available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Metal-doped Mo₂C (metal = Fe, Co, Ni, Cu) as catalysts on TiO₂ for photocatalytic hydrogen evolution in neutral solution

Jing Liu^a, Gary Hodes^c, Junqing Yan^{a,*}, Shengzhong (Frank) Liu^{a,b,#}

^a Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, Shaanxi, China

^b iChEM, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^c Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel

ARTICLE INFO

Article history:

Received 28 March 2020

Accepted 3 May 2020

Published 5 January 2021

Keywords:

3d metal

Doping

Mo₂CTiO₂

Photocatalysis

Water splitting

Hydrogen evolution

ABSTRACT

The neutral hydrogen evolution reaction (HER) is vital in the chemical industry, and its efficiency depends on the interior character of the catalyst. Herein, work function (W_F) engineering is introduced via 3d metal (Fe, Co, Ni, and Cu) doping for modulating the Fermi energy level of Mo₂C. The defective energy level facilitates the free water molecule adsorption and, subsequently, promotes the neutral HER efficiency. Specifically, at a current density of 10 mA/cm², Cu-Mo₂C exhibits the best HER performance with an overpotential of 78 mV, followed by Ni-Mo₂C, Co-Mo₂C, Fe-Mo₂C, and bare Mo₂C with 90, 95, 100, and 173 mV, respectively, and the corresponding Tafel slope values are 40, 43, 42, 56, and 102 mV/dec. The modified W_F can also lead to an enhanced photocatalytic efficiency owing to the lowered Schottky barrier and excellent carrier transition across the electrocatalyst–solution interface. When coupling the metal-doped Mo₂C samples with TiO₂, enhanced photocatalytic neutral HER rates are obtained in comparison to the case with bare TiO₂. Typically, the HER rates are 521, 404, 275, 224, 147, and 112 μmol/h for Cu, Ni, Co, Fe, bare Mo₂C, and bare TiO₂, respectively. Time-resolved photoluminescence spectroscopy (TRPS) and ultrafast transient absorption (TA) measurements are carried out to confirm the recombination and migration of the photogenerated carriers. The fitted τ values from the TRPS curves are 22.6, 20.5, 10.1, 4.7, 4.0, 2.5, and 1.9 ns for TiO₂, TiO₂-Mo₂C, TiO₂-Fe-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Ni-Mo₂C, TiO₂-Cu-Mo₂C, and TiO₂-Pt, respectively. Additionally, the fitted τ values from the TA results are 31, 73, and 105 ps for the TiO₂-Mo₂C, TiO₂-Cu-Mo₂C, and TiO₂-Pt samples, respectively. This work provides in-depth insights into the W_F modulation of an electrocatalyst for improving the HER performance.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The hydrogen evolution reaction (HER) via electrocatalytic

water splitting is regarded as one of the promising technological strategies for solving the energy problem in the near future [1–7]. The hydrogen evolution electrode, often the most critical

* Corresponding author. E-mail: junqingyan@snnu.edu.cn

Corresponding author. E-mail: liusz@snnu.edu.cn

We acknowledge support from the National Key Research Program of China (2017YFA0204800, 2016YFA0202403), the National Natural Science Foundation of China (21603136), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT_14R33), and the 111 Project (B14041).

DOI: 10.1016/S1872-2067(20)63589-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 1, January 2021

component for the HER, has been intensively investigated to integrate hydrogen generation into energy and industrial infrastructures. For the typical HER, there are three steps: (1) protons (in acid solution) or water molecules (in neutral or alkaline solution) are adsorbed on the reaction sites (M) of the electrode; (2) M–H bonds are formed under a slight electrode discharge; (3) Hydrogen generation through the combination of two nearby M–H or proton and M–H or water and M–H [8–10].

Previous experimental and theoretical studies have shown that water dissociation plays a significant role in achieving an efficient HER in neutral media [11–14]. An efficient approach to improving the kinetics of water dissociation involves accelerating the breaking of H–OH bonds by creating more surface-active sites [15–18]. Although the general design principle for achieving enhanced neutral HER efficiency has been regarded as accelerated water dissociation, design rules for developing more efficient neutral catalysts are still needed.

Besides the nature of the electrolyte and the electrode, the interface between them also determines the performance of the electrocatalyst, and thus, its character relates to the external expression of the activity [18–20]. In the semiconductor-solution interface, there is a classical model of carrier migration and reaction [21–23]; the initial energy difference between the Fermi level (E_{fermi}) of the semiconductor and the value of the redox couple is the intrinsic factor essential for ultimate performance [22,24,25]. Accordingly, a similar interface also exists for the electrocatalyst-solution system. As shown in Figure 1a, there are two different energy levels for the redox couple (O/R); thus, it is assumed that there is a quasi- E_{fermi} between the reduction and oxidation energy levels (W_{R} and W_{O} , respectively). In that manner, the E_{fermi} of one electrocatalyst needs to be equal to the quasi- E_{fermi} of the O/R couple after the equilibration. Once a bias is applied to the electrode, the electrons flow into the bulk of the material and induce the promotion of the electrode E_{fermi} , and the current appears across the interface. Notably, for the electron tunnel jump, the electron energy level remains unchanged. However, the surface adsorption of reaction precursors is crucial for the above reaction process owing to the limited lifetime of the electron in solution, on which further study is required.

Doping is known to weaken or strengthen the surface adsorption energy between materials and reaction intermediates [26–30]. It can also form additional energy levels near the E_{fermi} and change the electrode interfacial dipole layer to some extent [31–33]. Cation doping, particularly involving 3d transition metals (TMs, such as Fe, Co, Ni, and Cu), can provide more electron orbits through their 3d orbital hybridization with nonmetals, as shown in Figure 1b. The interface of the materials will present a positive charge property and can, thus, promote the oxygen absorption of water molecules [34–38]. In this case, the 3d TM doping is assumed to improve the water-splitting performance under the neutral condition, and this assumption still requires confirmation. Molybdenum carbide (Mo_2C) has been intensively studied as a high-efficiency HER electrocatalyst owing to its outstanding electrical conductivity [39–44] and its similar electronic structure as Pt-group metals [45,46], making it a

Fig. 1. Schematic diagram of the electron tunnel transition across the electrode-solution interface, (a) the bare and (b) the doped catalyst systems. E_{vac} , vacuum level; E_{f} , Fermi level; ϕ , work function; W_{O} and W_{R} are the reduction and oxidation energy levels of the O/R redox couples; $E^0_{1(\text{O/R})}$, the defined quasi- E_{fermi} of the redox couple; the electronic energy level of the electrode is scaled by E_{vac} , and the redox couple is the standard hydrogen electrode (SHE). The doping energy level is also shown in b.

potential substitute for Pt in the field of electrocatalysis. Tuning its solid-solution interface properties for achieving a high HER performance under a neutral condition has not been profoundly studied.

Herein, we report the 3d TM (Fe, Co, Ni, and Cu) -doped Mo_2C synthesized by a solid-state reaction for enhancing the water adsorption capacity at the early stage of an electrocatalytic reaction. The 3d TM doping brings the defective energy level around the E_{fermi} and, subsequently, promotes the electron tunnel transition across the solid to the Helmholtz layer in the solution (pH = 6.8). Cu- Mo_2C exhibits the best HER performance, followed by Ni-, Co-, and Fe-doped samples. Moreover, we investigate the modification of the surface of TiO_2 with the metal-doped Mo_2C and measure the photocatalytic hydrogen evolution performance.

