ISSN 1674-1056
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Citation: Chin. Phys. B . 2020, 29(5): 058104 . **doi:** 10.1088/1674-1056/ab8203
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Prediction of structured void-containing 1T-$PtTe_2$ monolayer with potential catalytic activity for hydrogen evolution reaction*

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(Received 5 January 2020; revised manuscript received 25 February 2020; accepted manuscript online 23 March 2020)

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted considerable attention because of their unique properties and great potential in nano-technology applications. Great efforts have been devoted to fabrication of novel structured TMD monolayers by modifying their pristine structures at the atomic level. Here we propose an intriguing structured 1T-$PtTe_2$ monolayer as hydrogen evolution reaction (HER) catalyst, namely, Pt_4Te_7, using first-principles calculations. It is found that Pt_4Te_7 is a stable monolayer material verified by the calculation of formation energy, phonon dispersion, and *ab initio* molecular dynamics simulations. Remarkably, the novel structured void-containing monolayer exhibits superior catalytic activity toward HER compared with the pristine one, with a Gibbs free energy very close to zero (less than 0.07 eV). These features indicate that Pt_4Te_7 monolayer is a high-performance HER catalyst with a high platinum utilization. These findings open new perspectives for the functionalization of 2D TMD materials at an atomic level and its application in HER catalysis.

Keywords: first-principles calculations, structured $PtTe_2$ monolayer, void-containing materials, HER catalyst

PACS: 81.16.Hc, 31.15.A–, 68.65.–k, 14.60.Cd **DOI:** 10.1088/1674-1056/ab8203

1. Introduction

Stimulated by the fascinating properties of graphene,[1] great efforts have been devoted to discovering and synthesizing more two-dimensional (2D) materials.[2–8] Compared to group-VI transition metal dichalcogenides (TMDs) (especially MoS_2 and WS_2), platinum dichalcogenides (PtS_2, $PtSe_2$, and $PtTe_2$), as one of the group-X TMDs, are still in their infancy.[9–11] Experimental research of few layered PtS_2 and monolayer $PtSe_2$ has made great progress,[12–16] and several novel physical phenomena have also been found in bulked $PtTe_2$.[17,18] However, so far there has been no available experimental data about monolayer $PtTe_2$. Despite the sporadic calculation reports on binary-phased Pt-Te nanosheets,[19,20] systematical theoretical investigations and potential applications for platinum and tellurium binary monolayer are still lacking and necessary.

To extend 2D materials' potential and to widen their applications, an advanced method is engineering pristine structures at atomic scales.[21–24] In fact, engineering surface atoms is a promising way to design catalysts for hydrogen evolution reaction (HER) in TMDs.[25–31] Except for the catalytic performance at the edges,[32,33] an inert basal plane of monolayer MoS_2 could further be used as HER catalysis by introducing sulfur vacancies or strain.[34,35] Vacancies in 2D TMDs are ubiquitous and play crucial roles in understanding electronic, optical, and catalytic properties and tailoring them for desirable applications.[36,37] Bulk $PtTe_2$ can be transformed from a chemically inert material into a catalyst in stable adsorption of hydroxyl groups after the introduction of defects and surface functionalization,[38] while the atomic level functionalization of $PtTe_2$ monolayer has not yet been reported.

In this paper, based on density functional theory (DFT) calculations, we screened the structural and electronic properties of platinum and tellurium binary structured nanosheets systematically, and found a stable structured 1T-$PtTe_2$ monolayer, namely Pt_4Te_7. Pristine 1T-$PtTe_2$ monolayer is an indirect band semiconductor with a gap of 0.67 eV. In contrast, Pt_4Te_7 monolayer is a mini-gap semiconductor, whose bandgap is only 28 meV. Its thermal and dynamical stability has also been confirmed by formation energy, *ab initio* molecular dynamics and phonon dispersion analysis. The electronic structure of Pt_4Te_7 makes it excellent catalytic performance for HER distinguished from its pristine plane 1T-$PtTe_2$ monolayer. The Gibbs free energy, a widely used descriptor for catalytic activity, is less than 0.07 eV for Pt_4Te_7, which is better than the best cathode material for HER, Pt bulk surfaces (−0.09 eV).[39] The stable void-containing structured 1T-$PtTe_2$ monolayers predicted in this study could be a benefit for searching other functionalized TMD materials.

