Theoretical interpretation on lead adsorption behavior of new two-dimensional transition metal carbides and nitrides

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ABSTRACT

The alkalization-intercalated MXene (Alk-MXene: $Ti_3C_2(OH)_2$) has recently confirmed as a new and effective material for removing Pb heavy metal. Herein, taking into account of the complexity and diversity of MXenes, the Pb adsorption behavior of different MXenes with the highest valuable applied structure of M_2X $(OH)_2$ (M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and X = C or N) has been systemically investigated by first principles calculations utilizing the generalized gradient approximation with the density functional theory, which paves a desirable trajectory for the applications of MXenes. Basically, the formation energies of $M_2N(O_2H_{2-2x}Pb_x)$ are lower than those of $M_2C(O_2H_{2-2x}Pb_x)$, suggesting the substitution of N is more effective for the Pb adsorption in contrast to C due to the different valence electron numbers between C and N atoms. In addition, the results show that the $Ti_2C(OH)_2$ is the most favorite one for the lowest mass fraction to lead removal. Notably, both $Sc_2C(OH)_2$ and $Zr_2C(OH)_2$ structures don't have the ability of Pb removal. The kinetics of the lead removal was elucidated on the variation of potential wells by virtue of the density of states and electron localization function.

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1. Introduction

A new family of two-dimensional layered transition metal materials (termed MXenes), recently have attracted numerous researchers due to their outstanding properties in catalysis chemistry and energy storage systems [1–6]. They consist of M (an early transition metal), X (C or N) and OH or F groups [7], which are synthesized by hydrofluoric acid etching MAX phases at room temperature [8]. MXenes possess excellent properties owing to their large surface areas in combination with a large number of surface groups, can be utilized to upload different metal atoms such as Li, K, Na, Mg for battery applications [5]. In addition, hydroxyl groups on the surface of alkalization intercalated MXenes can be potentially used in removing heavy-metal ions for environmental remediation by ion exchange [9], which is one of the most attraction options for industrial viewpoints to selectively trap toxic metals due to its suitable cost-effectiveness and simplicity of operation [10]. More recent results [11] demonstrate that the surface groups significantly affect the metal ion adsorption. For example, the residual of F and other hydrogen sites weakens the adsorption role of alk-MXene $Ti_3C_2(OH)_2$. However, the intercalation of X^+ (X = Li, Na, K) groups on the surface of $Ti_3C_2(OH)_2$ strengthens the adsorption behavior. It demonstrates that the alkalization intercalation treatment plays an important role in accelerating the adsorption of heavy metallic ions, which can be regarded as a simple and direct approach to large-scale applications.

However, the variety of MXene is over 60 dependent on the different element occupations. The properties are different with transition metals M and X due to their various electronic structures [12]. Taking into account the complexity of MXenes and their different inherent characteristics, it is of particular importance to understand their properties on metallic ions adsorption, which plays some implications in optimizing the properties of Pb removing. Meanwhile, it also provides some beneficial suggestions to synthesize the most efficient adsorbent for metal ions removing.

Recently, we firstly found lead uptake of alkalization-intercalated MXene ($Ti_3C_2(OH)_2$) [10]. And then the effect of the
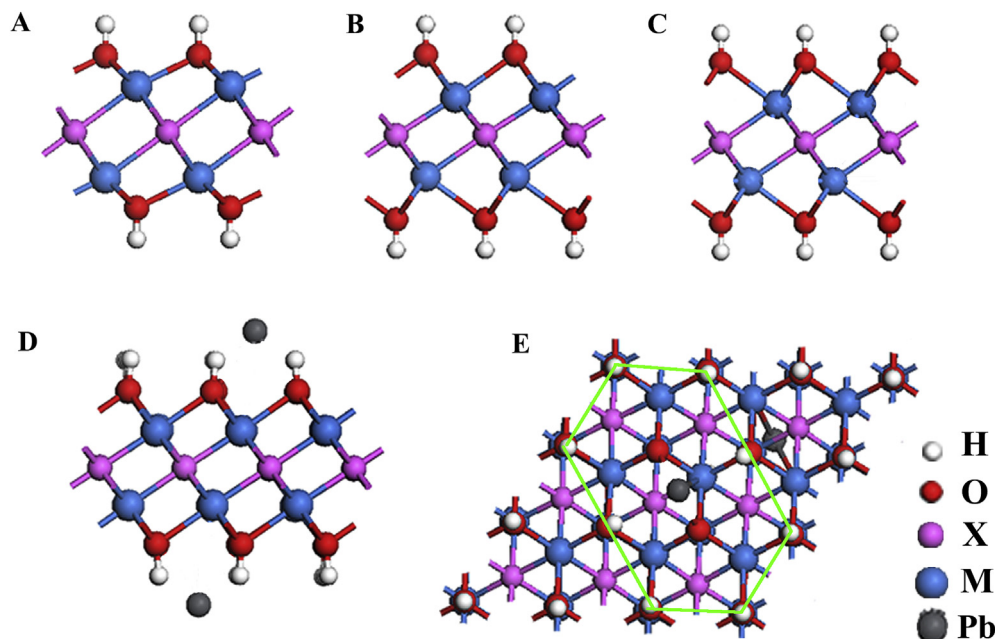
Fig. 1. The sketch maps of three different models of $M_2X\,(OH)_2$ MXene, and Pb adsorption on $M_2X\,(OH)_2$ MXene. (A) A $-M_2X\,(OH)_2$; (B) B $-M_2X\,(OH)_2$; (C) C $-M_2X\,(OH)_2$; (D) the side view of $M_2X\,(O_2H_{2-2x}Pb_x)$; (E) the top view of $M_2X\,(O_2H_{2-2x}Pb_x)$.