2. Experimental

Synthesis of undoped and metal-doped Mo_2C . Both the materials of MoO_3 and TiO_2 were purchased from Alfa Aesar Chemical Co. For the metal-doped samples, MoO_3 was mixed with metal chlorates in 50 mL of a deionized aqueous solution. The mixture was stirred for about 24 h and was, subsequently, subjected to centrifugation and drying. Thereafter, the obtained $\text{MO}_x\text{-MoO}_3$ was mixed with urea and ground evenly. After that, the mixture was calcined under N_2 condition, for 5 h at 600 °C. For the preparation of bare Mo_2C , the same process was carried out without chlorate addition.

Synthesis of $\text{TiO}_2\text{-M-Mo}_2\text{C}$. The photo-assisted impregnation method was used for loading M- Mo_2C onto the surface of TiO_2 . Typically, TiO_2 - and Mo_2C -based samples were mixed in 50 mL of a deionized aqueous solution. A 365-nm LED lamp was introduced under continuous stirring. After adsorption for 4 h, the product was centrifuged and dried.

Characterization. TEM was performed on a FEI Tecnai G2 F20 electron microscope at an acceleration voltage of 200 kV. The diffuse reflectance ultraviolet-visible (UV-Vis) spectra of

studied samples were recorded in the air against BaSO₄ on a Perkin-Elmer Lambda 950 spectrophotometer. The XRD patterns of the samples were recorded on a Rigaku Smartlab-9kW instrument using Cu K α X-ray ($\lambda = 1.54186 \text{ \AA}$) radiation at a scanning rate of $4^\circ/\text{min}$. The XPS spectra were acquired on a Kratos Axis Ultra DLD spectrometer with Al K α ($h\nu = 1486.6 \text{ eV}$) as the excitation source. Room-temperature PL spectroscopy and time-resolved fluorescence spectroscopy were conducted on a PerkinElmer LS55 fluorescence spectrophotometer. FTIR was carried out on a Bruker V70 spectrometer with a Pike heat chamber. The electrocatalytic water-splitting performances were carried out in a conventional three-electrode cell on a Zennium Zahner electrochemical workstation. The femto-second TA measurement was carried out using the techniques developed by Han and coworkers [61,62]. The samples were spined onto quartz glasses and then tested. The photocatalytic water splitting was performed in a vacuum system. Typically, a catalyst sample of 100 mg was suspended in 100 mL of a 10% methanol aqueous solution in the reaction cell. After evacuated for 30 min, the reactor cell was irradiated by the Xe lamp at 200 W. The gaseous products were analyzed using an on-line gas chromatograph equipped with a thermal conductivity detector.

3. Results and discussion

3.1. Synthesis and Characterization of the Mo₂C-based samples

The metal oxide-coated Mo₂C samples were synthesized via a two-step process, as shown in Figure 2a (See Experimental Section). The amount of metal was 10% (molar ratio) of Mo. Noteworthy, the molar ratio of the metals to Mo was measured by ICP to be ca. 1% for the 10% samples. Figure 2b gives the X-ray diffraction (XRD) patterns of the bare and metal oxide (MO_x)-loaded MoO₃; there was no difference between the MO_x

pattern and those of all the MO_x-loaded ones, and MO_x could not be detected, suggesting the limited MO_x amount and mild loading process. Figure 2c shows the XRD patterns of the Mo₂C samples, which all show the typical β -Mo₂C (PDF No. 35-0787) peaks [47–49].

No impurity peaks derived from MO_x or metal, other than those indicative of Mo carbides, can be observed. However, when we magnify the range of 2θ from 32° – 42° , (101) shifts to a larger 2θ , from the bare Mo₂C to Fe, Co, Ni, and Cu-doped Mo₂C (Figure S1), confirming the element radius change tendency. Moreover, the surface metal doping will introduce more surface defective sites, which are confirmed by the shift of the XRD peak and will be beneficial for water adsorption and splitting. Figure S2 gives the XRD patterns of the other doped metal contents, 5% and 15%. Similarly, the MO_x-loaded MoO₃ and the corresponding metal-doped Mo₂C samples all give the typical MoO₃ and Mo₂C patterns, respectively.

The morphology and microstructure of the as-prepared bare and metal-doped Mo₂C samples were measured by transmission electron microscopy (TEM). As shown in Figures S3a–e, the bare Mo₂C has a bulky shape, confirming that the high-temperature solid-state reaction will induce the created particle aggregation. Moreover, the precursor of MoO₃ is the typical thick-layered structure [27,50]. Similarly, the metal-doped Mo₂C samples show the bulk morphology with the small particles, further suggesting a strong reaction between MoO₃ and urea. The lattice structure of the above samples can be detected clearly by high-resolution TEM (HRTEM). As seen in the HRTEM images of Figures S3f–g, the bare and metal-doped Mo₂C samples all show a ca. 0.23 nm lattice, which is assigned to the (101) Mo₂C interplanar spacing [44,45]. Some slightly reduced interplanar spacing values can be found for the metal-doped samples in comparison to those of the bare Mo₂C, which are consistent with the above XRD result. The TEM images of the other metal-doped Mo₂C samples can be found in Figure S4. Clearly, all of them show a similar appearance with the bare Mo₂C, further suggesting a complete reaction between MoO₃ and urea.

The surface chemical constituents of the bare and metal-doped Mo₂C were investigated by XPS. The wide XPS spectra can be found in Figure S5. Mo and the doped metals (Fe, Co, Ni, and Cu) present detectable peaks, and no impurities (for example, C 1s) were found, suggesting that the metals were loaded by MoO₃ in the form of oxides (Figures 2a–ii). Moreover, the above result further confirms that the metals were absorbed and loaded by the MoO₃ surface after long-term stirring. Figure 3a gives the Mo 3d high-resolution XPS spectra of the bare and metal-doped Mo₂C. Clearly, there are three oxidation valences for all the Mo₂C samples. Typically, the binding energy (BE) values at 229.3, 230.8, and 233.1 eV are assigned to Mo²⁺, Mo⁴⁺, and Mo⁶⁺, respectively. The peak at 229.3 eV can be attributed to Mo ^{δ +} ($0 < \delta < 4$) [34–36]. The other two higher BE peaks can be attributed to MoO₂ and MoO₃ [47–49], suggesting that surface oxidation of Mo₂C in air occurs even for the metal-doped samples. Moreover, an obvious peak shift in the Mo 3d XPS results can be observed, suggesting that the metal doping introduced additional defect sites, which will be beneficial for the

Fig. 2. Preparation process of bare and MO_x-coated Mo₂C. (a) Schematic illustration of the synthesis of metal-doped Mo₂C: i) the MO_x precursors (metal chlorates) were dropwise added into the MoO₃ solution; ii) after stirring the above mixture, the metal oxides were formed on the surface of MoO₃; iii) the M-MoO₃ samples were mixed uniformly with urea and subsequently calcined in N₂ at 600 °C. (i) The ellipsoid indicates MoO₃, (ii) and the small black dots indicate the metal oxides. (b) The XRD patterns of M-MoO₃; (c) XRD patterns of M-Mo₂C.