*Project supported by the National Key R&D Program of China (Grant Nos. 2016YFA0202300, 2018YFA0305800, and 2019YFA0308500), the National Natural Science Foundation of China (Grant Nos. 61888102, 51872284, and 51922011), and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB30000000).

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2. Computational details

Density functional theory (DFT) calculations were carried out using the projector-augmented wave approach (PAW)[40] and the Perdew–Burke–Ernzerhof (PBE) developed exchange-correlation functional,[41] as implemented in the VASP.[42] The band structure calculation of Pt_4Te_7 is employed Heyd–Scuseria–Ernzerhof (HSE) hybrid functional. The cutoff energy was chosen at 500 eV, and the Brillouin zone was sampled using k-points of $7 \times 7 \times 1$. The convergence thresholds for energy and atomic forces were set as 1×10^{-5} eV and 0.01 eV/Å, respectively. The distance of vacuum space was set to larger than 20 Å. The phonon spectrum was computed with density functional perturbation theory (DFPT)[43] and post-treated by Phonopy code.[44] Molecular dynamic simulations were performed using the (4×4) $PtTe_2$ supercell and the NVT ensemble, and lasted for 10 ps with a time steps of 1.0 fs, which was controlled by the Nosé–Hoover method.[45]

3. Results and discussion

It is reported that bulk and layered $PtTe_2$ is stable in the octahedral 1T structure.[18] Similar to other TMD materials, the electronic properties of $PtTe_2$ are also thickness dependent.[10,11] Bulk 1T-$PtTe_2$ is semi-metallic, and monolayer $PtTe_2$ exhibits an indirect semiconducting feature with bandgap of 0.67 eV. The lattice parameters of 1T $PtTe_2$ were optimized to be $a = b = 4.0$ Å. We modified the monolayer structure of $PtTe_2$ by introducing voids at the atomic scale.

Different types of void-containing 1T-$PtTe_2$ monolayers are firstly investigated. A 2×2 supercell is selected for structural modification at atomic level. According to the number and location of missing Te atoms, we investigate four different structured monolayers as shown in Fig. 1. In one case, one Te atom is removed. The stoichiometry is Pt_4Te_7 (as shown in Fig. 1(a)). In the other three cases, one Te atom is removed from the first layer and one Te atom is removed from the third layer. The three structures are named as α-Pt_4Te_6, β-Pt_4Te_6 and γ-Pt_4Te_6 (Figs. 1(b)–1(d)). The optimized lattice constants of Pt_4Te_7 monolayer are $a = b = 7.8$ Å at the PBE level, which is slightly smaller than that of the perfect 1T-$PtTe_2$ monolayer ($2a = 2b = 8.0$ Å). The optimized lattice parameters of the other three Pt_4Te_6 are 7.7 Å, 7.8 Å, and 8.0 Å, respectively.

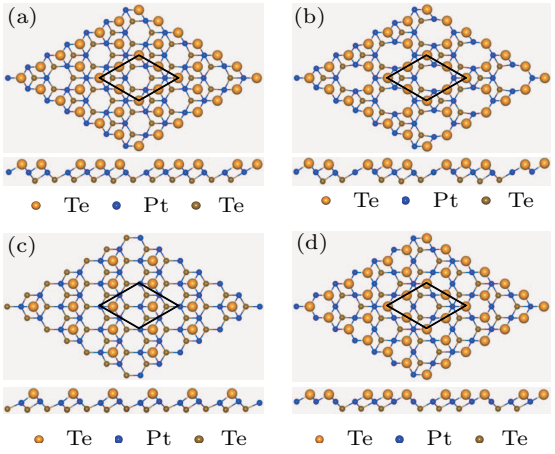


Fig. 1. Atomic structures of void-containing 1T-$PtTe_2$ monolayer. (a) Top and side view of Pt_4Te_7, in which one Te atom in the first atomic layer is removed in a 2×2 supercell, making the first layer looks like a Kagome pattern. (b) Top and side view of α-Pt_4Te_6, in which one Te atom from the first layer and one nearest-neighbor Te atom from the third layer are removed in a supercell. (c) Top and side view of β-Pt_4Te_6, in which two Te atoms from the first layer are removed in a supercell. (d) Top and side view of γ-Pt_4Te_6, in which one Te atom from the first layer and one next nearest-neighboring Te atom from the third layer are removed in a supercell. The supercell is shown in a black box. The Te atoms in the first and third atomic layers are represented by light orange and dark orange, respectively. The Pt atoms in the second atomic layer are represented by blue. For clarity, the atoms in the first atomic layer magnified, while the side view only shows the nearby atoms containing voids.

