Transition Metal-Promoted V$_2$CO$_2$ (MXenes): A New and Highly Active Catalyst for Hydrogen Evolution Reaction

Chongyi Ling, Li Shi, Yixin Ouyang, Qian Chen, and Jinlan Wang*

Developing alternatives to precious Pt for hydrogen production from water splitting is central to the area of renewable energy. This work predicts extremely high catalytic activity of transition metal (Fe, Co, and Ni) promoted two-dimensional MXenes, fully oxidized vanadium carbides (V$_2$CO$_2$), for hydrogen evolution reaction (HER). The first-principle calculations show that the introduction of transition metal can greatly weaken the strong binding between hydrogen and oxygen and engineer the hydrogen adsorption free energy to the optimal value $\approx$0 eV by choosing the suitable type and coverage of the promoters as well as the active sites. Strain engineering on the performance of transition metal promoted V$_2$CO$_2$ further reveals that the excellent HER activities can maintain well while those poor ones can be modulated to be highly active. This study provides new possibilities for cost-effective alternatives to Pt in HER and for the application of 2D MXenes.

1. Introduction

Hydrogen has been considered to be one of the most important candidates for the energy source of the next generation,[1,2] owing to the high energy density and environmentally friendly combustion product (H$_2$O). Hydrogen evolution from electrocatalytic water splitting is one of the most efficient ways, where an ideal catalyst would be the key factor to the production of hydrogen. Precious metal platinum (Pt) is the most popular electrocatalyst for hydrogen evolution reaction (HER).[3] However, the high cost and the insufficiency of Pt greatly hamper their practical utilization. To assure a sustainable hydrogen generation, tremendous efforts have been made to develop the earth abundant and cost-effective alternatives to Pt in the past few decades, including non-precious metal alloys, metal chalcogenides, metal carbides, metal nitrides, metal phosphides, and so on.[4–8] Among these alternatives, 2D layered materials (such as MoS$_2$) have gained broad interest recently because of their extremely large surface areas, low cost, and excellent catalytic activity.[9–11]

Very recently, a new class of 2D layered materials with a general formula of M$_n$X$_3$ labeled MXenes has been reported.[12–16] Shortly after the synthesis of MXenes,[12] their possible application as anode materials for Li ion batteries (LIBs) has been explored greatly and these MXenes exhibit good capability for high charge–discharge rates.[14,17–19] Besides LIBs, other applications, such as non-Li-ion batteries,[20,21] hydrogen storage,[22,23] supercapacitor,[24] and thermoelectric materials,[25] have also been investigated. MXenes were predicted to be potential heterogeneous catalysts owing to their high surface area and excellent thermostability as well.[26] Recalling the fact that the release of H$_2$ can always be observed during the synthesis process of MXenes,[12] it is very possible that MXenes may be good catalyst for HER, which is never reported yet.

In this work, we select vanadium carbides with fully oxygen terminated surface (V$_2$CO$_2$) as the representative to investigate the HER performance by employing first-principles calculations. Our results show that the strong hydrogen adsorption inhibits the pure V$_2$CO$_2$ as a potential HER catalyst. However, by introducing suitable transition metal atoms onto the surface, the H adsorption free energy can be tuned to be zero, comparable or even better than that of Pt (111) surface. The promotion effect is ascribed to the charge transfer between promoter atoms and surface O atoms. Moreover, the promotional HER performance shows good stability and can be further improved via external strain engineering.

2. Results and Discussion

Due to the high surface activity, all the MXenes produced to date are terminated by functional groups, such as OH, O, and F.[26] The terminated groups (T) in MXenes have also been investigated. MXenes were predicted to be potential heterogeneous catalysts owing to their high surface area and excellent thermostability as well.[26] Recalling the fact that the release of H$_2$ can always be observed during the synthesis process of MXenes,[12] it is very possible that MXenes may be good catalyst for HER, which is never reported yet.