Fig. 3. X-ray photoelectron spectroscopy (XPS) spectra of M-Mo₂C. (a) Mo 3d of the bare and metal-doped Mo₂C, (b) Ni 2p, (c) Cu 2p, (d) Fe 2p, and (e) Co 2p XPS spectra.

electrocatalytic activity. No change in the oxidation percentage of the doped samples is observed, suggesting that the content of the doped metals is low. For the Ni 2p XPS spectra of Ni-Mo₂C in Figure 3b, there are two main peaks located at 858.1 and 875.8 eV, attributable to Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺ [40], respectively. The Cu-Mo₂C sample shows a corresponding 2p XPS curve in Figure 3c; two main peaks are detected at 933.1 and 952.7 eV and assigned to Cu 2p_{3/2} and Cu 2p_{1/2} of Cu²⁺ [51], respectively. Figure 3d shows the 2p XPS spectra of the Fe-Mo₂C sample; two peaks located at 712.2 and 725.9 eV, attributed to Fe 2p_{3/2} and Fe 2p_{1/2} of Fe³⁺ [30], respectively, can be observed. Finally, for the Co sample in Figure 3e, four visible peaks located at 779.8, 786, 797.5, and 804 eV can be detected. Typically, the two peaks of 779.8 and 797.5 eV belong to Co²⁺

species, while the two peaks of 786 and 804 eV are attributed to the satellite features of Co²⁺ [34]. The above Ni, Cu, and Fe-doped samples, as well as the Co-doped one, all show the same valence state as the used chloride precursors, and no change in the valency of the metals occurred, suggesting that urea only reduces Mo and the metals doped into the Mo₂C lattice.

3.2. Neutral HER performance of Mo₂C-based samples

Figure 4 gives the HER performance of the undoped and metal-doped Mo₂C samples. Commercial 20% Pt/C was employed as a reference sample. As shown from the polarization curves in Figure 4a, the reference 20% Pt/C gives the best HER

Fig. 4. HER performance of Mo₂C-based samples. (a) Polarization curves recorded on glassy carbon electrodes. For all the samples, the catalyst loading was 0.2 mg/cm², and the scan rate was 5 mV/s. (b) The corresponding Tafel plots, derived from the polarization curves in (a). (c) The overpotentials of the samples for the current densities of 10, 50, and 500 mA/cm², also derived from the polarization results. (d) Electrochemical impedance spectroscopy (EIS), performed under the given applied potential of −0.1 V (vs. RHE). (e) The plots of Δj at 1.3 V vs. RHE against the scan rate; data obtained from the cyclic voltammetry (CV) curves in the region of 1.2–1.4 V vs. RHE are given in Figure S6. (f) Durability test of the undoped and doped Mo₂C catalysts at the applied potential of −0.1 V (vs. RHE). All samples were tested for 600 s.

performance with the fastest curve decline from the bias voltage of 0 to -0.4 V vs RHE. Evidently, the bare Mo_2C gives the lowest activity. All the doped samples show an enhanced HER performance in comparison with Mo_2C . Typically, $\text{Cu-Mo}_2\text{C}$ shows the best performance, followed by $\text{Ni-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, and $\text{Fe-Mo}_2\text{C}$, confirming that the $3d$ metal doping can accelerate the water adsorption and dissociation, subsequently promoting the HER activity of Mo_2C .

The Tafel slope can be derived from the Tafel equation ($\eta = j_0 + \text{Alog}(j)$), which presents the relationship between the electrochemical reaction kinetics and the overpotential. Figure 4b gives the corresponding Tafel slopes of the samples. For the commercial 20% Pt/C, the Tafel slope is 48.8 mV/dec, which is consistent with literature reports [18,19]. For the Mo_2C -based samples, the Tafel slopes are 102, 56, 42, 43, and 40 mV/dec for the bare Mo_2C , $\text{Fe-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$, and $\text{Cu-Mo}_2\text{C}$ (as shown in Table 1), respectively. Besides, a low Tafel slope implies fast carrier mobility; thus, the HER kinetics of $\text{Cu-Mo}_2\text{C}$ is similar to that of the 20% Pt/C reference. The reduced Tafel slopes from $\text{Fe-Mo}_2\text{C}$ to $\text{Cu-Mo}_2\text{C}$ further confirm the modulating effect of additional $3d$ electrons for surface H_{ads} desorption. The corresponding HER performance comparison can be found in Table S1, which shows the excellent HER activity of the $\text{Cu-Mo}_2\text{C}$ sample. Figure 4c shows the corresponding overpotential of the Mo_2C -based samples and the reference 20% Pt/C under three different current densities of 10, 50, and 100 mA/cm^2 . For the 20% Pt/C sample, the overpotentials of 61, 103, and 130 mV were obtained at current densities of 10, 50, and 100 mA/cm^2 , respectively. For the Mo_2C -based cathodes at 10 mA/cm^2 , the overpotentials were 100, 95, 90, 78, and 173 mV for $\text{Fe-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$, $\text{Cu-Mo}_2\text{C}$, and bare Mo_2C , respectively, suggesting that the $3d$ metal doping can boost and modulate the neutral HER activity of Mo_2C . Under two high current density conditions, the samples still show the same trend of overpotential decline (see Table 1), further confirming that the $3d$ electron doping can accelerate the water adsorption and dissociation behavior. Figure 4d gives the corresponding electrocatalytic EIS results of the Mo_2C -based samples. Clearly, the five samples show the semicircle change with a specific trend. It was reported that the radius of the arc translates into the relative impedance of the carrier interface migration [27,28], and evidently, the Cu -doped sample gives the smallest interface impedance. Specifically, the EIS spectra were fitted using the circuit model, as shown in Figure S6. R_s and R_{ct} are the interface impedances of the electron transfer across the glassy carbon electrode–catalyst and catalyst–solution interfaces, and C_{dl} is the interfacial capacitance of the cata-

lyst–solution interface. Table 1 presents the corresponding fitted results of the three parameters. Clearly, the R_s value is almost constant (ca. 5.8 Ω/cm^2), suggesting a similar impedance for the carriers across all the electrode–catalyst interfaces. However, for the catalyst–solution interface, the R_{ct} values are 119, 89.6, 46.5, 33.8, and 23.2 Ω/cm^2 for Mo_2C , $\text{Fe-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$, and $\text{Cu-Mo}_2\text{C}$, respectively. The decreased interface impedance suggests that the $3d$ metal doping can improve the carrier migration and water adsorption. Next, the electrochemically active area (E_{aa}) was calculated by measuring the electrochemical double-layer capacitor (C_{dl}). Typically, CV was carried out at different scan rates of 20, 40, 60, 80, and 100 mV/s in the range of 1.2 – 1.4 V vs. RHE, as shown in Figure S7. The plots of Δj at 1.3 V vs. RHE against the scan rate are shown in Figure 4e, and the slopes were used to express double the C_{dl} values [27,28]. The C_{dl} values were calculated to be 0.047, 0.06, 0.1, 0.16, and 0.24 F/cm^2 for Mo_2C , $\text{Fe-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$, and $\text{Cu-Mo}_2\text{C}$, respectively (Table 1). Thus, E_{aa} shows an increasing trend from Fe - to Cu -doped Mo_2C . The stability of the samples was further checked, as shown in Figure 4f. All the Mo_2C -based electrodes show relatively stable performance under an applied bias of 100 mV. We also evaluated the HER performance in strong acid and alkaline solutions, as shown in Figure S8. The doping concentration is also crucial for the HER performance in a neutral solution. As shown in Figure S9, all the metals exhibit the same trend of improved performance with increasing metal concentration.