Table 1
Total energy of models A, B and C for $M_2X\,(OH)_2$ (M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta; X = C, N). The most stable models are highlighted in bold-typeface.

| M_2C	Model A (eV)	Mode B (eV)	Model C (eV)	M_2N	Model A (eV)	Mode B (eV)	Model C (eV)
Sc_2C	**−50.069**	−49.894	−49.286	Sc_2N	**−51.558**	−51.292	−51.003
Ti_2C	**−52.479**	−52.340	−52.124	Ti_2N	**−53.052**	−52.786	−52.769
V_2C	**−52.377**	−51.990	−52.144	V_2N	**−52.425**	−52.044	−52.242
Cr_2C	**−50.793**	−50.308	−50.403	Cr_2N	**−50.673**	−50.060	−50.023
Mo_2C	**−53.115**	−52.739	−52.956	Mo_2N	**−52.339**	−51.989	−51.758
Nb_2C	**−54.595**	−54.273	−54.594	Nb_2N	−53.964	−54.070	**−54.187**
Zr_2C	−54.167	**−54.173**	−54.036	Zr_2N	**−54.399**	−54.244	−54.361
Hf_2C	−56.853	**−56.863**	−56.719	Hf_2N	**−56.868**	−56.771	−55.801
Ta_2C	−57.892	−57.589	**−58.030**	Ta_2N	−56.845	−57.327	**−57.498**

external-layered sites (solution compositions) on adsorption and the adsorption kinetics of different heavy-metal ions have been interpreted by first principles with density functional theory. Herein, as a continuous work reported previously, some deep and detailed issues relevant to the different internal-layered sites have be clarified for further extending its potential applications based on the first principles calculations: (i) Whether all of M_2X-type MXenes have the lead removal ability; (ii) How does M and X site in MXenes affect the adsorption process; (iii) Which M_2X-type MXenes is the most effective for Pb removing.

2. Computational method

All calculations have been performed with the *Vienna ab initio Simulation Package* (VASP) code [13] based on density functional theory (DFT). We employed the exchange-correlation function based on generalized gradient approximation (GGA) with the Perdue-Burke-Ernzerhof (PBE) [14]. The ion-electron interaction was treated by the projector augmented wave (PAW) method [15]. The energy cutoff was set at 520 eV, and we have used ($4 \times 4 \times 1$), k-point grids for 3×3 supper cells of MXenes. The Methfessel-Paxton smearing scheme [16] with the smearing width of 0.1 eV was applied to the Brillouin-zone integrations and the magnitude of the force acting on each atom became less than 0.005 eV/Å. The

positions of atoms and the cell parameters were fully optimized by using the conjugate gradient method and the total energy of the optimized structures were well-converged, 10^{-6} eV per cell. For all simulations, the van der waals (vdW) interaction is included using a dispersion correction term with DFT-D3 method [17,18]. The electronic structures including density of states (DOS) and electron localization function (ELF) [19] were obtained using $12 \times 12 \times 1$ k points. A large vacuum space of 20 Å was used for avoid any interaction between MXene sheets.

The chemical reaction of heavy metals Pb uptake of alk-MXene is shown as following:

$$2M_2X(OH)_2 + xPb(NO_3)_2 \rightarrow 2M_2X(O_2H_{2-2x}Pb_x) + 2xHNO_3 \quad (1)$$
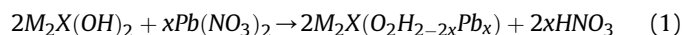
The formation energy (E_f) of chemical reaction to describe the stability of Pb uptake of alk-MXene is defined as the following:

$$E_f = E_{tot(M_2X(O_2H_{2-2x}Pb_x))} + 2xE_{tot(HNO_3)} - E_{tot(M_2X(OH)_2)} \\ - xE_{tot(Pb(NO_3)_2)} \quad (2)$$

where E_{tot} is the total energy of corresponding substance. According to this definition, a negative E_f indicates that it is energetically favorable for the reagents to form more stable products and vice versa.