

High catalyst performance of two-dimensional Ti₃B₃N₃S₆ for hydrogen evolution reaction

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Abstract. Single-atom catalysts (SACs) for the hydrogen evolution reaction (HER) is an efficient electrochemical pathway to produce the green production. However, the development of HER process is hampered by the lack of high-performance electrocatalysts. In this work, we proposed a new π -d conjugated structure of the Ti₃B₃N₃S₆ monolayer as the single-atom catalysts for the HER process by using the density functional theory (DFT) calculations. The calculated results show that the Ti atom is active site of the Ti₃B₃N₃S₆ monolayer with the high catalytic activity ($\Delta G_H = -0.14$ eV) for HER. The electronic properties of the Ti₃B₃N₃S₆ monolayer were explored by the electron localization function (ELF), Bader charge analysis and the polarized density of states (PDOS) density analysis. The Ti₃B₃N₃S₆ monolayer can promote the electronic transfer during the HER process, which indicates that the Ti₃B₃N₃S₆ monolayer can be considered to investigate the catalytic activity for HER. The Gibbs free energy of H atoms adsorption on the Ti₃B₃N₃S₆ monolayer is -0.14 eV. Furthermore, the origin of high catalytic activity for the Ti₃B₃N₃S₆ monolayer was explored by the analysis of the PDOS of the H adsorption on the Ti₃B₃N₃S₆ monolayer. Therefore, our work proposes a new and high catalytic single-atom catalyst for the HER.

Keywords: hydrogen evolution reaction; Two-dimensional monolayer; Ti₃B₃N₃S₆ monolayer.

1. Introduction

Due to increased environmental pollution and the global scarcity of resources, the pollution-free and high energy density fuel gains widespread attention. Hydrogen (H₂) is an ideal energy carrier of sustainable energy source for its high energy density and environmental friendliness. The electro-chemical water splitting for the production of H₂ through hydrogen evolution reaction (HER) process plays a critical role as a promising and sustainable method for large-scale hydrogen production. So far, platinum-based catalysts are regarded as the best catalysts for HER. However, the limited earth resources of the noble metals hamper their large-scale application. Exploring new catalysis for HER with resource-rich and non-noble metal elements is one promising pathway for the mass production of hydrogen.

In recent years, embedding single transition metal (TM) atoms into 2D substrates have been widely explored as effective electrocatalysts for HER process. Owing to their tunable electronic structures and low coordinated configurations, these single-atom catalysts (SACs) are developed to improve the electrocatalytic performance of catalysts for the HER process. SACs can effectively prevent the occurrence of clusters in the reaction process due to the interaction between the metal atom and the substrate, such as Ti, V, Mn and Co-silience [1], Sc, Ti and V-CuPS₃[2] and Ni-P₄[3]. At the same time, the non-

noble transition metals are cheap and well-resourced on the earth. However, so far many catalysts cannot achieve high metal atom loadings. This becomes a serious problem as the high loading of metal atoms is crucial to increase the number of exposed active sites, thus significantly improving catalytic efficiency of the catalysts for HER. Therefore, the design of a rational, highly atomically loaded and cheap catalyst is the subject of our work.

Moreover, as an analogue of benzene (C₆H₆), borazine (B₃N₃H₆) is electronically and isostructurally similar to benzene. Borazine exhibits delocalized π ring currents localized on the nitrogen atoms, while it has a lower level of aromaticity. Recently, there a new π conjugated structure of the B₃N₃ ring was explored the dynamical and mechanical stabilities [4]. Therefore, the transition metal atom and B₃N₃S₆ could form a new π -d conjugated structure with high stability.

Herein, we proposed a new 2D structure of the Ti₃B₃N₃S₆ monolayer to study the catalytic activity for the HER process and investigate the origin of high catalytic activity by using the density functional theory (DFT) simulations. The calculated results show that the Ti atom is the active center of the Ti₃B₃N₃S₆ monolayer with ΔG_H of -0.14 eV, which shows that the Ti₃B₃N₃S₆ monolayer is a high electrocatalyst for the HER. Furthermore, the electronic structure (including PDOS, ELF and Bader

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charge) of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer was explored for the HER process.