The specific surface areas (SSAs) of the samples are given in Table 1, and they all show similar values around 12 m^2/g , suggesting that the exposed reaction areas of the materials are the same; the metal doping with the corresponding change in the intrinsic properties leads to the above enhanced electrocatalytic activity.

3.3. *M-Mo₂C* for boosting *TiO₂* photocatalytic HER

3.3.1. Synthesis and characterization of *TiO₂-M-Mo₂C*

TiO_2 has been researched widely in the fields of photocatalysis and photovoltaics [52–60]. In the photocatalytic HER processes, the separation and migration of photogenerated holes or electrons in TiO_2 depend on the cocatalyst properties [54]. Here, we used the impregnation method for loading $\text{M-Mo}_2\text{C}$ samples onto the TiO_2 surface. The XRD patterns in Figure 5a show the typical TiO_2 peaks for all the studied samples. Owing to the low Mo_2C loading (mass percent, ca. 2%), no peaks from Mo_2C can be detected.

The UV-Vis-NIR diffuse reflection absorption spectra of the

Table 1

Summary of the HER performance of the undoped and metal-doped Mo_2C in 0.5 M Na_2SO_4 .

Sample	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	η_{10} (mV)	η_{50} (mV)	η_{100} (mV)	Tafel (mV/dec)	SSA ^a (m^2/g)	C_{dl} ^b (F/cm^2)
Mo_2C	5.92	119	173	283	360	102	12.3	0.047
$\text{Fe-Mo}_2\text{C}$	5.83	89.6	100	161	200	56	11.7	0.06
$\text{Co-Mo}_2\text{C}$	5.83	46.5	95	145	178	42	13.4	0.1
$\text{Ni-Mo}_2\text{C}$	5.69	33.8	90	137	172	43	10.8	0.16
$\text{Cu-Mo}_2\text{C}$	5.88	23.2	78	127	160	40	11.9	0.24

^a Specific surface area, obtained from Figure S11; ^b Obtained from Figure 4e; the slope is $2 \times C_{\text{dl}}$.

Fig. 5. Physico-chemical properties of the bare TiO_2 and $\text{TiO}_2\text{-M-Mo}_2\text{C}$ samples. (a) XRD patterns; (b) UV-Vis-NIR diffuse reflection (K-M absorption) spectra; (c) Room-temperature PL spectra; (d) Ti 2p XPS peaks.

samples are shown in Figure 5b. Clearly, there is some noticeable change in the visible region, suggesting the existence of Mo_2C samples. The bare TiO_2 shows an absorption cutoff edge of ca. 394 nm, which is consistent with the anatase phase [53], and there is a slight difference for the Mo_2C -loaded samples.

The room-temperature photoluminescence (PL) characteristics are shown in Figure 5c. All the samples give the ca. 394 nm PL peak, attributed to the band-gap transition recombination of anatase TiO_2 . However, there are some differences in the samples from the bare TiO_2 to $\text{TiO}_2\text{-Cu-Mo}_2\text{C}$. Specifically, $\text{TiO}_2\text{-Mo}_2\text{C}$ gives almost the same PL peak as the bare TiO_2 , while for the doped Mo_2C , a small redshift can be found. This shift could be explained by a transition from the defect levels in the doped Mo_2C to the valence band of TiO_2 . Moreover, the normalized PL intensity decreases with increasing electrocatalytic activity of the doping metal, suggesting an increasing order of carrier separation from Fe to Cu.

XPS measurements were carried out to detect the valence states of the TiO_2 and $\text{TiO}_2\text{-M-Mo}_2\text{C}$ samples. For the O 1s XPS spectra in Figure S10a, the main peak at 529.8 eV for all samples can be found, and this peak is assigned to the lattice oxygen in TiO_2 [52–54]. For the $\text{TiO}_2\text{-Cu-Mo}_2\text{C}$ sample, an additional peak occurs at 531.4 eV, which is assigned to surface hydroxide groups [53], suggesting that the adsorption of water is influenced by the surface metal doping. For the Mo 3d XPS

spectra in Figure S10b, the curves are similar to those of the Mo_2C -based samples in Figure 3a, with the three main peaks at ca. 229, 322.6, and 236.1 eV assigned to Mo^{2+} , Mo^{4+} , and Mo^{6+} , respectively. However, there is a slight left shift from $\text{TiO}_2\text{-Mo}_2\text{C}$ (Mo^{2+} , 228.9 eV) to $\text{TiO}_2\text{-Cu-Mo}_2\text{C}$ (Mo^{2+} , 229.1 eV), suggesting that the interaction between TiO_2 and Mo_2C is enhanced from Mo_2C to Cu-doped Mo_2C . For the Ti 2p XPS spectra shown in Figure 5d, two main typical Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at ca. 458.3 and 464.2 eV can be found for all the samples. However, there is an obvious shift from the bare TiO_2 peak to the $\text{TiO}_2\text{-Cu-Mo}_2\text{C}$ peak, confirming the strong interaction between TiO_2 and the co-catalysts. As shown in the scanning electron microscopic (SEM) image in Figure S12a, the sample is made up of aggregated nanoparticles of ~50 nm in size. The TEM results in Figure S12b confirm the morphology with a nanoparticle size of 60–100 nm. The dark regions are assigned to the Cu- Mo_2C component. The HRTEM image in Figure S12c clearly shows two different lattice structures with lattice spacing values of ca. 0.24 and 0.18 nm from TiO_2 (004) and Mo_2C (102), respectively. The TEM mapping results in Figures S12d–i suggest a uniform elemental distribution. The TEM images for the samples of $\text{TiO}_2\text{-Mo}_2\text{C}$, $\text{TiO}_2\text{-Fe-Mo}_2\text{C}$, $\text{TiO}_2\text{-Co-Mo}_2\text{C}$ and $\text{TiO}_2\text{-Ni-Mo}_2\text{C}$ can be found in Figure S13 and show similar images as the Cu sample in Figure S12b.

Fig. 6. Photocatalytic HER performance of TiO₂-M-Mo₂C samples. (a) HER activity, 2% TiO₂-Pt was used as the reference sample. (b) The hydrogen evolution rate with mean errors. (c) The stability test of the TiO₂-Cu-Mo₂C sample. The reference Pt sample was prepared by photodeposition. For the cycle measurements, the catalyst was treated via centrifugation, dried, and reused six times, and the reaction time was 12 h.