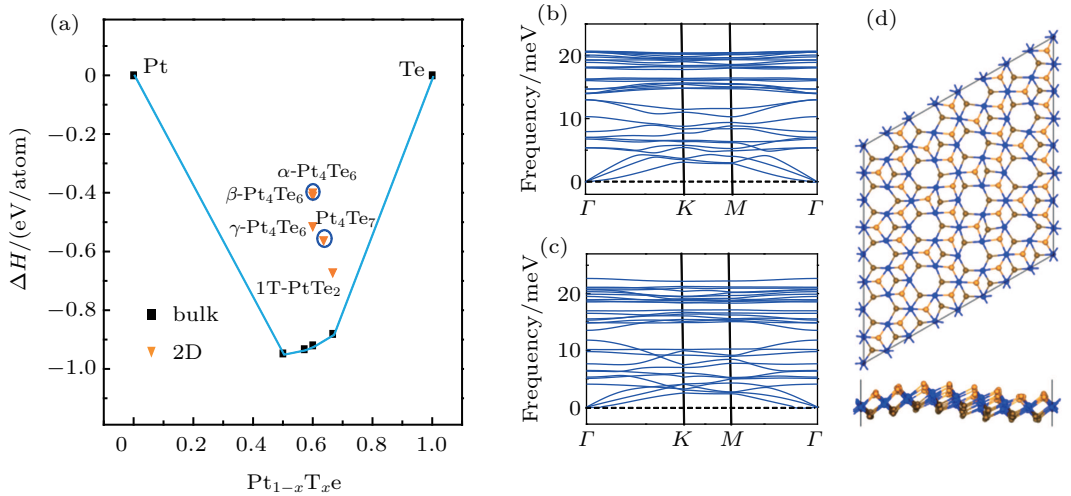


Fig. 2. Stability of void-containing 1T-$PtTe_2$ monolayer. (a) Formation energy of void-containing 1T-$PtTe_2$ monolayer. The black square indicates the formation energy of bulk structures and are connected by blue lines. The bulk Pt–Te binary has multiple structures,[46] chemical components from left to right are Pt, PtTe, Pt_3Te_4, Pt_2Te_3, $PtTe_2$, Te, respectively. The orange triangles represent formation energies of 2D structures. (b)–(c) Phonon dispersion of monolayer Pt_4Te_7 and α-Pt_4Te_6 along the high-symmetry directions of the Brillouin zone. (d) Snapshots of the equilibrium structure of Pt_4Te_7 monolayer at 400 K at the end of 10 ps first-principles molecular dynamics simulation.

The stability of the structured 1T-$PtTe_2$ monolayers is checked by calculating the formation energy which indicates the energy difference during the formation of the 2D material from its constituent elements at 0 K and 0 atm. The equation for the energy changes of formation of the structured $PtTe_2$ monolayer is

$$\Delta E\left(Pt_{1-x}Te_x\right) = E_{tot}\left(Pt_{1-x}Te_x\right) - \sum n_i \mu_i^0,$$

where E_{tot} is the total energy per formula unit of the structured $PtTe_2$ monolayer and μ_i^0 is the chemical potential of each element. Here we use the energy of Pt and Te from their bulk phase. We can find that the energy value of the perfect 1T-$PtTe_2$ monolayer is -0.668 eV as shown in Fig. 2(a), which is slightly higher than the formation energy of the bulk phase $PtTe_2$ (-0.881 eV). The value of Pt_4Te_7 monolayer is -0.559 eV. The three Pt_4Te_6 monolayers are -0.407 eV, -0.396 eV and -0.511 eV, respectively. Although Pt_4Te_7 and three Pt_4Te_6 have less energy favored than monolayer $PtTe_2$, the formation energies are still negative, which means that the formation of these patterned materials is not forbidden from energetic perspective. Monolayer materials with similar formation energy, such as monolayer $MoTe_2$,[47] have already been fabricated experimentally.[48,49]

The kinetic stability of these structured 1T-$PtTe_2$ monolayers is further studied by checking the existence of imaginary frequency in the phonon dispersion, which is widely used to test the structural stability.[50] For Pt_4Te_7 monolayer, as shown in Fig. 2(b), the absence of imaginary modes in the entire Brillouin zone confirms its dynamical stabilities. For the Pt_4Te_6 monolayer, there are imaginary frequencies for β- and γ-Pt_4Te_6, indicating that these two structures are not stable. For α-Pt_4Te_6, the phonon dispersion is shown in Fig. 2(c). There is no imaginary frequency indicating its kinetic stability. Through the verification of the stability, we can obtain two stable novel structured monolayer materials, namely, Pt_4Te_7 and α-Pt_4Te_6.

