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Short Communication

High-throughput screening of MXenes for hydrogen storage via graph neural network

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Keywords: Hydrogen storage MXene Machine learning Multi-scale simulations	To better understand the recent experiment on hydrogen storage in MXene multilayers [Nature Nanotechnol. 2021, 16, 331], we propose a multiscale workflow to computationally screen 23,857 compounds of MXene for hydrogen storage in near ambient condition. By using density functional theory simulation to produce the dataset, we trained physics-informed atomistic line graph neural networks to predict hydrogen's adsorption performance on MXenes, which is further validated through grand canonical Monte Carlo simulation. As a result, ScYC is identified to exhibit a hydrogen storage capacity of 5.7 wt% at 230 K and 100 bar, showing the promise for hydrogen storage.		

1. Introduction

The increasing concentration of carbon dioxide in the atmosphere has resulted in global warming, climate change, and a host of other environmental issues. One of the most promising solutions to achieving carbon neutrality is to use hydrogen energy, which has high gravimetric energy density, renewability and zero CO₂ emission, showing the potential to replace fossil fuels in the future's sustainable energy system [1–4]. However, one main obstacle that hinders the vast commercial application of hydrogen energy is lack of hydrogen storage materials with both high gravimetric and volumetric density under near ambient conditions [4,5]. The search target set by US Department of Energy for 2025 requires 5.5 wt% and 40 g/L hydrogen with an operating temperature range of -40 °C to 60 °C [6]. To balance the energetics of storage and kinetics of release, the desirable adsorption energy window is 20 ~ 80 kJ/mol for fast reversible hydrogen storage under near ambient temperature and moderate pressure (less than 100 bar).

In a recent experimental study, S. Liu et al. [7] applied incompletely etching strategy to prepare multilayer Ti_2CT_x (T: functional group) that has an unprecedented 8.8 wt% hydrogen uptake at room temperature and 60 bar pressure. The storage mechanism was attributed to a nano-pump-effect-assisted weak chemisorption due to the existence of fluorine functional group and narrow interlayer distance (~7 Å). From the computational aspect, several studies [8–12] discussed the adsorption

mechanism and hydrogen storage performance of specific compounds of MXene. Nevertheless, the current studies have only covered a very small part of the MXene compounds as compared with the more than 23,000 MXenes as reported in MXenes database (aNANt) [13].

To explore the hydrogen storage materials more effectively and efficiently, it is necessary to apply high-throughput computational screening together with machine learning methods [14-18]. For physisorption type hydrogen storage materials, Ahmed and Siegel [18] selected 8,282 candidates for hydrogen storage by screening 918,734 metal organic frameworks through extremely randomized trees algorithm and GCMC simulation. For chemisorption type hydrogen storage materials, Rahnama et al. [15,16] predicted the hydrogen weight percentage and optimal material composition of metal hydrides with several supervised machine learning models based on Hydrogen Storage Materials Database. For quasi-molecular adsorption governed by Kubas interaction, however, no studies are reported to utilize high-throughput computational screening with machine learning. The main underlying reason lies in fact that the interactions with hydrogen are more complicated due to electron donation and back-donation between transition metal's unfilled d orbitals and hydrogen's σ orbital [19], so it is expensive and time-consuming to precisely calculate the adsorption energy of hydrogen on adsorbent, and high level computational methods are required [20,21] which is different from physisorption [22] where the weak Van de Waals interaction can be reliably described by non-

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bonding parameters of conventional force field.

Based on the physics insight of Kubas effect, the electrons in hydrogen's σ orbital transfer to the empty d orbital of transition metal and the electron in transition metal's d orbital undergoes a back-donation process to the hydrogen's σ^* orbital, resulting in elongated H-H bond length in a quasi-molecular form. According to this picture, we can distinguish whether the hydrogen is in quasi-molecular state by checking H-H bond length and the distance between hydrogen and transition metal, instead of calculating the precise hydrogen adsorption energy. On the basis of these factors, we design a new workflow to screen MXene space for hydrogen storage, as shown in Fig. 1.

