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Full Length Article

Exploring adsorption behavior and oxidation mechanism of mercury on monolayer Ti_2CO_2 (MXenes) from first principles

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ABSTRACT

Developing low-cost, high adsorption capacity, and recyclable mercury sorbents is an important step for control of mercury in coal-fired flue gas. However, few sorbents meet all the requirements. Herein, we explore the adsorption behavior and oxidation mechanisms of mercury on 2D Ti_2CO_2 (MXenes) monolayer and defective Ti_2CO_2 monolayer with an Ov (Ov-Ti_2CO_2) through first-principles computations based on density functional theory (DFT). Our calculation results show that Hg^0 adsorption on Ti_2CO_2 and Ov-Ti_2CO_2 monolayers are mainly physisorption and chemisorption mechanisms, respectively. Moreover, the presence of a single oxygen vacancy on Ti_2CO_2 monolayer can improve the interaction between the mercury and Ov-Ti_2CO_2 monolayer, thereby enhancing the adsorption energy of mercury by 66 kJ/mol. Hg^0 has a strong interaction with Ti atom on Ov-Ti_2CO_2 monolayer by the atomic orbital hybridization and overlap. The adsorption of HgO molecule on Ti_2CO_2 and Ov-Ti_2CO_2 monolayers are chemisorption processes. Furthermore, electron density difference analysis indicates that the remarkable charge accumulation across the interface is closely related to the strong interaction between HgO molecule and Ti_2CO_2 or Ov-Ti_2CO_2 monolayers. The three-step reaction processes ($Hg^0 \rightarrow$ Hg(ads) → HgO(ads) → HgO) are taken place on Ti_2CO_2 and Ov-Ti_2CO_2 monolayers, resulting in the formation of gaseous HgO molecule. The energy barrier for the Hg^0 oxidation reaction step on Ov-Ti_2CO_2 monolayer (54.85 kJ/mol) is about half of that on Ti_2CO_2 monolayer (104.73 kJ/mol). The desorption steps of the resultant HgO molecule from Ti_2CO_2 and Ov-Ti_2CO_2 monolayers are the rate-determining steps, which need external energies of about 119.3 and 183.2 kJ/mol, respectively.

1. Introduction

Mercury is recognized as one of the most harmful environmental contaminants due to its volatility, persistence, and neurological health impacts, which has caused more and more widespread concerns in recent years [1]. In order to limit the emission of mercury from coal combustion, the United States Environmental Protection Agency (U.S. EPA) promulgated the first national standards – Mercury and Air Toxics Standards (MATS) in December 2011 [2]. After that, the Minamata Convention on Mercury entered into force on August 16, 2017 [3]. Extensive research efforts around the world have been devoted to reduce mercury releases over the last decade [4], because the high vapor pressure and low solubility of elemental mercury (Hg^0) make it difficult to remove from the combustion flue gas [5]. Various promising sorbents or catalysts with good adsorption performance toward Hg^0 removal have been extensively studied, including activated carbon [6], metal oxides [7–11], metal sulfides [12,13], *h*-BN [14], and pure metals [15–18]. Nonetheless, only activated carbon (AC) has been commercialized so far [19]. However, AC-based sorbents show the inability to be regenerated, and thus incurring high operating costs. In addition, AC decorated by the halides may cause secondary pollution. To this end, the ongoing search for new low-cost alternative sorbents/catalysts for Hg^0 removal is of paramount significance.

MXenes are a newly discovered class of two-dimensional (2D) materials comprising carbides and/or nitrides of transition metals with the general formula $M_{n+1}X_nT_x$ (n = 1–3, M = early transition metal, e.g., Ti and/or Mo, X = C and/or N) [20]. Since the first MXene was synthesized in 2011 [21], this new 2D material has attracted great attention [22–24]. Due to the use of aqueous medium during synthesis, MXenes flakes are generally terminated with surface moieties (–OH, –O,