C. Y. Ling, L. Shi, Y. X. Ouyang, Dr. Q. Chen, Prof. J. L. Wang
Department of Physics
Southeast University
Nanjing 211189, China
E-mail: jlwang@seu.edu.cn

Prof. J. L. Wang
Synergetic Innovation Center for Quantum Effects and Applications (SICQEA)
Hunan Normal University
Changsha 410081, China

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DOI: 10.1002/advs.201600180
atoms on one surface and above the hollow sites of M₂X₃ on the other surface. Different MXenes and T groups have different ground state structures. We considered all the possible absorption sites and found that the O atom favorably absorbs above the hollow site of C₃V₃. The stability of partial and fully oxidized V₂C was also evaluated by computing the formation energies and the fully oxidized V₂C is always thermodynamically most favorable when the chemical potential exceeds −7 eV, which corresponds to the ultralow oxygen partial pressure (see Figure S2a,b in the Supporting Information for more details). The stability of fully oxidized vanadium carbides is further evaluated by ab initio molecular dynamics simulation. As shown in Figure S2c (Supporting Information), the structure remains well even at a temperature of 1000 K, indicative of the high thermodynamic stability of V₂CO₂. Therefore, fully oxidized vanadium carbides (V₂CO₂) is selected as the study prototype in this work.

We first study the HER catalytic activity of pure V₂CO₂ by computing the reaction free energy of hydrogen adsorption at different hydrogen coverage (12.5%, 16.7%, and 25% monolayer (ML) H coverage on one surface), where the H atom prefers to adsorb on the top site of surface O atoms. The calculated ΔG_H is −0.45, −0.42, and −0.37 eV for 12.5%, 16.7%, and 25% ML H coverage (see Figure S1, Supporting Information), respectively, indicative of the strong interaction between H and surface O. Thus, the pure V₂CO₂ is not a good catalyst for HER activity.

Since the high H binding strength causes the poor performance of V₂CO₂ in HER, it is natural to seek the way to weaken the interaction between H and O to improve the HER activity. In fact, when H adsorbs on surface O atom, the combination of H 1s orbital and O 2pz orbital will form a fully filled bonding orbital (σ) and a partially filled anti-bonding orbital (σ*). According to molecular orbital theory, the H bonding strength is determined by the occupancy of the partially filled anti-bonding orbital, that is, the higher σ* occupancy, the weaker binding strength. So if we can introduce an electron donor (such as metal atoms) onto the surface, the O atom will receive extra electron from the donor, leading to more filled p-states of O atom. As a result, σ* occupancy will increase when forming the H—O bond on the surface of V₂CO₂. Meanwhile, the extra electron that surface O gained will also lead to less charge transfer from H to O. Therefore, the interaction between H and O will be weakened and the HER performance will be improved greatly (Figure 1). To verify this point, we study the HER performance of transition metal (TM) absorbed V₂CO₂.

For TM-promoted V₂CO₂, the TM atoms prefer to locate above the hollow sites of O₃V₃ and form three TM—O and