2. Results and discussions

2.1. MXene's hydrogen adsorption geometry database

The MXene's hydrogen adsorption geometry database is constructed in our previous work [23] as stated below. First, the hydrogen adsorption geometries of selected MXenes (about 10 percent of the aNANt database with no fifth period transition metal involved) were calculated through DFT calculation. Note that this step only involved geometry optimization with DFT, thus saving one to two orders of magnitude of time compared with binding energy calculation, which makes highthroughput simulation possible in our study. Then, using results from the last step as dataset, two successive ALIGNNs were trained. The first one is for H2 quasi-molecule classifier, judging whether the H-H bond length stretches too much (>0.9 Å in this study) that is out of the scheme of Kubas interaction. The second ALIGNN is H₂ adsorption geometry predictor, using multi-regression form to predict the H-H bond length and the distance between transition metal and the geometry center of two hydrogen atoms (denoted as H_{com}). By adding a bond-order term to the loss in the second model, we introduce the physics of bond order to the graph neural network, transforming this model to a physicsinformed version with higher accuracy. Next, aforementioned ALIGNN models are used to predict the remaining dataset, giving four hydrogen adsorption geometry labels, i.e. H₂ bond length (d_{H1}, d_{H2}) and adsorption distance (d_{MH1}, d_{MH2}) (see Fig. 1), to 9,883 MXene compounds with two quasi-molecule H₂ labels.

2.2. ScYC for hydrogen storage

Among the whole predicted database, 46 MXenes with both hydrogen bond lengths greater than 0.755 Å are selected to be the candidates of KHSMs (see the supplemental material for the whole list). Among them, ScYCH₂ is the lightest one with the promise for hydrogen storage as further verified with GCMC simulation based on ab-initio force field.

The dynamical stability of ScYCH2 is verified through the harmonic phonon dispersion in Fig. S1(c), and the thermal stability is also examined by machine learning force field accelerated ab-initio molecule dynamics (AIMD) as implemented in VASP. Fig. S1(d) shows the change of free energy during a 10-ps AIMD simulation with a timestep of 1 fs. At 500 K, the free energy only fluctuates around a corresponding constant value during the whole simulation, and the final structure remains stable without bond breakings, suggesting the stability of ScYCH2 at 500 K.

To validate ScYCH₂'s performance on hydrogen storage, we carried out an ab-initio force field GCMC simulation. The potential energy surface of hydrogen on ScYCH₂ is scanned under the scheme of electrostatic embedding approach [24]. Three regions, including a quantum cluster region, a charged effective core potential region and a point charge region, are divided to model the solid material. H₂'s adsorption energies and configurations are illustrated in Figure S2. More details of computational implementation can be found in Methods section. We use the following Morse potential to describe the interaction of H₂ with atoms in ScYCH₂,

$$U_{ij} = \varepsilon \left[\left(1 - e^{-k^* \left(r_{ij} - \sigma \right)} \right)^2 - 1 \right]$$
(1)

where ε stands for the depth of the potential well, k measures the width of the potential well, σ is a distance at which the potential equals zero and r_{ij} is the distance between particle i and j. The fitted parameters are listed in Table 1. As is shown in Fig. 2, the fitted force field parameters can reproduce the potential energy curves from ab-initio calculations perfectly, with R² of 0.99995 and 0.99998 for H₂ on the up and bottom side of ScYCH₂ respectively. When the distance D is larger than 3 Å, the interaction energy between H₂ and sorbent decays nearly linearly rather than exponentially as in other KHSMs [25]. Here we attribute such kind of near linear decay as the long-range interaction effect between hydrogen and MXenes. Therefore, under near ambient conditions, each TM site is expected to adsorb more than one H₂ molecule for better performance on hydrogen storage. Using the *ab-initio* fitted force field, this assumption is further confirmed by GCMC simulations, which

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Fitted parameters of Morse potential for interaction between ScYCH2 and H2.

Term (H _{com} -)	ε (kcal/mol)	K (Å-1)	(Å)
Sc	1.94602	1.87417	2.49443
Y	2.55953	1.65069	2.71605
С	1.99966	1.28576	3.58235
Н	0.31721	0.94347	3.69991



Fig. 1. Workflow for the high-throughput screening of MXene for hydrogen storage via graph neural network and multiscale simulation.



Fig. 2. Potential energy curves of H_2 on (a) up side and (b) bottom side of ScYCH₂ substrates derived from *ab-initio* calculations with cluster method. Inserts are the side views of quantum cluster region in our calculations.

introduces temperature and pressure for a better description of real hydrogen storage conditions. More details on force fitting methods and GCMC simulation implementation are given in the Methods section.