2. Computational Details

The Vienna ab initio Simulation Package (VASP) code was used to all energy calculations[5]. The electronic exchange correlation was performed by the Perdew – Burke – Ernzerhof (PBE) function based on the generalized gradient approximation (GGA)[6]. The Brillouin zones was performed by the Monkhorst – Pack mesh of $3 \times 3 \times 1$. The z-direction was set to 15 Å to avoid the weak interactions of van der Waals interaction. The energy cutoffs was set to 520 eV. The energy and force convergences were set to 10^{-5} eV and 0.02 eV/Å, respectively.

The Gibbs free energy of H adsorption (ΔG_H) on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer is used to evaluate the HER catalytic performance, which can be calculated by the following equation:

$$\Delta G_H = \Delta E_H + \Delta ZPE - T\Delta S, \quad (1)$$

Where the ΔE_H is the total energy of H adsorption on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer. ΔZPE is zero-point energy difference. T is set to 300 K. ΔS is the entropy difference. The calculated value of $\Delta ZPE - T\Delta S$ is 0.24 eV.

3. Results and discussion

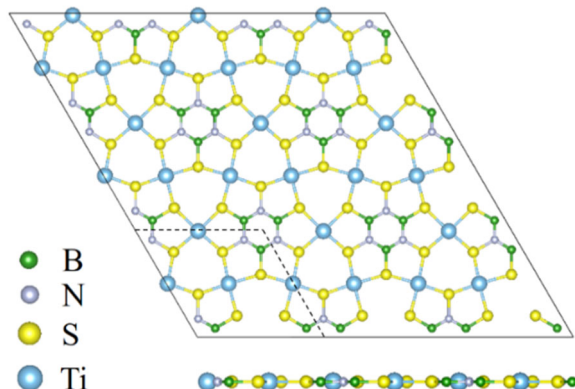


Figure 1. The top and side views of $3 \times 3 \times 1$ supercell of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer. The green, sliver, yellow and blue cells represent B, N, S and Ti atoms. The dotted plot represents a unit cell.

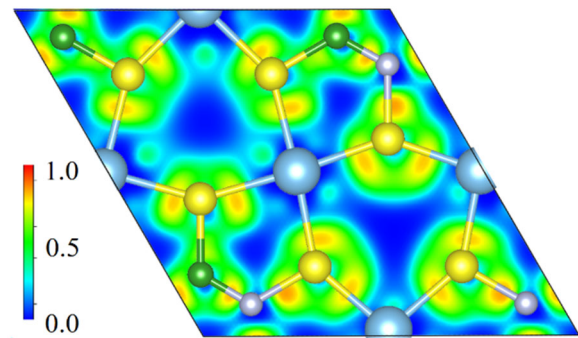


Figure 2. Electron localization function (ELF) map at isosurface value of 0.50 a.u. The values of ELF are between 0.0 and 1.0.

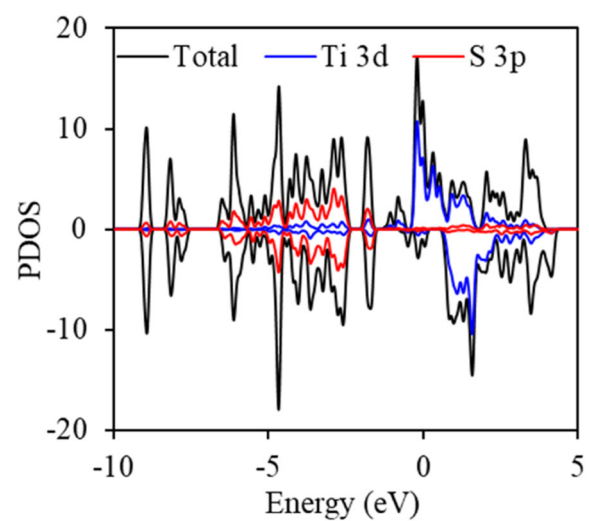


Figure 3. The PDOS of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer. The black, blue and red lines are DOS of the total, 3d orbital of Ti atom and 3p orbital of S atom. The Fermi energy is located at 0 eV.