![Figure 1. The scheme of modulating the HER performance of V₂CO₂ by introducing transition metal onto the surface. a) The combination of H 1s orbital and O 2pz orbital forms a fully filled bonding orbital and a partially filled anti-bonding orbital, in which the occupancy of anti-bonding orbital will determine the strength of H—O bond. b) Charge transfer from H to O will occur when H adsorbs on O; by introducing a TM atom onto the surface, O will gain extra electrons from TM, leading to less charge transfer from H to O and a higher occupancy of anti-bonding orbital when forming the H—O bond.](image-url)
three TM—V bonds with neighboring O and V atoms, respectively. The calculated binding energies ($E_b$) between different TM atoms and V$_2$CO$_2$ are illustrated in Table S1 (Supporting Information), and they are all larger than 1.0 eV, indicative of the strong binding strength between TM atoms and V$_2$CO$_2$. The stability of TM-promoted V$_2$CO$_2$ is further evaluated by ab initio molecular dynamics simulation. As shown in Figure S3 (Supporting Information), no structure reconstruction is found to occur in all of the cases under the temperature of 353 K. Even the temperature increases to 500 K, which far exceeds the typical experimental reaction temperature, the structures of the TM-V$_2$CO$_2$ still remain in good shape, indicative of the high stability of pure V$_2$CO$_2$, suggesting that introducing the TM onto the surface of V$_2$CO$_2$ can indeed weaken the H—O binding strength and thereby improve the HER performance. Most importantly, the Δ$G_{H}$ at T$_3$ site of 25% ML Ni-V$_2$CO$_2$ (denoted as “T$_3$(25% ML-Ni)” for the sake of concision), T$_0$(16.7% ML-Co), T$_1$(16.7% ML-Co), and T$_3$ site of 25% ML Ni-V$_2$CO$_2$ is only $−0.01$, $−0.04$, $−0.05$, $0.03$, and $−0.03$ eV, respectively. The $|ΔG_{H}|$ at these sites are even smaller than the $ΔG_{H}$ of Pt(111) surface ($≈0.09$ eV), indicating the extremely high catalytic activity for HER. Other sites, such as T$_3$(12.5% ML-Co) and T$_2$(12.5% ML-Ni) have $|ΔG_{H}|$ ($≈0.1$ eV) to that of Pt(111) surface. Therefore, these TM-promoted V$_2$CO$_2$ are expected to have HER performances that are comparable to or even better than the Pt surface.

Moreover, the HER catalytic activities of TM-V$_2$CO$_2$ show strong dependence on the types and coverage of the promoters as well as the active sites. First, at the same level of promoter coverage and the same type of active site, the calculated $ΔG_{H}$ always decreases from Fe- to Co- to Ni-V$_2$CO$_2$. For example, at the T$_3$ site of V$_2$CO$_2$ with 25% ML promoter coverage, the calculated $ΔG_{H}$ is 0.31 eV for Fe-V$_2$CO$_2$, 0.10 eV for Co-V$_2$CO$_2$, and $−0.01$ eV for Ni-V$_2$CO$_2$, respectively. Second, for a given active site and a given promoter type, the calculated $ΔG_{H}$ always increases with the increase of the promoter coverage. This can

Figure 2. The structures and computational models of a) 12.5%, b) 16.7%, and c) 25% ML TM-promoted V$_2$CO$_2$, where the blue, gray, red, and green balls present the V, C, O, and TM atoms, respectively. d) Calculated reaction free energies of hydrogen absorption $ΔG_{H}$ of V$_2$CO$_2$ with 12.5%, 16.7%, and 25% ML TM coverage as a function of promoter and active site. The blue and red lines present the variations of $ΔG_{H}$ with the changes of promoter type and active site, respectively. The yellow and transparent planes present the cases of 12.5% and 16.7% ML TM covered V$_2$CO$_2$, respectively, which can describe the effect of the coverage of TM on the $ΔG_{H}$. (Supporting Information)
The promotional effect of TM on HER performance of V$_2$CO$_2$ can be ascribed to the significant charge transfer between promoter atom and surface O atoms. Through Bader charge analysis, for pure V$_2$CO$_2$, each surface O atom gains about 0.895 e from surrounding V atoms (see Table 1). For the TM promoted V$_2$CO$_2$, the electrons that surface O atoms received (N$_e$) range from 0.899 to 0.967 e (Table 1 and Figure 3a), larger than those in pure V$_2$CO$_2$. As discussed above, these extra electrons will lead to more p-states of O atom and increase the σ* occupancy in TM promoted V$_2$CO$_2$. As a result, the H–O bond of TM-V$_2$CO$_2$ is weakened, as compared with that in pure V$_2$CO$_2$ and eventually increases ΔG$_{H}$. Moreover, different TM promoters cause different charge transfer, which is determined by the intrinsic electronegativity of the TM. As the electronegativity order of these three TMs follows: Fe (1.83) < Co (1.88) < Ni (1.92), Fe will provide the largest charge transfer to O atom, followed by Co and Ni. As a result, at 12.5% ML TM coverage, the charge near the active sites of Fe-promoted V$_2$CO$_2$ is the densest, followed by Co- and Ni-promoted systems (Figure 3b-d). For other TM coverage, similar tendency is observed, as shown in Table 1 and Figure 3a. Correspondingly, the H–O bond in Fe-promoted V$_2$CO$_2$ is always weaker than that in Co- and Ni-promoted systems. Therefore, the ΔG$_{H}$ in Ni-V$_2$CO$_2$ is always the smallest, followed by Co-V$_2$CO$_2$ and Fe-V$_2$CO$_2$. As more TM atoms surround the active site (from T$_0$ to T$_1$ to T$_2$ to T$_3$), the number of received electrons of O atom increases for all TM-promoted systems. As a result, the H–O binding strength is attenuated and ΔG$_{H}$ is thus enhanced. With the increase of Ni coverage from 12.5% ML (Figure 3d) to 16.7% ML (Figure 3e), the charge density at the same type of active site always increases. For other promoters, the received charge of a certain site at a lower TM coverage is also less than that at a higher TM coverage (Table 1 and Figure 3a). Therefore, the H–O bond is weakened and ΔG$_{H}$ is augmented with the increase of TM coverage. These results are in perfect accord with the promoter type, coverage and active site dependent behaviors discussed above, which shed light on the nature of the promotional effects of transition metals on the catalytic activity.