As is shown by the GCMC calculated isotherms in Fig. 3(a), the highest H_2 excess uptakes are around 100 bar. A maximum gravimetric storage capacity of 4.3 wt% for ScYCH₂ is found at 230 K, 100 bar and remains 3.3 wt% at 330 K. The intriguing part is that more than 80 per cent of capacity can be reached near 25 bar owning to the relatively strong Kubas interaction. Such result is in consistent with the experiment findings in Ti₂CT_x [7].

The process of hydrogen storage on ScYCH₂ is further revealed in Fig. 3(b-c) for H₂'s density profiles at 298 K, 100 bar. The side view (see Fig. 3(b)) implies a two-layer hydrogen storage mechanism, including a layer of H₂ adsorption through Kubas effect (yellow bubbles) and another layer with H₂ adsorption through charge polarization (blue stripe). The previously mentioned long-range interaction effect (see Fig. 2(a-b)) gives rise to this unique phenomenon and ensures a good hydrogen storage ability under near ambient conditions. Fig. 3(c) gives the pattern of H₂'s density of the Sc side from the top view. On each Sc site (purple atom), there are two potential adsorption sites (yellow bubbles). This pattern is also valid for the Y side. Besides, H₂ density at the yttrium side is more condense than that at the scandium side, so it is safe to conclude that the introduction of Y elevates the volumetric storage capacity but might jeopardizes the gravimetric capacity owing to its heavy elemental mass. To further explore the impact of Y, we built up a similar structure Sc1.75Y0.25CH2 with reduced yttrium abundance, as is shown in Fig. 4(a-b). In consequence, the potential energy surfaces

of Sc_{1.75}Y_{0.25}CH₂ (see Fig. 4(d-e)) have shallower potential wells (about -2 and -4 kcal/mol) compared to ScYCH₂ (about -8 and -8 kcal/mol) owing to the weakening of charge polarization effect. The results of Bader charge analysis [47] (Table S2-3) also suggests that Y can increase the charge polarization in our system. Therefore, the hydrogen storage capacity of Sc_{1.75}Y_{0.25}CH₂ is not as good as ScYCH₂ even though it is 22% lighter than the latter compound. This result suggests that the fifth period elements can play a vital role in KHSMs despite its heavy weight.

Besides the quasi-molecular adsorption, the chemically adsorbed hydrogen atoms in ScYCH₂ will also contribute to the overall hydrogen storage capacity, as is verified by previous experimental work on a similar MXene material, Ti₂CT_x [7]. The adsorption energy for H atoms at Sc side and Y side is -3.339 eV and -3.487 eV (see Fig. S1(a-b) for their configurations), which contributes up to 1.4 wt% to the overall hydrogen storage capacity.

3. Conclusions

In summary, motivated by the recent experiment on hydrogen storage in MXene multilayers and the reported MXenes database (aNANt), for the first time we screened 23,857 compounds of MXene by using the high-throughput simulation, physics-informed graph neural network and multi-scale modeling methods. ScYC is identified from 46 candidates with high hydrogen storage performance. The intrinsic gravimetric storage capacity of ScYC reaches 5.7 wt% at 230 K and 100 bar, synergistically operated by the Kubas interaction with transition metal sites and the polarization with the functional groups. Our work deepens



Fig. 3. (a) Predicted H₂ excess adsorption isotherms for ScYCH₂ at 230 K, 298 K and 330 K; (b) side view of a snapshot of the calculated H₂'s density at 298 K,100 bar and (c) is the top view.



Fig. 4. Hydrogen storage ability of $Sc_{1.75}Y_{0.25}CH_2$ (or $Sc_7YC_4H_8$). (a) side view of optimized unit cell of $Sc_{1.75}Y_{0.25}CH_2$ and (b) is the top view; (c) predicted H_2 excess adsorption isotherms for $ScYCH_2$ at 230 K, 298 K and 330 K; (d) potential energy curves of H_2 on upper side of $Sc_{1.75}Y_{0.25}CH_2$ substrates derived from *ab-initio* calculations with cluster method and (e) is potential energy curves of H_2 on the lower side. Inserts are the side views of quantum cluster region in our calculations.

the understanding of existing experiments, and provides the new candidate for hydrogen storage. Furthermore, the strategy of using the activated H-H bond length and the distance from the substrates as the descriptors in machine learning assisted screening can be readily generalized to other fields like CO_2 capture and N_2 fixation.

