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Hydrogen adsorption, dissociation and diffusion on two-dimensional Ti_2C monolayer

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ABSTRACT

The adsorption, dissociation and diffusion of hydrogen on two-dimensional (2D) Ti_2C monolayer with and without carbon vacancies have been investigated by first-principles calculations based on density functional theory. Weak molecular physisorption was observed for the adsorption of H_2 on 2D Ti_2C monolayer with end-on configuration. However, for the side-on configuration, the H_2 molecule decomposes spontaneously and then the two H atoms prefer to bond to the surface Ti atoms at the monolayer. Based on the chemical bonding analysis, the mechanism of the dissociation of H_2 has been elucidated. Moreover, the hydrogen diffusion on the Ti_2C surface with and without carbon vacancies was investigated. A better hydrogen diffusion property was found for the Ti_2C monolayer with carbon vacancies. The energetics for H penetration from surface to the solute site in the bulk was also studied.

Introduction

Hydrogen is considered one of the most promising green energy carriers because of several inherent advantages including abundance, high energy density, and non-polluting nature [1–3]. For the last decades, many efforts have been made to find out the potential hydrogen storage mediums with high storage capacity and excellent hydrogen adsorption/desorption behavior. Among the most widely studied materials, carbon nanostructures, such as carbon nanotubes and graphene, have drawn lots of attention due to the light weight, large surface area, and structural diversity [4–7]. However, the interaction between H_2 molecules and carbon-based materials is mainly limited to van der Waals forces. The relative weak interaction leads to H_2 molecular physisorption at the surface of carbon nanostructures which can be used for hydrogen storage only at very low temperatures around that of liquid nitrogen [8]. In order to increase the strength of hydrogen binding in carbon nanostructures, a number of methodologies have been performed. It was found that the binding energies can be strengthened by doping and decorating with transition metals (TM) atoms [9–13]. Unfortunately, however, in most cases TM atoms tend to aggregate on the surface of carbon nanostructures, which decreases the strengthening effects.

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Previous works have found that the hydrogen adsorption in non-stoichiometric titanium carbide, TiC_x, is energetically favorable and a capacity of 2.9 wt% is easily reached [14,15]. It seems that titanium carbide may be a potential hydrogen storage material. Very recently, a new family of two-dimensional (2D) transition metal carbides called "MXene", including Ti_2C, V_2C, Nb_2C, Ti_3C_2, Ta_4C_3, TiNbC, $(V_{0.5}, Cr_{0.5})_3C_2$, and Ti_3CN_x, was successfully synthesized by selective extraction of "A" layers from MAX phases [16–20]. MXene has a crystal structure with alternately arranged TM and C atomic layers along *c* axis, where TM atomic layers are exposed on the surface (Fig. 1). The monolayers of MXenes have attracted great interest because of its potential applications in energy storage system [21–23], separation membranes for ion separation [24], wastewater treatment as oxidants [25], and mediator-free biosensor as immobilization matrix [26,27]. Recently, based on first-principles calculations, Hu and co-workers revealed the reversible hydrogen storage capacity of 3.4 wt% for 2D Ti_2C [28] and 3.6 wt% for 2D Sc_2C [29]. Because of their unique structural characteristics, MXene monolayers are expected to be promising candidates for hydrogen storage. Therefore, it is very crucial to reveal the hydrogen storage properties of MXene monolayers. In the present work, we studied the hydrogen adsorption, diffusion, and molecular dissociation on the 2D Ti_2C monolayer by first-principles calculations. The energetics for the hydrogen diffusion in the vicinity of Ti_2C surface and in the lattice interior was investigated. Moreover, the Ti_2C monolayer is usually not defect-free experimentally due to the limitations of the selective extraction method and more carbon vacancy (CV) can be induced with the increase of heating temperature [30]. Thus, the effect of carbon vacancy on the adsorption and diffusion of hydrogen in 2D Ti_2C was also investigated.