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and –F groups) [25]. Furthermore, theoretical computation illustrated that the MXenes surface modified by the –O group shows more stable than that the –OH and –F groups decorated surface for most MXenes [26]. Significantly, the surface O-terminated Mxenes have shown promise in various applications (e.g., Li-ion batteries [27], fuel cells [28], hydrogen evolution [29–31], CO oxidation [32,33], and gas sensors [34]), because of their tunable surface terminations. Additionally, Zhang et al. [32] investigated the thermal stability of Ti/Ti_2CO_2 and found that the Ti/Ti_2CO_2 is slightly reconstructed until the temperature is up to 800 K. Thus, the Ti_2CO_2 monolayers may be relative stable. Lee et al. [35] reported a new functionalization property and application of $Ti_3C_2T_x$ MXene in wastewater purification and found that the magnetic $Ti_3C_2T_x$ MXene (MGMX) nanocomposite presented excellent Hg(II) removal performance. Interestingly, for the synthesis process of MXenes, the vacancies are usually unavoidable. Sang et al. [36] found that different point defects that are prevalent on the surface of monolayer titanium carbides. Zhang et al. [37] reported a defective Ti_2CO_2 monolayer with oxygen vacancies (Ov) that can promote the reduction of CO_2. Based on the previous reports, the presence of point defects or vacancies on the MXenes has a crucial effect on the function of MXenes. It is therefore expected that the Ov in Ti_2CO_2 monolayer would alter the interaction between the substrate and the Hg adatom. Recalling the fact that the surface of MXenes can be tunable during its synthesis process, it is likely that MXenes can serve as novel sorbents for Hg^0 removal from flue gas, which is never reported yet.

In the present work, we explore the adsorption behavior and oxidation mechanism of mercury on the monolayer Ti_2CO_2 (MXenes) in both its bare and oxygen vacancy forms by first principles calculations. The first step is to investigate the interaction between Hg^0/HgO and substrates and followed by the detailed discussion of the corresponding electronic properties. On the basis of the adsorption energy and electronic properties analysis, we propose the adsorption mechanism of Hg^0 and HgO on the monolayer Ti_2CO_2 and defective Ti_2CO_2 with O atom vacancy. Finally, we analyze the reaction pathway of Hg^0 oxidation for revealing the contribution of each elementary reaction step to heterogeneous mercury transformation over monolayer Ti_2CO_2 (MXenes).

2. Computational methodology

Density functional theory calculations were carried out using the $DMol^3$ code [38]. The electron exchange–functional was calculated using Perdew – Burke–Ernzerhof (PBE) [39] described by generalized gradient approximation (GGA) [40]. To describe the weak interaction, the Tkatchenko – Scheffler [41] correction scheme was adopted. The atomic orbital was treated with the double numerical plus polarization (DNP) basis set and DFT semicore pseudopotentials (DSPPs) were used for the interactions between the ion core and the valence electrons. The convergence criteria in total energy, maximum force, and maximum displacement were set at 10^{-5} Hartree, 0.002 Hartree/Å, and 0.005 Å, respectively. The electronic self-consistent field (SCF) tolerance was set at 10^{-6} Hartree. The *k*-points sampling of the Brillioun zone was done using a 23 × 23 × 1 mesh for the unit cell and a 12 × 12 × 1 mesh for the supercell (3 × 3 unit cell). A 25 × 25 × 1 *k*-point grid was used for calculations of electronic properties. The electron density difference of Hg^0 and HgO adsorption on Ov-Ti_2CO_2 monolayer were calculated by using the CASTEP modules (detailed theoretical methods in the supporting information).