3.3.2. Photocatalytic HER performance of TiO₂-M-Mo₂C

The photocatalytic activities of the TiO₂ and TiO₂-Mo₂C samples were quantified and the 2% TiO₂-Pt was used as a reference. From the plot of activity against reaction time (Figure 6a), all the samples essentially exhibit a linear growth for hydrogen production. Typically, the TiO₂-Pt reference shows the highest activity, in the decreasing order of activity: TiO₂-Cu-Mo₂C, TiO₂-Ni-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Fe-Mo₂C, TiO₂-Mo₂C, and bare TiO₂, indicating that the various Mo₂C species act as electrocatalytic sites, and the activities of these sites depend on the doping metal. The reaction rate together with the mean error is shown in Figure 6b. The TiO₂-Pt reference sample gives a hydrogen generation rate of 625 μmol/h. For the TiO₂-Mo₂C samples, the reaction rates are 521, 404, 275, 224, and 147 μmol/h for Cu, Ni, Co, Fe, and bare Mo₂C samples, respectively, while the bare TiO₂ gives 112 μmol/h. Thus, while the catalytic effect of the undoped Mo₂C loading is low, for the metal-doped Mo₂C, the reaction times are promoted by factors of 2, 2.5, 3.6, and 4.65 for Fe, Co, Ni, and Cu, respectively, further confirming that more 3d electrons can promote the photogenerated electron transfer across the TiO₂-cocatalyst interface. The stability of the Mo₂C-Cu photocatalyst was measured by cycling over 2 h periods (Figure 6c). Clearly, no obvious increase or decrease can be detected, confirming the well-set interface of TiO₂ and Mo₂C. For the samples of the other four metal-doped Mo₂C, the HER performance is shown in Figure S14, the photocatalytic HER is also sensitive to the cocatalyst content. The apparent quantum efficiency (AQY) under LED-365 was measured to be 78.12% according to the following equation:

$$\text{AQY} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% = \frac{\text{number of evolved H}_2 \times 2}{\text{number of incident photons}} \times 100\%$$

Table S2 gives the comparison of Mo₂C-based co-catalysts

for the photocatalytic H₂ generation rate and shows the clear enhanced effect of TiO₂.

3.3.3. Photogenerated carrier interfacial separation

The interfacial separation and migration of photogenerated electrons and holes can be studied by EIS under illumination. An aqueous solution of 0.5 M Na₂SO₄ was used as the electrolyte and a 365 nm LED device as the source of illumination. As shown in Figure S15a, all the TiO₂-Mo₂C-based samples give similar curves for the EIS plots with the trend of reducing arc size from TiO₂-Mo₂C through TiO₂-Fe-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Ni-Mo₂C, and TiO₂-Cu-Mo₂C, suggesting a decrease in the resistance. Figure S15b gives the fitting circuit diagram according to the studied interfaces; the parameters of R₁, R₂, and R₃ are the carrier resistances across the electrode-catalyst, TiO₂-Mo₂C, and catalyst-solution interfaces, respectively. C₁ and C₂ are the corresponding interface capacitances. Table S3 gives the fitted results. Clearly, R₁ does not show any obvious change (0.35 Ω/cm²), suggesting the same electrode-catalyst interface. For R₂, there is a decrease from 6.25 to 3.4 Ω/cm² for TiO₂-Mo₂C to TiO₂-Cu-Mo₂C, suggesting that the interface resistance is reduced owing to the energy level change of Mo₂C owing to different 3d metal dopings. R₃ also gives the same trend with R₂. For C₁ and C₂, there is almost no change in the former and the latter increases with a maximum value obtained for TiO₂-Cu-Mo₂C. As we have mentioned above, the additional 3d electron metal doping will introduce defect energy levels and, thus, decrease the interface barrier of the semiconductor and Mo₂C for carrier migration. The EIS result of the TiO₂-Pt reference is also given in Figure S16. Note that only two interfaces exist in the TiO₂-Pt sample; thus, two resistances are given. The fitted R₂ gives 168 Ω/cm², which is larger than that of the TiO₂-M-Mo₂C sample (Table S3).

The photogenerated carrier recombination and separation were further studied via time-resolved photoluminescence spectroscopy (TRPS) and ultrafast transient absorption (TA)

Fig. 7. (a) Time-resolved PL spectra of all samples; the excitation and emission wavelengths are 320 and 390 nm, respectively. The ultrafast transient absorption kinetics of (b) TiO₂-Mo₂C, (c) TiO₂-Cu-Mo₂C, and (d) the TiO₂-Pt reference. The pump wavelength is 320 nm, and the probed wavelength is 525 nm.

spectroscopy. For the TRPS in Figure 7a, the samples under study show the obvious decay in the range of 30 ns with the bare TiO₂, affording the slowest decay. However, for the Mo₂C-loaded TiO₂ samples, the PL curves decay increasingly rapidly in the order of TiO₂-Fe-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Ni-Mo₂C, and TiO₂-Cu-Mo₂C. It should be noted that the TiO₂-Pt reference sample exhibits the fastest decay. The TRPS curves were fitted using the equation, $y = ae^{(-x/\tau)} + y_0$. The fitted τ values for the samples are 22.6, 20.5, 10.1, 4.7, 4.0, 2.5, and 1.9 ns for TiO₂, TiO₂-Mo₂C, TiO₂-Fe-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Ni-Mo₂C, TiO₂-Cu-Mo₂C, and TiO₂-Pt, respectively. We chose only the three samples of TiO₂-Mo₂C, TiO₂-Cu-Mo₂C, and the reference TiO₂-Pt for the TA measurements. As shown in Figures 7b–d, the three samples show qualitatively similar TA decay curves. The TA results were also fitted using a one time-constant equation: $y = ae^{(-x/\tau)} + y_0$. As given in Figures 7b–d, the τ values are 105, 73, and 31 ps for TiO₂-Mo₂C, TiO₂-Cu-Mo₂C, and TiO₂-Pt, respectively. Since Pt acts as the receiving center for the photogenerated electrons from the semiconductor [55], the Mo₂C loading can also carry out this electron transfer. Moreover, Cu doping can boost the activity more than 2.4 times compared with the bare Mo₂C, further confirming the effect of a high number of 3d electrons for increasing the electron transfer.

3.3.4. Mechanism of metal doping for assisting Mo₂C HER

To better understand the intrinsic driving force for facilitating the electron transfer across the catalyst-solution or semiconductor-cocatalyst interfaces, the work function (W_F) values of the bare and doped Mo₂C on TiO₂ samples were measured by

ultraviolet photoelectron spectroscopy (UPS). As shown in Figure 8a, all the samples show a similar E_{fermi} location, and the 3.6 eV peak can also be observed, which is consistent with literature reports [34]. Moreover, all the samples give a main cutoff value of ca. 13.5 eV. However, there are some noticeable tails for the doped samples in comparison to the undoped bare Mo₂C, confirming the defective energy levels. The specific W_F' values for the Mo₂C based samples can be calculated via the following equation: $W_F' = 21.2$ (He I UV energy) – ($E_{\text{cutoff}} - E_{\text{fermi}}$) (eV). Thus, the W_F values are 3.58, 3.9, 4.2, and 3.7 eV for Cu-Mo₂C, Co-Mo₂C, Fe-Mo₂C, and Ni-Mo₂C, respectively. Figure 8b shows the corresponding energy level structures of the undoped and metal-doped Mo₂C samples together with the W_F' , and the main W_F value of the doped Mo₂C is 7.7 eV.