Moreover, we carried out first-principles molecular dynamics simulations to check the structural stability at finite temperature (400 K). Figure 2(d) is a snapshot for a 4×4 Pt_4Te_7 supercell after 10 ps MD run. The structure remains intact throughout the whole MD run, indicating that monolayer Pt_4Te_7 is thermodynamically stable. On the other hand, α-Pt_4Te_6 is screened out because the structure becomes disorder in the MD simulation.

After confirming the stability of Pt_4Te_7, we explored its electronic properties. As shown in Fig. 3(a), Pt_4Te_7 monolayer exhibits semiconductor character with a mini-gap of 28 meV. This nearly metallic feature may exhibit feasible physical properties in electrode candidate materials.

Therefore, we investigate the hydrogen evolution reaction (HER) catalytic performance of monolayer Pt_4Te_7. For HER catalytic performance, ΔG_H is known to scale with activation energies and has been successfully used as a descriptor for correlating theoretical predications with experimental measurements of catalytic activity for various systems.[26] For the pristine monolayer 1T-$PtTe_2$, ΔG_H is about 1 eV (Fig. 3(b)), indicating that the monolayer 1T-$PtTe_2$ is inert for HER. When periodic Te atom vacancies are introduced (i.e., the structured monolayer Pt_4Te_7), the ΔG_H decreases to 0.06 eV. We attribute this significant improvement to the small bandgap of Pt_4Te_7. As already demonstrated in other TMD materials,[34] such as MoS_2, the improvement of HER catalytic performance can be achieved by the semiconducting-to-metallic transition. Compared to the pristine $PtTe_2$ which has a bandgap of 0.5 eV, the band gap of Pt_4Te_7 monolayer is only 28 meV, which is very closely metallic.

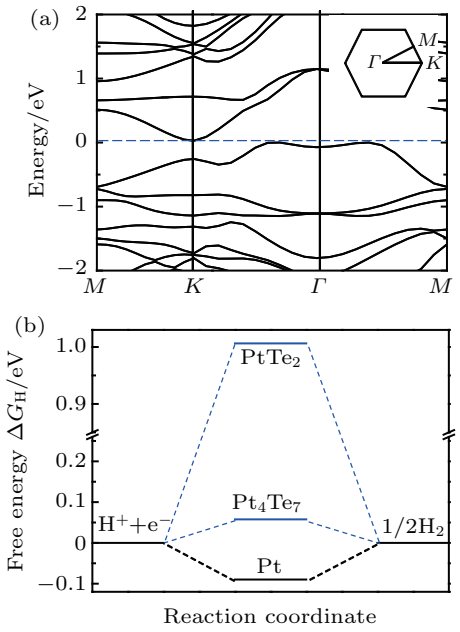


Fig. 3. Energy band structures and HER catalytic performance of Pt_4Te_7. (a) The energy band structure of monolayer Pt_4Te_7, which show a band gap of 28 meV at HSE06 level. The inset shows the Brillouin zone with high-symmetry points. (b) The Gibbs free-energy profile of HER for monolayer Pt_4Te_7.

4. Conclusions

In summary, we have modified the 1T phase monolayer $PtTe_2$ at the atomic level and found a structured void-containing monolayer, Pt_4Te_7, based on comprehensive DFT calculations. According to our results, Pt_4Te_7 is a stable 2D monolayer material which is verified by the calculation of formation energy, phonon dispersion and *ab initio* molecular dynamics simulations. This void-containing Pt_4Te_7 is predicted to have excellent HER catalytic performance due to the exposure of Pt atoms in the sandwiched structure. These findings open new perspectives for the functionalization of 2D TMD materials at the atomic level.

Acknowledgements

A portion of the research was performed in CAS Key Laboratory of Vacuum Physics. Computational resources were provided by the National Supercomputing Center in Tianjin.

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