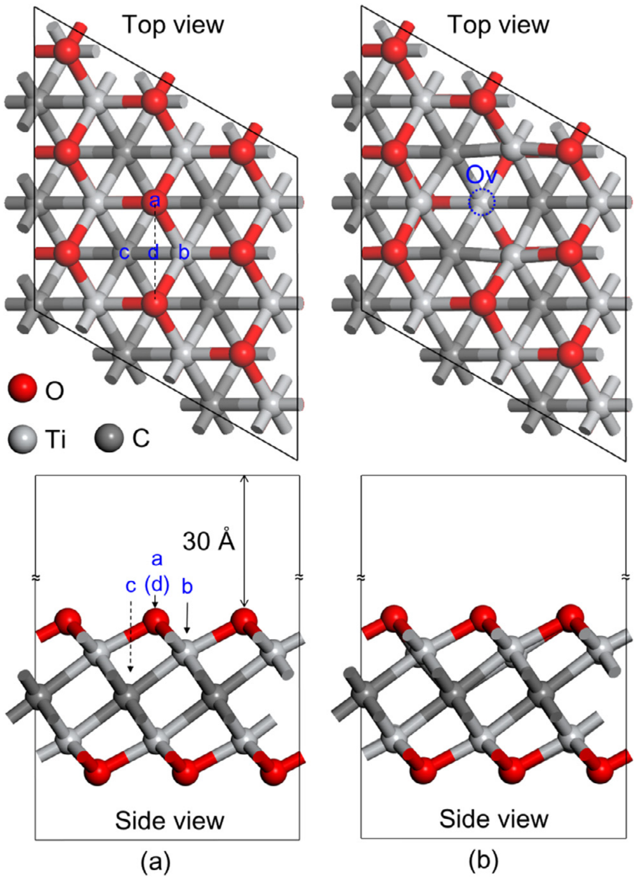

Fig. 1. Top and side views of the optimized (a) Ti_2CO_2 monolayer and (b) defective Ti_2CO_2 monolayer with an oxygen vacancy (dashed circle). a, b, c, and d represent the adsorption sites of O-top, Ti-top, C-top, and O-bri, respectively.

A 2D Ti_2CO_2 monolayer slab with a 3 × 3 surface geometric configuration (Fig. 1a) was chosen as the substrate, which is sandwiched with stacking O—Ti—C—Ti—O in the vertical direction by two O monolayers on the top and bottom, two Ti monolayers as the sublayers and one C monolayer in the center. To minimize the undesirable nonperiodic interactions, we introduced a vacuum layer of 30 Å along the lattice vector (c direction here). The space group of the monolayer Ti_2CO_2 is $P3^-ml$. The optimized lattice parameter is 3.03 Å with a deviation of 0.33%, which is in line with previous reported value [42,43]. The small deviation suggests that the calculations are reliable. The 3 × 3 Ti_2CO_2 supercell used here is consistent with early reports [32,33]. Meanwhile, the calculated adsorption energies of Hg^0 listed in Table S1 suggest that both the 3 × 3 and 4 × 4 supercells give almost the same values. Moreover, the Ti_2CO_2 exhibits a semiconducting nature with an indirect band gap of 0.24 eV in GGA-PBE level of theory (Fig. S1), which is consistent with other theoretical studies [43–45]. To model the defective Ov-Ti_2CO_2 with a single oxygen vacancy (Fig. 1b), one O functional group was removed from the pristine 3 × 3 monolayer Ti_2CO_2 supercell. The formation energy of oxygen vacancy ($E_{form}(Ov)$) is obtained by:

$$E_{form}(Ov) = E_{Ov\text{-}Ti_2CO_2} + 1/2E_{O_2} - E_{Ti_2CO_2} \quad (1)$$

where $E_{Ov\text{-}Ti_2CO_2}$, $1/2E_{O_2}$, and $E_{Ti_2CO_2}$ describe the optimized total energies of the monolayer Ti_2CO_2 with a single oxygen vacancy, half of the O_2 molecules, and pristine Ti_2CO_2 monolayer, respectively. The obtained oxygen vacancy formation energy is 4.34 eV, which is much small comparing with that of sulfur defects in MoS_2 (6.27 eV) [46]. The sulfur defects on MoS_2 was successfully prepared [47]. Therefore, Ov in Ti_2CO_2 monolayer could be obtained easily in a similar way. No obvious reconstruction is observed around the O vacancy, which is similar to that in the pristine Ti_2CO_2. The O—Ti bonds lengths of 1.946 Å around the O vacancy are shorter than that of the primitive O—Ti (1.962 Å). As mentioned above, the Ti_2CO_2 is semiconducting in nature. However, introduction of Ov in the system results in a semiconductor to metal transition (Fig. S1), which may be favor for the adsorption of Hg^0.

The adsorption energies (E_{ads}) of Hg^0 and HgO on Ti_2CO_2 and Ov-Ti_2CO_2 surfaces are calculated as follows:

$$E_{ads} = E_{(adsorbate/substrate)} - E_{adsorbate} - E_{substrate} \quad (2)$$