To confirm that the metal dopant energy levels can contribute to free water adsorption, in-situ Fourier transform infrared spectroscopy (FTIR) was carried out under a flow of water-saturated N₂. The Mo₂C background was removed from the FTIR signal, and the signals of water adsorption were detected directly. As shown in Figure S17, there is one main peak at 3240 cm⁻¹, which is assigned to water molecules and is observed for both the undoped and metal-doped Mo₂C samples. However, the normalized intensities are different, as shown in Figure 8c. Typically, the Cu-Mo₂C sample gives the highest intensity, followed by Ni-, Co-, and Fe-doped Mo₂C, while the undoped Mo₂C affords the lowest intensity, thereby confirming that the low W_F can assist water adsorption. As noted above, the free water molecules are the reaction precursors for the HER under the neutral condition; thus, the water adsorption will facilitate the subsequent breakage of the H–OH bond, as

Fig. 8. Mechanism of metal doping for promoting carrier transfer at the interfaces. (a) UPS of the different Mo₂C samples. (b) The corresponding energy level schematic diagrams of the bare and metal-doped Mo₂C. (c) FTIR intensity of the adsorbed water molecules on the bare and metal-doped Mo₂C. The in-situ FTIR was carried out by a water-saturated N₂ flow; (d) the near-linear relationship between the W_F and the HER overpotential of the metal-doped Mo₂C samples.

shown in Figure S18. Furthermore, the adsorbed water molecule layer can assist the electron tunneling to the electrolyte, where the electron energy does not change. We considered that there may be a linear relationship between the energy level of the catalyst and the overpotential. As shown in Figure 8d, the defect W_F values are plotted with the HER overpotential with the HER current densities of 10, 50, and 100 mA/cm², and a close to linear relationship is established, suggesting that the small W_F can promote the carrier interface transfer in a linear manner.

For the co-catalyst-based photocatalytic water splitting, the interface between the semiconductor and electrocatalyst is vital for the electron transfer [54–55]. Owing to the higher W_F of the electrocatalyst than that of the semiconductor, a Schottky barrier can form in the n-type semiconductor, which opposes electron transfer from the semiconductor to the electrocatalyst. Thus, lowering the W_F of the electrocatalyst will be an effective strategy for enhancing the overall photon-to-current conversion efficiency. The W_F of anatase TiO₂ is typically in the range of 4.0–4.5 eV; thus, the energy level diagram can be drawn as shown in Figure S19. In consideration of the efficient HER performance of the Mo₂C-based samples, the enhanced photocatalytic hydrogen evolution can be also achieved.

4. Conclusions

Herein, W_F engineering in Mo₂C was researched via doping with different 3d electron metal compounds (Fe, Co, Ni, and Cu)

to explore the enhanced neutral HER performance. Undoped and metal-doped Mo₂C were synthesized via urea reduction under N₂. Owing to the low content of doped metals, the phase, lattice structure, and the surface Mo valence states of the obtained Mo₂C samples were almost the same for all the samples. However, they exhibited regular changes in HER activity. Typically, the Cu-Mo₂C showed the best HER with an overpotential of 78 mV at 10 mA/cm², followed by Ni-Mo₂C, Co-Mo₂C, Fe-Mo₂C, and bare Mo₂C with overpotentials of 90, 95, 100, and 173 mV, respectively. The corresponding Tafel slope values are 40, 43, 42, 56, and 102 mV/dec. The interface resistances and capacitances were measured by EIS plots and CV curves, and it was found that the Cu-doped sample gives the smallest resistance across the solid-solution interface and the largest interface capacitance. UPS was used to measure the W_F changes due to the metal doping. The W_F values of Cu, Ni, Co, and Fe-doped Mo₂C are 3.58, 3.7, 3.9, and 4.2 eV, respectively, although the W_F of Mo₂C is 7.7 eV. In-situ FTIR measurements were carried out for quantifying free water adsorption on undoped and doped Mo₂C samples and showed that the low W_F values of the doped samples assisted water adsorption. This is also consistent with the electrocatalytic results.

These electrocatalysts were further used as co-catalysts of a TiO₂ photocatalyst. Owing to the low W_F of the metal-doped Mo₂C, the presumed Schottky barrier between TiO₂ and Mo₂C could be lowered, which favored the photogenerated electron transfer from TiO₂ to electrocatalyst. The photocatalytic HER performance was enhanced for the metal-doped Mo₂C system

in comparison to the undoped sample. Typically, for the TiO₂-Mo₂C samples, the HER rates are 521, 404, 275, 224, 147, and 112 μmol/h for Cu, Ni, Co, Fe, bare Mo₂C, and bare TiO₂, respectively. This work can help to understand the effect of *W_F* modulation on the HER performance of an electrocatalyst and to design more efficient water-splitting systems.