Figure 1 shows the top and side views of $3 \times 3 \times 1$ supercell of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer, where the dotted box indicates the unit cell. The green, sliver, yellow and blue cells represent B, N, S and Ti atoms. Each $\text{B}_3\text{N}_3\text{S}_6$ ring is connected to six S atoms, and a Ti atom is connected to four S atoms. After structural optimization, all atoms of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer are in the same plane, and the lattice constants are $a = b = 9.18 \text{ \AA}$, $c = 15 \text{ \AA}$, $\alpha = \beta = 60^\circ$, $\gamma = 120^\circ$. It is essential to know the electronic properties of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer for catalytic HER performance. To investigate electronic properties of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer, the electron localization function (ELF) and the polarized density of states (PDOS) were investigated, and the calculated results are shown in Figures 2 and 3. For the ELF of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer as shown in Figure 2, the ELF values of Ti-S bonds are lower than 0.5, which indicated that the bond of Ti-S is ionic bond. At the same time, the B-S and B-N bonds are covalent due to the ELF values are greater than 0.5.

At the same time, the Bader charge of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer are calculated, and the calculated results show that the Ti atom transfer about 0.23 electrons to the S atom, which indicates that the transition atom can transfer electrons efficiently in the catalytic process. Therefore, the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer can generate effective electrons transfer during the HER process.

Moreover, the partial density of states (PDOS) of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer are investigated, and the calculated result was shown in Figure. 3. The black, blue and red lines are DOS of the total, 3d orbital of Ti atom and 3p orbital of S atom. The results show that the Fermi energy level (E_F) is crossed by the electronic states, and the Ti atoms contribute the majority of the electronic state, which indicated that the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer is metal conductive. The above results indicated that the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer can promote the electronic transfer during the HER process. Therefore, the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer is considered to investigate the catalytic activity for HER process.

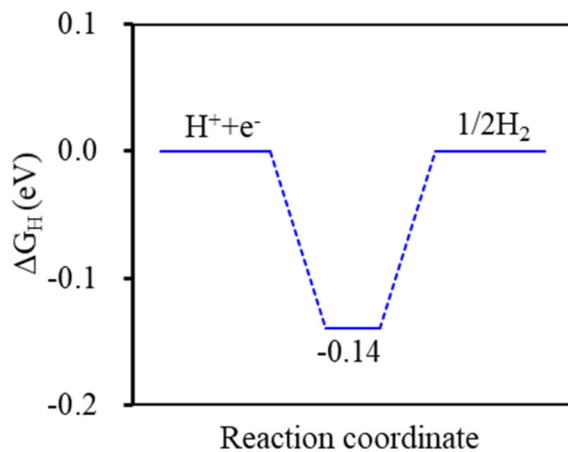


Figure 4. The diagram of Gibbs free energy for HER on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer.

According to the previous studies, the sites of the transition metal atom would be the active catalytic center of the HER process. Therefore, the H atom adsorption site on surface of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer is the Ti atom in our work. Therefore, the Gibbs free energy diagram was investigated in Figure 4. The Gibbs free energy of adsorbed H atoms (ΔG_H) to evaluate HER performance has been widely accepted. At the same time, the closer the value of ΔG_H is to 0 eV, the better the catalytic effect, i.e., the catalyst can effectively adsorb H atoms without being too tightly adsorbed to allow the H atoms to be released. Fig. 4 shows the diagram of Gibbs free energy for HER on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer. The value of ΔG_H is -0.14 eV for the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer, which indicates that the Ti atom can effectively adsorb H atoms and can easily release H_2 molecules during the HER catalytic process. Therefore, based on the above, the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer can be act as a novel and efficient electrocatalyst for the HER process.