A complete HER is a multistep reaction. The first step is the hydrogen adsorption, named Volmer reaction, in which a proton gains an electron from the surface of catalyst or electrode to form adsorbed hydrogen. The subsequent step has two possibilities: one is the homolytic Tafel reaction, 2H$_{ad}$ → H$_2$; the other is the heterolytic Heyrovsky reaction, H$_{ad}$ + H$^+$ + e$^-$ → H$_2$. The pathway of the second step is strongly dependent on the inherent properties of the catalyst or electrode. Above discussion belongs to Volmer reaction. To give a comprehensive understanding of the HER process of TM-V$_2$CO$_2$, we further explore possibilities of Tafel mechanism or Heyrovsky mechanism. In fact, all the active sites that present high activity for Volmer reaction will maintain their catalytic activity for Heyrovsky reaction. Therefore, the second step of HER on the surface of TM-promoted V$_2$CO$_2$ can follow the Heyrovsky mechanism. To verify whether the reaction can also follow the Tafel mechanism, we select 16.7% Fe- and Co-promoted V$_2$CO$_2$ as prototypes and calculate the ΔG$_{f}$ for the adsorption of the second hydrogen. As shown in Figure S5 (Supporting Information), with the adsorption of the second hydrogen, the ΔG$_{f}$ greatly increases from ~0.04 and ~0.10 eV to 0.42 and 0.37 eV for Fe- and Co-V$_2$CO$_2$, respectively, indicating that the second HER step of TM-promoted V$_2$CO$_2$ may not follow the Tafel mechanism. To further verify this, the activation barriers following Tafel mechanism are calculated. As shown in Figure S6 (Supporting Information), relative high energy barriers need to be overcome, i.e., 2.13 and 2.22 eV for Fe- and Co-V$_2$CO$_2$.