References

- [1] I. Roger, M. A. Shipman, M. D. Symes, *Nat. Rev. Chem.*, **2017**, 1, 0003.
- [2] J. Staszak-Jirkovsky, C. D. Malliakas, P. P. Lopes, N. Danilovic, S. S. Kota, K. C. Chang, B. Genorio, D. Strmcnik, V. R. Stamenkovic, M. G. Kanatzidis, N. M. Markovic, *Nat. Mater.*, **2016**, 15, 197–203.
- [3] Z. Fang, L. Peng, Y. Qian, X. Zhang, Y. Xie, J. J. Cha, G. Yu, *J. Am. Chem. Soc.*, **2018**, 140, 5241–5247.
- [4] C. Zhu, A. L. Wang, W. Xiao, D. Chao, X. Zhang, N. H. Tiep, S. Chen, J. Kang, X. Wang, J. Ding, J. Wang, H. Zhang, H. J. Fan, *Adv. Mater.*, **2018**, 30, 1705516.
- [5] L.-L. Feng, M. Fan, Y. Wu, Y. Liu, G.-D. Li, H. Chen, W. Chen, D. Wang, X. Zou, *J. Mater. Chem. A*, **2016**, 4, 6860–6867.
- [6] C.-T. Dinh, A. Jain, F. P. G. de Arquer, P. De Luna, J. Li, N. Wang, X. Zheng, J. Cai, B. Z. Gregory, O. Voznyy, B. Zhang, M. Liu, D. Sinton, E. J. Crumlin, E. H. Sargent, *Nat. Energy*, **2019**, 4, 107–114.
- [7] M. J. Kenney, J. E. Huang, Y. Zhu, Y. Meng, M. Xu, G. Zhu, W.-H. Hung, Y. Kuang, M. Lin, X. Sun, W. Zhou, H. Dai, *Nano Res.*, **2019**, 12, 1–5.
- [8] N. Mahmood, Y. Yao, J. W. Zhang, L. Pan, X. Zhang, J. J. Zou, *Adv. Sci.*, **2018**, 5, 1700464.
- [9] J. Xing, F. Lin, L. Huang, Y. Si, Y. Wang, L. Jiao, *Chin. J. Catal.*, **2019**, 40, 1352–1359.
- [10] L. Zhang, L. Han, H. Liu, X. Liu, J. Luo, *Angew. Chem. Int. Ed.*, **2017**, 56, 13694–13698.
- [11] P. Kuang, T. Tong, K. Fan, J. Yu, *ACS Catal.*, **2017**, 7, 6179–6187.
- [12] Q. Sun, L. Wang, Y. Shen, M. Zhou, Y. Ma, Z. Wang, C. Zhao, *ACS Sustain. Chem. Eng.*, **2018**, 6, 12746–12754.
- [13] K. Li, J. Zhang, R. Wu, Y. Yu, B. Zhang, *Adv. Sci.*, **2016**, 3, 1500426.
- [14] X. Lu, J. Xie, X. Chen, X. Li, *Appl. Catal. B*, **2019**, 252, 250–259.
- [15] J. Miao, F. X. Xiao, H. B. Yang, S. Y. Khoo, J. Chen, Z. Fan, Y. Y. Hsu, H. M. Chen, H. Zhang, B. Liu, *Sci. Adv.*, **2015**, 1, e1500259.
- [16] J. Liu, D. Zhu, T. Ling, A. Vasileff, S.-Z. Qiao, *Nano Energy*, **2017**, 40, 264–273.
- [17] X. Ren, D. Wu, R. Ge, X. Sun, H. Ma, T. Yan, Y. Zhang, B. Du, Q. Wei, L. Chen, *Nano Res.*, **2018**, 11, 2024–2033.
- [18] G. Qu, Y. Zhao, G. Zhao, Y. Zhou, S. Cai, Y. Kang, C. Xu, *Electrochim. Acta*, **2019**, 298, 943–949.
- [19] S. Drouet, J. Creus, V. Colliere, C. Amiens, J. Garcia-Anton, X. Sala, K. Philippot, *Chem. Commun.*, **2017**, 53, 11713–11716.
- [20] D. Dinda, M. E. Ahmed, S. Mandal, B. Mondal, S. K. Saha, *J. Mater. Chem. A*, **2016**, 4, 15486–15493.
- [21] P. Wang, S. Xu, F. Chen, H. Yu, *Chin. J. Catal.*, **2019**, 40, 343–351.
- [22] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.*, **2010**, 110, 6446–6473.
- [23] K. Maeda, K. Domen, *J. Phys. Chem. Lett.*, **2010**, 1, 2655–2661.
- [24] T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.*, **2014**, 43, 7520–7535.
- [25] L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F. Robles-Hernandez, S. Baldelli, J. Bao, *Nat. Nanotechnol.*, **2014**, 9, 69–73.
- [26] Y. R. Zheng, P. Wu, M. R. Gao, X. L. Zhang, F. Y. Gao, H. X. Ju, R. Wu, Q. Gao, R. You, W. X. Huang, S. J. Liu, S. W. Hu, J. Zhu, Z. Li, S. H. Yu, *Nat. Commun.*, **2018**, 9, 2533.
- [27] J. Yan, L. Kong, Y. Ji, Y. Li, J. White, S. Liu, X. Han, S.-T. Lee, T. Ma, *Commun. Chem.*, **2018**, 1, 95.
- [28] H. Wu, L. Kong, Y. Ji, J. Yan, Y. Ding, Y. Li, S. T. Lee, S. Liu, *Adv. Mater. Interfaces*, **2019**, 6, 1900308.
- [29] J. Yan, P. Li, Y. Ji, H. Bian, Y. Li, S. Liu, *J. Mater. Chem. A*, **2017**, 5, 21478–21485.
- [30] J. Yan, H. Wu, P. Li, H. Chen, R. Jiang, S. Liu, *J. Mater. Chem. A*, **2017**, 5, 10173–10181.
- [31] H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.*, **2003**, 125, 3082–3089.
- [32] X. Yang, A. Wolcott, G. Wang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang, Y. Li, *Nano Lett.*, **2009**, 9, 2331–2336.
- [33] F. Wang, C. Di Valentin, G. Pacchioni, *J. Phys. Chem. C*, **2012**, 116, 8901–8909.
- [34] H. Lin, N. Liu, Z. Shi, Y. Guo, Y. Tang, Q. Gao, *Adv. Funct. Mater.*, **2016**, 26, 5590–5598.
- [35] H. Ang, H. T. Tan, Z. M. Luo, Y. Zhang, Y. Y. Guo, G. Guo, H. Zhang, Q. Yan, *Small*, **2015**, 11, 6278–6284.
- [36] X. Zheng, Y. Chen, X. Zheng, G. Zhao, K. Rui, P. Li, X. Xu, Z. Cheng, S. X. Dou, W. Sun, *Adv. Energy Mater.*, **2019**, 9, 1803482.
- [37] R. Luo, M. Luo, Z. Wang, P. Liu, S. Song, X. Wang, M. Chen, *Nanoscale*, **2019**, 11, 7123–7128.

Graphical Abstract

Chin. J. Catal., 2021, 42: 205–216 doi: 10.1016/S1872-2067(20)63589-6

Metal-doped Mo₂C (metal = Fe, Co, Ni, Cu) as catalysts on TiO₂ for photocatalytic hydrogen evolution in neutral solution

Jing Liu, Gary Hodes, Junqing Yan*, Shengzhong (Frank) Liu*
 Shaanxi Normal University, China; Dalian Institute of Chemical Physics,
 Chinese Academy of Sciences, China; Weizmann Institute of Science, Israel

Metals (Fe, Co, Ni and Cu) doped Mo₂C samples are reported to promote the water adsorption performance, and then boost the neutral HER activity for working as the co-catalysts of TiO₂.

- [38] Y. Shi, Y. Zhou, D.-R. Yang, W.-X. Xu, C. Wang, F.-B. Wang, J.-J. Xu, X.-H. Xia, H.-Y. Chen, *J. Am. Chem. Soc.*, **2017**, 139, 15479–15485.
- [39] Y. Y. Chen, Y. Zhang, W. J. Jiang, X. Zhang, Z. Dai, L. J. Wan, J. S. Hu, *ACS Nano*, **2016**, 10, 8851–8860.
- [40] Z. Y. Yu, Y. Duan, M. R. Gao, C. C. Lang, Y. R. Zheng, S. H. Yu, *Chem. Sci.*, **2017**, 8, 968–973.
- [41] Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong, Y. Li, *ACS Nano*, **2016**, 10, 11337–11343.
- [42] W. Zhang, H. Zhang, J. Xu, H. Zhuang, J. Long, *Chin. J. Catal.*, **2019**, 40, 320–325.
- [43] Z. Shi, K. Nie, Z.-J. Shao, B. Gao, H. Lin, H. Zhang, B. Liu, Y. Wang, Y. Zhang, X. Sun, X.-M. Cao, P. Hu, Q. Gao, Y. Tang, *Energy Environ. Sci.*, **2017**, 10, 1262–1271.
- [44] H. Ang, H. Wang, B. Li, Y. Zong, X. Wang, Q. Yan, *Small*, **2016**, 12, 2859–2865.
- [45] K. Xiong, L. Li, L. Zhang, W. Ding, L. Peng, Y. Wang, S. Chen, S. Tan, Z. Wei, *J. Mater. Chem. A*, **2015**, 3, 1863–1867.
- [46] J. Shen, R. Wang, Q. Liu, X. Yang, H. Tang, J. Yang, *Chin. J. Catal.*, **2019**, 40, 380–389.
- [47] C. Wan, Y. N. Regmi, B. M. Leonard, *Angew. Chem. Int. Ed.*, **2014**, 53, 6407–6410.
- [48] F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu, X. W. Lou, *Angew. Chem. Int. Ed.*, **2015**, 54, 15395–15399.
- [49] M. Li, Y. Zhu, H. Wang, C. Wang, N. Pinna, X. Lu, *Adv. Energy Mater.*, **2019**, 9, 1803185.
- [50] J. Yan, L. Li, Y. Ji, P. Li, L. Kong, X. Cai, Y. Li, T. Ma, S. Liu, *J. Mater. Chem. A*, **2018**, 6, 12532–12540.
- [51] X. Zhang, X. Zhu, L. Lin, S. Yao, M. Zhang, X. Liu, X. Wang, Y.-W. Li, C. Shi, D. Ma, *ACS Catal.*, **2016**, 6, 912–918.
- [52] R. Shen, J. Xie, Q. Xiang, X. Chen, J. Jiang, X. Li, *Chin. J. Catal.*, **2019**, 40, 240–288.
- [53] Y. Zhu, Z. Zhang, N. Lu, R. Hua, B. Dong, *Chin. J. Catal.*, **2019**, 40, 413–423.
- [54] J. Wang, B. Liu, K. Nakata, *Chin. J. Catal.*, **2019**, 40, 403–412.
- [55] L. Kong, Y. Ji, Z. Dang, J. Yan, P. Li, Y. Li, S. F. Liu, *Adv. Funct. Mater.*, **2018**, 28, 1800668.
- [56] A. Meng, L. Zhang, B. Cheng, J. Yu, *Adv. Mater.*, **2019**, 31, 1807660.
- [57] A. Meng, J. Zhang, D. Xu, B. Cheng, J. Yu, *Appl. Catal. B*, **2016**, 198, 286–294.
- [58] C. Li, W. Yang, Q. Li, *J. Mater. Sci. Technol.*, **2018**, 34, 969–975.
- [59] G. Huang, X. Liu, S. Shi, S. Li, Z. Xiao, W. Zhen, S. Liu, P. K. Wong, *Chin. J. Catal.*, **2020**, 41, 50–61.
- [60] Q.-F. Liu, Q. Zhang, B.-R. Liu, S. Li, J.-J. Ma, *Chin. J. Catal.*, **2018**, 39, 542–548.
- [61] B. Yang, K. Han, *Acc. Chem. Res.*, **2019**, 52, 3188–3198.
- [62] C.-J. Zhao, K. Han, *Acc. Chem. Res.*, **2012**, 45, 404–413.