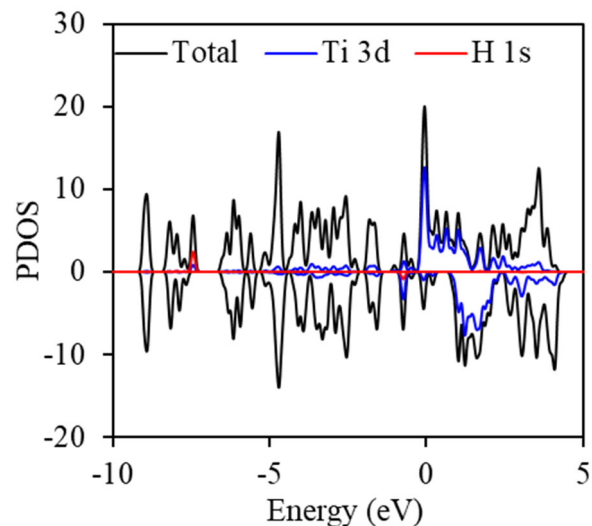


Figure 5. The partial density of states of H adsorption on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer. The black, blue and red lines are density of states of the total, 3d orbital of Ti atom and 1s orbital of H atom. The Fermi energy level is located at 0 eV.

To understand the high catalytic mechanism for the HER process on the surface of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer, the PDOS of the H adsorption on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer was investigated in Figure 5, and the calculated results show that the 1s orbital of H atom with 3d orbital of Ti atoms generate hybridization from the coupling of electronic states, which indicates that the H atom can be adsorbed on the Ti atom of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer on the HER process. The density states are below the E_F , which can be full filled, which indicates that the Ti atoms achieve effective charge transfer on the HER process. Therefore, the electronic analysis of the H adsorption on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer proved the H atoms can be stable adsorbed during the HER process, and the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer has the great catalytic performance of the HER.

4. Conclusion

In this paper, we investigated the catalytic activity of $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer for HER by using the DFT calculation. The calculated results implied that the Ti atom is the active center with the ΔG_H value of -0.14 eV, which indicates that the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer can be acted as a good sing-atom catalyst for the HER process. The electronic properties of the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer, i.e., the partial density of states, Bader charge and electron localization function, are investigated to get the potential of the performance of the HER. At the same time, the origin of excellent catalytic performance was studied by a series of electronic structure analysis, which shows that the s orbital of H atom with d orbital of Ti atoms generate hybridization from the coupling of electronic states. The electronic analysis of the H adsorption on the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer proved the H

atoms can be stable adsorbed during the HER process, and the $\text{Ti}_3\text{B}_3\text{N}_3\text{S}_6$ monolayer has the great catalytic performance of the HER. Therefore, our work proposed a new and excellent two-dimensional electrocatalyst for the HER process.

References

1. Sun, Y. X., Huang, A. J. Wang, Z. G, et al. Transition metal atom (Ti, V, Mn, Fe, and Co) anchored silicene for hydrogen evolution reaction. *Rsc Adv.* 9. (2019) 26321-26326.
2. Sun, Y. X., Huang, A. J., Li, Z. J., et al. Transition Metal Atoms Anchored on CuPS3 Monolayer for Enhancing Catalytic Performance of Hydrogen Evolution Reactions. *Electrocatalysis-Us.* 13. (2022) 494-501.
3. Yang, Y. et al. Insights into the Origin of High Activity of Ni5P4(0001) for Hydrogen Evolution Reaction. *J Phys Chem C.* 127. (2023) 5385-5394.
4. Abdullahi, Y. Z. Antiferromagnetic semiconductor in porous boron nitride (B6N6) sheet: First-principles investigation. *Computational and Theoretical Chemistry.* 1197. (2021) 113155.
5. Kresse, G. & Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B.* 54. (1996) 11169-11186.
6. Perdew, J. P. et al. Atoms, Molecules, Solids, and Surfaces - Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys Rev B.* 46. (1992) 6671-6687.