### Table 1. Calculated ΔE$_{H}$, ΔG$_{H}$, and charge transfer at different active sites of different TM-V$_2$CO$_2$.

| System     | Coverage | Active site | ΔE$_{H}$ [eV] | ΔG$_{H}$ [eV] | Ne [e]  |
|------------|----------|-------------|---------------|---------------|---------|
| Fe-V$_2$CO$_2$ | 12.5% ML | T$_0$       | -0.58         | -0.21         | 0.912   |
|            |          | T$_1$       | -0.53         | -0.16         | 0.927   |
|            |          | T$_2$       | -0.28         | 0.09          | 0.941   |
|            | 16.7% ML | T$_0$       | -0.41         | -0.04         | 0.918   |
|            |          | T$_1$       | -0.34         | 0.03          | 0.933   |
|            |          | T$_2$       | -0.22         | 0.15          | 0.941   |
|            | 25% ML   | T$_0$       | -0.06         | 0.31          | 0.967   |
| Co-V$_2$CO$_2$ | 12.5% ML | T$_0$       | -0.60         | -0.23         | 0.909   |
|            |          | T$_1$       | -0.60         | -0.23         | 0.924   |
|            |          | T$_2$       | -0.40         | -0.03         | 0.932   |
|            | 16.7% ML | T$_0$       | -0.47         | -0.10         | 0.913   |
|            |          | T$_1$       | -0.42         | -0.05         | 0.929   |
|            |          | T$_2$       | -0.30         | 0.07          | 0.932   |
|            | 25% ML   | T$_0$       | -0.27         | 0.10          | 0.952   |
| Ni-V$_2$CO$_2$ | 12.5% ML | T$_0$       | -0.72         | -0.35         | 0.899   |
|            |          | T$_1$       | -0.66         | -0.29         | 0.918   |
|            |          | T$_2$       | -0.52         | -0.15         | 0.923   |
|            | 16.7% ML | T$_0$       | -0.60         | -0.23         | 0.905   |
|            |          | T$_1$       | -0.53         | -0.16         | 0.918   |
|            |          | T$_2$       | -0.45         | -0.08         | 0.927   |
|            | 25% ML   | T$_0$       | -0.38         | -0.01         | 0.946   |

be seen vividly from Figure 2d that the yellow plane which presents the case of 12.5% ML promoter coverage is always under the transparent plane which describes the situation of 16.7% ML promoter coverage. Third, the HER activity is also sensitive to the transparent plane which describes the situation of 16.7% ML T$_0$ to T$_2$ and to T$_3$ site, leading to the increase of V$_2$CO$_2$, the electrons that surface O atoms received (N$_e$) range from 0.899 to 0.967 e (Table 1 and Figure 3a), larger than those in pure V$_2$CO$_2$. As discussed above, these extra electrons will lead to more p-states of O atom and increase the σ* occupancy in TM promoted V$_2$CO$_2$. As a result, the H–O bond of TM-V$_2$CO$_2$ is weakened, as compared with that in pure V$_2$CO$_2$ and eventually increases ΔG$_{H}$. Moreover, different TM promoters cause different charge transfer, which is determined by the intrinsic electronegativity of the TM. As the electronegativity order of these three TMs follows: Fe (1.83) < Co (1.88) < Ni (1.92), Fe will provide the largest charge transfer to O atom, followed by Co and Ni. As a result, at 12.5% ML TM coverage, the charge near the active sites of Fe-promoted V$_2$CO$_2$ is the densest, followed by Co- and Ni-promoted systems (Figure 3b-d). For other TM coverage, similar tendency is observed, as shown in Table 1 and Figure 3a. Correspondingly, the H–O bond in Fe-promoted V$_2$CO$_2$ is always weaker than that in Co- and Ni-promoted systems. Therefore, the ΔG$_{H}$ in Ni-V$_2$CO$_2$ is always the smallest, followed by Co-V$_2$CO$_2$ and Fe-V$_2$CO$_2$. As more TM atoms surround the active site (from T$_0$ to T$_1$ to T$_2$ to T$_3$), the number of received electrons of O atom increases for all TM-promoted systems. As a result, the H–O binding strength is attenuated and ΔG$_{H}$ is thus enhanced. With the increase of Ni coverage from 12.5% ML (Figure 3d) to 16.7% ML (Figure 3e), the charge density at the same type of active site always increases. For other promoters, the received charge of a certain site at a lower TM coverage is also less than that at a higher TM coverage (Table 1 and Figure 3a). Therefore, the H–O bond is weakened and ΔG$_{H}$ is augmented with the increase of TM coverage. These results are in perfect accord with the promoter type, coverage and active site dependent behaviors discussed above, which shed light on the nature of the promotional effects of transition metals on the catalytic activity.
respectively. Therefore, we can conclude that the HER on the surface of Fe- and Co-promoted V$_2$CO$_2$ follows the Heyrovsky mechanism rather than the Tafel mechanism.