4. Methods for computation and simulation

4.1. Periodic crystal's simulation

DFT calculations for optimizing the hydrogen adsorption geometry are carried out with the Vienna ab initio simulation package (VASP) [26]. Generalized gradient approximation [27], projector-augmented wave method [28] and Per w-Burke-Ernzerhof (PBE) functional [29] with Grimme's semi-empirical DFT-D3 scheme [30] including Becke-Jonson damping [31] for the correction of dispersion interaction are employed. In energy calculations, the convergence criteria of all calculations are set as 1.0×10^{-5} eV for total energy and 0.01 eV/Å for Hellmann-Feynman force. K-points in Monkhorst-Pack scheme with a reciprocal space resolution of $2\pi \times 0.02$ Å⁻¹ are used. The phonon spectrum is calculated through the finite displacement approach as implemented in the phonopy code [32].

4.2. Hydrogen-MXene potential energy surface

All potential energy curve calculations are carried out with ORCA 5.0.3 package [33–35]. We constructed the cluster models through an electrostatic embedding approach [24]. First, a cluster containing 62 atoms centered with the adsorption site is carved out from a $21 \times 21 \times 1$ MXene supercell. The remaining atoms around the cluster are reduced to point charges, which are based on density derived electrostatic and

chemical (DDEC) charges via Chargemol package [36]. To keep up ligand field around surface ions and avoid electron spill-out effect, a boundary region is introduced where the charged effective core potentials [37–39] replace point charges (except hydrogen atoms that have no effective core potential available). The bond length of the hydrogen molecule at each given distance from the cluster is fully optimized while atoms of MXene cluster are kept constrained. According to benchmark studies [20,21], we optimize the adsorption geometry through hybrid functional PBE0-D3BJ [30,31,40] with basis set of def2-SV(P) [41] for sorbent atoms and def2-TZVP(-f) for hydrogen molecule, and calculate the accurate adsorption potential energy surface using the functional of ω B97M-V [42] and the def2-TZVPD basis set. The auxiliary basis def2/J [43] is used to speed up calculations under the scheme of identity approximation for the Coulomb integrals while the exchange terms are calculated with the "chain-of-spheres" method [44].

4.3. GCMC simulations

All GCMC simulations are carried out within the framework of RASPA2.0 code [45]. After convergence test as shown in Fig. S3, each GCMC simulation contains 5,000 cycles for equilibration and 5,000 cycles for production. Each cycle includes N Monte Carlo moves (insertion, deletion, translation, rotation and re-insertion), where N is the larger number of 20 and the number of hydrogen molecules. All MXene adsorbent geometrical configurations from DFT optimization are used as rigid frameworks in GCMC simulations. The non-bonded interactions between hydrogen and adsorbent are described by the abinitio fitted Morse potential. The Darkrim-Levesque parameter [46] is used to describe the interaction between hydrogen molecules. A cutoff of 12.8 Å is adopted for all the non-bonded potentials, Eward summation rule is used for Coulomb potentials. The excess adsorbed hydrogen is

given by,

$$m_{\rm ex} = m_{\rm abs} - \rho(\mathbf{T}, \mathbf{P}) \bullet \mathbf{V}_{\rm free} \tag{2}$$

where $m_{\rm ex}$ and $m_{\rm tot}$ are the masses of excess and absolute adsorbed H₂ molecule respectively, $\rho(T, P)$ is the density of H₂ at temperature T and pressure P, V_{free} is the void volume of the given structure. The weight capacity of hydrogen storage reads,

weight capacity =
$$\frac{m_{\rm ex}}{m_{\rm framework} + m_{\rm ex}} \times 100\%$$
 (3)

where $m_{\text{framework}}$ is the mass of the framework.

CRediT authorship contribution statement

Jiewei Cheng: Data curation, Investigation, Software, Visualization, Validation, Writing – original draft, Writing – review & editing. Tingwei Li: Software, Visualization, Writing – original draft. Yongyi Wang: Software, Visualization, Writing – original draft. Ahmed H. Ati: Software. Qiang Sun: Investigation, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Qiang Sun reports financial support was provided by China Scholarship Council.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

The following files are available free of charge Supporting Information including stability information, bader charge and adsorbed H₂'s configurations (PDF)Possible KHSMs candidates (PDF). Supplementary data to this article can be found online at https://doi.org/10.1016/j.aps usc.2023.158560.

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