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Electronic and transport properties for $Ti_3C_2O_2$ under the influence of a vertical electric field and stacking number

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ABSTRACT

The effect of a vertical electric field on the structural, electronic, and transport properties of $Ti_3C_2O_2$ with varying numbers of layers was systematically investigated by means of the first-principles method. This result demonstrated that the related properties of $Ti_3C_2O_2$ could be effectively tuned by the stacking number and the vertical electric field. When the vertical electric field increased to 2 V/Å, the energy bands of the monolayer and multilayers of the $Ti_3C_2O_2$ were separated obviously. However, the external vertical field could not open a band gap in the two dimensional $Ti_3C_2O_2$. Its transmission coefficients and thermoelectric power factors increased linearly with the increase of the stacking number. It revealed that the trilayer Ti_3C_2 had the potential of being a thermoelectric material. The transport properties for a dual-gated $Ti_3C_2O_2$ model were examined using non-equilibrium Green's functions. The results clearly confirmed that the vertical electric field could manipulate the transport properties of $Ti_3C_2O_2$, and the corresponding mechanisms are also discussed in detail.

1. Introduction

The unique physical and chemical properties of two-dimensional (2D) materials provide exciting opportunities for discovering unexpected phenomena, and expanding their numerous applications. The rapid development of graphene can be attributed to its successful research and application in recent decades [1–3]. Currently, more new 2D materials, beyond graphene, have been discovered, such as: hexagonal boron nitride (h-BN), transition-metal dichalcogenides (MoS_2, WS_2) and oxides and hydroxides [4]. Even though these 2D materials possess extraordinary structural, electronic, and mechanical properties, researchers are still trying to discover more new 2D materials.

Recently, a new family of 2D early transition-metal carbides and carbonitrides called MXenes has been discovered [5,6]. The new 2D materials possess extraordinary electrical, mechanical, and chemical properties, while their structures are very similar to graphene [7]. In 2011, Naguib et al. [8] first synthesized the new 2D transition-metal carbides and carbonitrides by removing the A layer from the MAX phase with hydrofluoric acid, where MAX is a family of ternary early transition-metal carbides, carbonitrides, and nitrides. M is an early transition metal, A is an A-group element in groups 13 and 14, and X is carbon or nitrogen. Moreover, they found that the sheet resistances of MXenes was comparable to that of multilayer graphene [9]. Consequently, many theoretical and experimental investigations have been carried out to explore their basic properties and potential applications [10–20].

For example, Naguib et al. [10] calculated the elastic and electronic properties of the 2D transition-metal carbides Ti_2C, Ti_3C_2, Ti_4C_3, V_2C, Cr_2C, Zr_2C, Hf_2C, Ta_2C, Ta_3C_2 and Ta_4C_3, and found that these materials possess high elastic moduli when stretched along the basal planes. Moreover, these new 2D materials have been found to be promising electrode materials for Li-ion and non-Li-ion batteries [11–13]. Hu et al. [14] investigated the hydrogen storage properties of Ti_2C, Sc_2C, and V_2C, and the results showed that they were good candidates for reversible hydrogen storage materials under ambient conditions. Furthermore, $Ti_3C_2(OH)$ has the unique behavior of lead adsorption [15]. Xie et al. [16–18] studied the structural, electronic, optical, and elastic properties of the $Ti_{n+1}X_n$ (X = C, N, n = 1–3) monolayers. The thermoelectric properties of the monolayer and multilayer of M_2C and M_2N were also investigated, and showed that Mo_2C was potentially a thermoelectric material [19]. Yu et al. [20] studied the adsorption of NH_3, H_2, CH_4, CO, CO_2, N_2, NO_2, and O_2 on the monolayer of Ti_2CO_2 by using the first-principles method. This work demonstrated that Ti_2CO_2

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was a potential gas sensor or capturer of NH_3 with high sensitivity and selectivity.

These previous studies demonstrated the potential applications of MXenes in many areas, such as energy storage [11–13], gas sensors [20], photocatalytic materials [21], biosensors [22], and transparent and conductive electrodes [23]. However, investigations on the potential applications of MXenes in nanoelectronic devices are still in preliminary stages. Berdiyorov [24,25] first investigated the effect of lithium and sodium ion adsorption on the electronic transport properties of Ti_3C_2, and the transport properties of Ti_3C_2 with surface functionalization also was discussed. The electronic transport properties of 2D $Ti_3C_2T_x$/graphene nanocomposite films were examined, and it was found that it possessed a high (metallic) electrical conduction [26]. Furthermore, the electronic and transport properties of Ti_2CO_2 nanoribbons were also studied [27]. The results showed that MXenes could be a promising candidate material in nanoelectronic devices.