金属(Fe, Co, Ni, Cu)掺杂的Mo₂C催化剂在TiO₂表面用于中性条件光催化分解水产氢

刘 晶^a, 盖瑞侯得^c, 闫俊青^{a,*}, 刘生忠^{a,b,#}

^a陕西师范大学, 应用表面与胶体化学教育部重点实验室, 陕西省能源新材料与器件重点实验室,
陕西省能源新技术工程实验室, 材料科学与工程学院, 陕西西安710119, 中国

^b中国科学院大连化学物理研究所, 中国科学院洁净能源创新研究院, 能源材料化学协同创新中心(iChEM),
辽宁大连116023, 中国

^c魏茨曼科学研究院, 雷霍沃特, 以色列

摘要: 中性条件下的分解水产氢(HER)是化工领域的重要反应之一, 其效率取决于催化剂的内在特性. 在本工作中, 我们利用3d金属(Fe, Co, Ni, Cu)对Mo₂C进行掺杂来调节其费米能级, 从而达到催化剂可在中性条件下吸附水并提高最终活性的目的. 首先, 利用简单浸渍法将四种金属的前驱体吸附到MoO₃表面, 然后通过煅烧一步合成金属掺杂的Mo₂C. 产物Mo₂C的XRD峰位移动以及XPS表征结果表明, 四种金属通过掺杂进入到了Mo₂C晶格. 利用HRTEM以及相应的元素面扫分析, 也证明金属确实掺杂进入了Mo₂C体相. 考察了Mo₂C基催化剂在中性条件下电解水产氢的性能, 结果表明, 在10 mA/cm²条件下, Cu-Mo₂C催化剂表现出最优的HER性能, 其次, 是Ni-Mo₂C, Co-Mo₂C, Fe-Mo₂C和纯Mo₂C, 它们的过电位分别为78, 90, 95, 100和173 mV, Tafel斜率分别是40, 43, 42, 56和102 mV/dec. 利用阻抗测试详细分析了催化剂-反应液界面电阻 R_{ct} 的变化情况, 样品Mo₂C, Fe-Mo₂C, Co-Mo₂C, Ni-Mo₂C和Cu-Mo₂C拟合后的 R_{ct} 值分别为119, 89.6, 46.5, 33.8和23.2 ohm/cm², 表明金属掺杂能明显降低催化剂的反应界面电阻. 由于电催化过程的主要研究对象是表面双电层, 所以我们利用循环伏安法计算了催化剂表面双电层的数值, 得到上述五个样品的 C_{dl} 数值分别为0.047, 0.06, 0.1, 0.16和0.24 F/cm², 双电层的提高为催化剂表面提供了更多的反应位点.

考虑了到光解水的界面反应实质也是电催化过程, 我们通过浸渍方法将催化剂负载到锐钛矿TiO₂表面, 考察调控的功函数对光催化效率的影响. XPS表征验证了M-Mo₂C负载于TiO₂表面. 负载助催化剂的TiO₂-M-Mo₂C样品均表现出了优于纯TiO₂的光解水产氢性能. 样品TiO₂-Cu-Mo₂C, TiO₂-Ni-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Fe-Mo₂C, TiO₂-Mo₂C和纯TiO₂的产氢速率分别为21, 404, 275, 224, 147和112 μmol/h. 利用瞬态荧光研究了载流子在助催化剂和TiO₂两相的界面迁移, 通过单指数拟合得到样品TiO₂, TiO₂-Mo₂C, TiO₂-Fe-Mo₂C, TiO₂-Co-Mo₂C, TiO₂-Ni-Mo₂C, TiO₂-Cu-Mo₂C和TiO₂-Pt的荧光寿命分别是22.6, 20.5, 10.1, 4.7, 4.0, 2.5和1.9 ns, 说明不同金属掺杂的Mo₂C对提取光生电子的效果不同, 元素Cu最有效. 进一步利用瞬态吸收光谱研究了TiO₂-Mo₂C, TiO₂-Cu-Mo₂C和TiO₂-Pt三个样品的载流子迁移, 同样采用单指数拟合得到的荧光寿命分别为105, 73和31 ps, 进一步说明掺杂Cu后助催化剂Mo₂C对于提取TiO₂的光生电子寿命具有很好的促进作用. 利用UPS技

术探究了金属掺杂后 Mo_2C 的缺陷能级位置,从计算结果可以看出,元素Cu掺杂后 Mo_2C 具有更深的缺陷能级,该能级对吸附水具有促进作用.利用原位红外光谱对样品进行了水蒸气吸附测试,结果表明, Mo_2C , $\text{Fe-Mo}_2\text{C}$, $\text{Co-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$ 和 $\text{Cu-Mo}_2\text{C}$ 样品依次的吸附水性能提升.综上,我们利用3d金属对助催化剂进行了缺陷调控来调变其对水的起始吸附过电位,该工作对设计性能优异的光解水助催化剂具有一定的借鉴意义.

关键词: 3d金属; 掺杂; Mo_2C ; TiO_2 ; 光催化; 水分解; 产氢

收稿日期: 2020-03-28. 接受日期: 2020-05-03. 出版日期: 2021-01-05.

*通讯联系人. 电子信箱: junqingyan@snnu.edu.cn

#通讯联系人. 电子信箱: liusz@snnu.edu.cn

基金来源: 国家重点研发计划(2017YFA0204800, 2016YFA0202403); 国家自然科学基金(21603136); 长江学者和创新团队发展计划(IRT_14R33); 高等学校学科创新引智计划(“111计划”, B14041).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).