Strain engineering has been proved to be an efficient way to tune the physical and chemical properties of 2D materials, including MXenes$^{[29–31]}$ which may have influence on the HER performance as well. Moreover, the real HER experiments are generally very complicated. Materials may suffer deformations and form curved surfaces, in which the concave and convex can be regarded as suffering compressive and tensile strain, respectively. We select 12.5% ML TM covered V$_2$CO$_2$ which contains T$_0$, T$_1$, and T$_2$ sites and the 25% ML TM covered V$_2$CO$_2$ which contains T$_3$ site as representatives to study the strain influence on the HER performance of the TM-promoted V$_2$CO$_2$. Here, the biaxial strain is considered and defined as $\varepsilon = \Delta a/a_0$, where the $a_0$ and $\Delta a + a_0$ are the lattice constants of the unstrained and strained supercells, respectively. Thus, the positive or negative values of $\varepsilon$ correspond to the tensile or compressive strain, respectively.

Figure 4 presents the reaction free energy for hydrogen adsorption at T$_0$, T$_1$, and T$_2$ sites of V$_2$CO$_2$ with the promoter coverage of 12.5% ML and at T$_3$ sites of V$_2$CO$_2$ with the coverage of 25% ML as a function of strain. A general tendency is observed, that is, the $\Delta G_H$ monotonously decreases with the increase of $\varepsilon$. Consequently, for strong H binding strength systems that have relatively negative $\Delta G_H$, the compressive strain can improve their HER performance. For example, the $\Delta G_H$ of T$_0$ (12.5% ML-Co) and T$_1$ (12.5% ML-Fe) sites is $-0.24$ and $-0.16$ eV at unstrained state and reduces to $-0.09$ and $-0.03$ eV under $-2.5\%$ strain, respectively. On the contrary, the tensile strain is an efficient way to improve the HER performance of weak H binding strength systems, such as T$_3$(25% ML-Co) site, whose $\Delta G_H$ will decrease from 0.10 to 0.03 eV when applying a 2.5% tensile strain on it. Moreover, the HER catalytic performance of V$_2$CO$_2$ can even be tuned to reach the optimal $\Delta G_H$ of 0 eV by applying a biaxial strain, i.e., T$_2$(12.5% ML-Co) under $-0.5\%$ strain and T$_3$(25% ML-Ni) under $-0.27\%$ strain. Most interestingly, for highly active sites such as T$_2$(12.5% ML-Co) and T$_3$(25% ML-Ni) sites, the calculated $|\Delta G_H|$ is always smaller than 0.1 eV within a relatively wide range of strain, indicating their highly catalytic stability when used in real condition.
Figure 4. Calculated free energy for hydrogen adsorption $\Delta G_\text{H}$ at a) $T_0$ (12.5% ML), b) $T_1$ (12.5% ML), c) $T_2$ (12.5% ML), and d) $T_3$ (25% ML) sites as a function of strain. The purple, blue, and green lines represent Fe-, Co-, and Ni-promoted systems, respectively.

The strain engineering HER performance of TM-promoted V$_2$CO$_2$ can be profoundly understood in light of the partial density of states of surface O under different strain. As clearly illustrated in Figures S7–S18 (Supporting Information), the p-orbital DOS of surface O atom in TM-promoted V$_2$CO$_2$ shows an upward shift with the increase of $\varepsilon$. These upward shifts will lead to fewer filled p-states, and less $\sigma^*$ occupancy with the increase of $\varepsilon$; as a consequence, the binding strength of H–O bond will be enhanced and the $\Delta G_\text{H}$ is accordingly decreased.