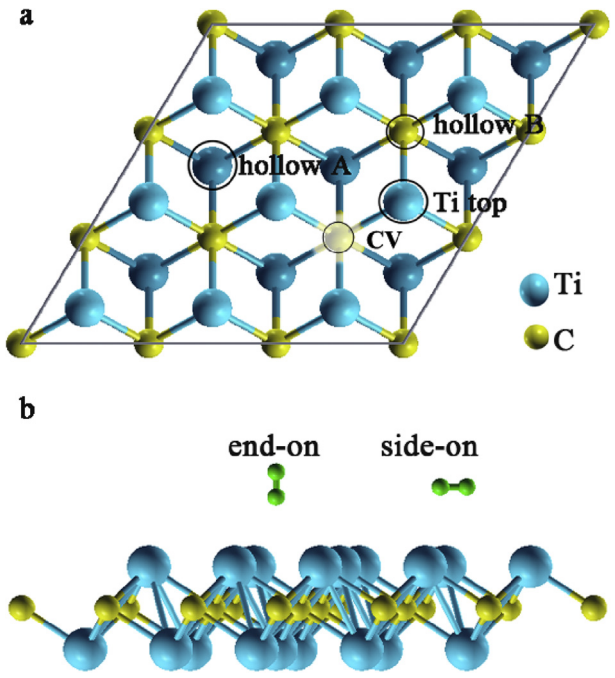

Fig. 1 – (a) Top view of a Ti_2C monolayer showing the Ti top, carbon vacancy (CV), hollow A and B sites for hydrogen adsorption. (b) Side view of the H_2 adsorption on Ti_2C: the side-on and end-on modes.

Computational methods

All density functional theory (DFT) calculations were performed within the DFT framework as implemented in Vienna Ab initio Simulation Package [31,32]. The effects of the approximation to the exchange-correlation energy were treated by the generalized gradient approximation. The plane-wave cutoff energy was set to 400 eV in all calculations. $3 \times 3 \times 1$ supercell was used together with $3 \times 3 \times 1$ *k*-point meshes. The self-consistent cycle was iterated for each calculation until the total energy was converged to within 10^{-4} eV. The model of Ti_2C structure was constructed appropriately by removal the Al atoms from its parent Ti_2AlC phase. A vacuum space of 20 Å was introduced to eliminate the interaction between adjacent Ti_2C layers. Ti_2C monolayer consists of a monatomic hexagonal C plane between two monatomic hexagonal Ti planes and forms a Ti–C–Ti sandwich structure (Fig. 1). The calculated lattice constant is $a = 3.037$ Å, which is in good agreement with previous calculation [33]. $3 \times 3 \times 1$ units in a supercell were used to study the adsorption of hydrogen on the monolayer. The mode of $3 \times 3 \times 1$ Ti_2C supercell with one carbon vacancy (CV) is designed to investigate the effect of CV on the adsorption and diffusion of hydrogen.

Results and discussion

Molecular hydrogen adsorption on 2D Ti_2C monolayer

Firstly, the adsorption of a single H_2 molecule on the Ti_2C $3 \times 3 \times 1$ supercell with or without carbon vacancy was investigated. As depicted in Fig. 1, there are eight typical adsorption configurations for the adsorption of a hydrogen molecule, i.e., the end-on (with the H–H bond is normal to the Ti_2C surface) and side-on (with the H–H bond is parallel to the Ti_2C surface) coordinations of the H_2 molecule to three different adsorption sites (Ti top, hollow site A, hollow site B, and CV) on the Ti_2C surface. In this work, the adsorption energy E_{ads} of H_2 is calculated according to the following equation:

$$E_{ads} = E(Ti_2C + H_2) - E(Ti_2C) - E(H_2) \quad (1)$$

where $E(Ti_2C + H_2)$, $E(Ti_2C)$, and $E(H_2)$ are the calculated total energy of Ti_2C supercell with adsorbed H_2, Ti_2C supercell with or without carbon vacancy, and a gas phase H_2 molecule, respectively.

For the end-on configuration, the adsorption energies, bond lengths, and Bader charges of H_2 adsorbed on the three different adsorption sites are summarized in Table 1. Compared with free H_2 molecule, the calculated H–H bond lengths are nearly unchanged, which means that the adsorbed H_2 still keep molecular configuration. The binding energy for H_2 adsorbed on Ti top, hollow A, hollow B and CV site is calculated to be −0.072, −0.075, −0.070, and −0.075 eV respectively. Bader charge analysis shows that nearly no