\(_3\)C@RGO and WC@RGO heterostructure.

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