3. Conclusion

In summary, we study the HER performance of fully oxidized vanadium carbides V$_2$CO$_2$ with and without the promotion of transition metals within the framework of first-principle calculations. Our calculations show that pure V$_2$CO$_2$ is not an ideal catalyst for HER, while it can be engineered to be an excellent HER catalyst by introducing the TM atoms onto the surface. The influences of the TM promoter type, coverage, and

the active site on the HER performance of V$_2$CO$_2$ are further explored in details and Fe-promoted, 16.7%–25% ML Co-promoted, and 25% ML Ni-promoted systems are found to be the best catalysts for HER activity with the optimal $\Delta G_\text{H}$ of $\approx$0 eV. Moreover, these TM-promoted catalysts show good catalytic stability and can be further modulated by applying external strain as well. It is worth pointing out that assembling various TM onto the surfaces of materials can be easily realized in experiment, while the size and coverage can also be controlled by adjusting the ratio of reactants, react time, type, and amount of surfactant. Therefore, these TM promoted V$_2$CO$_2$ are expected to be a kind of easy-synthesized and highly active catalytic system for HER. In short, the findings unveiled here would open a new window for the application of 2D MXenes and for the development of cost-effective alternatives to Pt in HER.

4. Experimental Section

All first-principle calculations were performed by using projector augmented wave method as implemented in the Vienna ab initio simulation package. The generalized gradient approximation in the Perdew–Burke–Ernzerhof form and a cut-off energy of 600 eV for plane-wave basis set were adopted. The convergence threshold was $10^{-3}$ eV for energy and $0.02$ eV Å$^{-1}$ for force, respectively. To avoid the interaction between two periodic units, a vacuum space at least 20 Å was used. Both non-polarized and spin-polarized calculations were employed to determine the ground state structures. Supercells consisting of 4 $\times$ 2 $\times$ 1 and 2 $\times$ 2 $\times$ 1 unit cells of V$_2$CO$_2$ ML were used for 12.5% ML, 16.7% ML, and 25% ML hydrogen adsorbed or promoter covered systems, respectively, as shown in Figure S1 in the Supporting Information. The corresponding Brillouin zone was sampled by Monkhorst–Pack k-point mesh of 4 $\times$ 8 $\times$ 1, 5 $\times$ 9 $\times$ 1, and 9 $\times$ 9 $\times$ 1, respectively.

The HER catalytic activity of materials can be evaluated by the reaction free energy of hydrogen adsorption ($\Delta G_\text{H}$) as defined by

$$\Delta G_\text{H} = \Delta E_\text{H} + \Delta E_{ZPE} - T\Delta S_\text{H}$$

where $\Delta E_\text{H}$ is the hydrogen adsorption energy

$$\Delta E_\text{H} = E_{\text{System+H}} - E_{\text{System}} - \frac{1}{2} E_\text{H}$$

in which $\Delta E_{\text{System+H}}$ and $E_{\text{System}}$ are the energies of V$_2$CO$_2$ systems with and without H adsorption, respectively. $\Delta E_{ZPE}$ and $\Delta S_\text{H}$ are the zero-point energy difference and the entropy difference between the adsorbed and the gas phase, respectively. The $\Delta E_{ZPE}$ can be obtained via vibrational frequency calculation. The $\Delta S_\text{H}$ can be regarded as $\Delta S_\text{H} \equiv \frac{1}{2} S_\text{H}$ due to the fact that the vibrational entropy in the adsorbed state is small according to previous studies. The optimal value for HER is $\Delta G_\text{H} = 0$, which means that the smaller values of $|\Delta G_\text{H}|$, the better HER performance of materials.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the NSFC (21525311, 21373045, 11404056) and NSF of Jiangsu (BK20130016) and SRDFP (2013002110029, 20130092120042) in China. The authors thank the computational resources at the SEU and National Supercomputing Center in Tianjin.

Received: May 9, 2016
Revised: May 20, 2016
Published online: June 28, 2016

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