The electronic and transport properties of 2D materials are very sensitive to the stacking number and external electric field. For example, studies have found that the band gap of bilayer and multilayer graphene could be opened under an external vertical electric field, while monolayer graphene remained zero-gap semimetallic [28,29]. Moreover, the band gap of the 2D silicene, germanene, multilayer phosphorene, and MoS_2 could also be effectively tuned by an external electric field, and its size and effective carrier mass increased linearly with the electric field strength [30–33]. However, there are few studies about the effects of the stacking number and vertical electric field on the electronic and transport properties of MXenes. Two-dimensional Ti_3C_2, as a typical representative of MXene family, is the most studied. Ti_3C_2 has been proved to be very promising applications as anode materials for lithium or non-lithium ion batteries [11,34], and exhibits peculiar optical properties [35,36]. But the effects of the stacking number and vertical electric field on the related properties of Ti_3C_2 are not explored yet. Moreover, experimentally observed MXenes are always functionalized.

In this work, the structural, electronic, and transport properties of monolayer and multilayer Ti_3C_2 with functional groups O under a vertical electric field was systematically studied by using the Atomistix Toolkit (ATK) code, which combines the non-equilibrium Green's function (NEGF) techniques with density functional theory (DFT) method [37–39]. The exchange–correlation potential was described by the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) method [40]. This choice is justified by the fact that GGA-PBE can provide accurate results for 2D MXenes materials [16,27,41]. It found that the related properties of $Ti_3C_2O_2$ could be effectively tuned by the stacking number and the vertical electric field. These studies might stimulate potential applications of 2D MXenes materials in the nanoelectronic device field.

2. Computational methods

In 2014, $Ti_3C_2T_x$ (T = O or F) was synthesized by etching Al from Ti_3AlC_2, and it had a hexagonal structure, space group $P6_3/mmc$, with $a = b = 3.0505$ Å and $c = 19.86$ Å [42]. The structure of the monolayer $Ti_3C_2O_2$ was built with a vacuum space of 15 Å along the z direction. Its structure can be described as six C atoms near each Ti atom, which formed an edge-shared TiC_6 octahedral structure [12]. The optimized lattice constants, $a = 3.09$ Å, were in good agreement with other reported theoretical results [10]. Each Ti—C—Ti—C—Ti forms a slab with five atomic layers, which is called as a quintuple layer (QL). The multilayer structure was constructed by arranging the quintuple layers over each other to form an AB stacked structure, as shown in Fig. 1. The surfaces of monolayer and multilayer Ti_3C_2 are functionalized with O group. In order to demonstrate the effects of interlayer interaction on the electronic and thermoelectric properties, the interlayer functional groups are not considered. The vertical electric field was applied along the z direction by inserting metallic gate electrodes. Moreover, no constraints were imposed while applying the vertical electric field, and the interlayer distance was also optimized under the vertical electric field.

Intralayer possesses strong covalent bonding, and while interlayer is weak van der Waals (vdW). The Troullier-Martins pseudopotential and double-zeta polarized (DZP) basis set were used to describe atomic inner and outer electronic state [43]. The vdW correction based on Grimme's scheme (PBE-D2) is adopted to consider the weak interlayer vdW forces [44]. This approach is successful in describing similar structure with graphene [45,46]. The geometry optimization was performed by Broyden-Fletcher-Goldfarb-Shanno minimization [47]. The convergence criteria of the geometry optimization were set to 0.05 eV/Å for the force and 0.001 eV/Å^3 for the stress. An energy cutoff of 30 Hartree was used for the wave function. According to the Monkhorst-

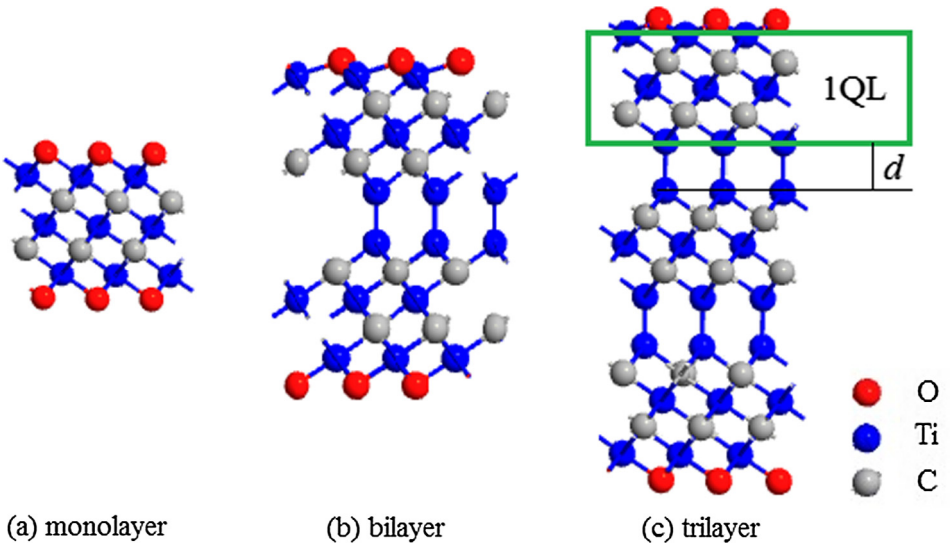

Fig. 1. Layered $Ti_3C_2O_2$ structure.