

# Carbon dioxide adsorption of two-dimensional carbide MXenes

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**Abstract:** Two-dimensional carbide MXenes ( $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{V}_2\text{CT}_x$ ) were prepared by exfoliating MAX phases ( $\text{Ti}_3\text{AlC}_2$  and  $\text{V}_2\text{AlC}$ ) powders in the solution of sodium fluoride (NaF) and hydrochloric acid (HCl). The specific surface area (SSA) of as-prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  was  $21 \text{ m}^2/\text{g}$ , and that of  $\text{V}_2\text{CT}_x$  was  $9 \text{ m}^2/\text{g}$ . After intercalation with dimethylsulfoxide, the SSA of  $\text{Ti}_3\text{C}_2\text{T}_x$  was increased to  $66 \text{ m}^2/\text{g}$ ; that of  $\text{V}_2\text{CT}_x$  was increased to  $19 \text{ m}^2/\text{g}$ . Their adsorption properties on carbon dioxide ( $\text{CO}_2$ ) were investigated under 0–4 MPa at room temperature (298 K). Intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$  had the adsorption capacity of  $5.79 \text{ mmol/g}$ , which is close to the capacity of many common sorbents. The theoretical capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$  with the SSA of  $496 \text{ m}^2/\text{g}$  was up to  $44.2 \text{ mmol/g}$ . Additionally, due to high pack density, MXenes had very high volume-uptake capacity. The capacity of intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$  measured in this paper was  $502 \text{ V}\cdot\text{v}^{-1}$ . This value is already higher than volume capacity of most known sorbents. These results suggest that MXenes have some advantage features to be researched as novel  $\text{CO}_2$  capture materials.

**Keywords:** MXenes; specific surface area (SSA); adsorption; carbon dioxide

## 1 Introduction

Carbon dioxide ( $\text{CO}_2$ ) is the most relevant contributor to greenhouse effect. However, over the past decades, the emission of  $\text{CO}_2$  and other greenhouse gases is continuously increased. Anthropogenic  $\text{CO}_2$  emissions are mainly due to combustion process, and a number of other industrial processes, such as hydrogen production, give some contributions also. In order to decrease  $\text{CO}_2$  content in atmosphere, it is necessary to look for a

suitable material to adsorb and capture  $\text{CO}_2$ .

In general, pressure and/or temperature swing approaches are used to capture  $\text{CO}_2$  in porous materials. The porous materials, as  $\text{CO}_2$  sorbents, should have superior properties in terms of capacity, stability, kinetics, selectivity, and regeneration [1]. Up to now, a wide range of sorbents for  $\text{CO}_2$  capture, have been used and studied, including metal organic frameworks (MOFs) [2], functionalized porous silica [3], activated carbon [4], zeolites [5], metal oxides, and microporous polymers [6]. Among these sorbents, MOFs exhibit very high  $\text{CO}_2$  uptake up to  $54.4 \text{ mmol/g}$  under high pressures (5 MPa) at 298 K [2]. Despite the excellent adsorption capacities, MOFs are much more expensive

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than commercially available activated carbons. In addition, MOFs are water sensitive; they can chemisorb water, and/or their porous structure can be destroyed upon exposure to water vapor. Up to now, it is still a great deal of research effort to design and synthesize high performance porous materials for CO<sub>2</sub> sorbents.

In 2011, a two-dimensional (2D) transition metal carbide with the name of MXene was prepared [7] and gained significant attention due to their excellent properties in many fields [8–12]. MXenes are prepared by selectively etching away A-site element from MAX ( $M_{n+1}AX_n$ ) phases with hydrofluoric acid or fluoride salt solution [7,13], where M is an early transition metal, A usually belongs to the groups IIIA and IVA, and X is carbon and/or nitrogen. Due to high surface energy, the surface of MXenes prepared in etching solution is always terminated with F, OH, and/or O [14]. Thus  $M_{n+1}X_nT_x$  is normally used as the chemical formula of MXene, where  $T_x$  represents the terminated F, OH, or O groups. By now, more than 10 MXenes, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> [15], Ti<sub>2</sub>CT<sub>x</sub> [16], V<sub>2</sub>CT<sub>x</sub> [17], etc. have been successfully synthesized and many more are predicted [18–22].

Due to the unique structure and properties, MXenes are extensively researched in many areas, such as microwave absorption and shielding [23–25], supercapacitors [26,27], ion battery [21,28–30], etc. Moreover, due to stacking structure, MXenes have a large amount of interlayer space. The interlayer space is suitable for gas adsorption. From theoretical calculation [31], MXenes with oxygen functional groups could adsorb NH<sub>3</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, etc. Our group has investigated the adsorption properties of MXene on some gases through theories and experiments, and found that MXenes can have important application in hydrogen storage [8,32] and methane adsorption [16,33]. At present, as the authors know, there is no research on the CO<sub>2</sub> adsorption of MXenes.

Following this idea, in this work, we synthesized two kinds of MXenes: Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, V<sub>2</sub>CT<sub>x</sub>, and researched the CO<sub>2</sub> adsorption of MXenes. The main purpose of this work was to clarify the relation between MXenes' microstructure and their CO<sub>2</sub> adsorption properties. And based on this work, the possibility of employing them as carbon dioxide capture media was explored.

## 2 Experiments

### 2.1 MXene nanosheets preparation

MXenes (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, V<sub>2</sub>CT<sub>x</sub>) with 2D structure in this

work were produced by immersing MAX phase (Ti<sub>3</sub>AlC<sub>2</sub>, V<sub>2</sub>AlC) powders in etching solution. Ti<sub>3</sub>AlC<sub>2</sub> powders and V<sub>2</sub>AlC powders were synthesized in a tube furnace. The experimental details to synthesize those powders were reported in Ref. [34] for Ti<sub>3</sub>AlC<sub>2</sub> powders and in Refs. [35,36] for V<sub>2</sub>AlC powders. The etching solution was composed of NaF ( $\geq 99.8$  wt%, Sinopharm Chemical Reagent Co., Beijing, China) and HCl (6 mol/L, Shuangshuang Chemical Co., Yantai, China) solution. 2 g Ti<sub>3</sub>AlC<sub>2</sub> powders were soaked in NaF (2 g) and HCl (40 mL) solution at 333 K for 48 h to obtain Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. 2 g V<sub>2</sub>AlC powders were soaked in NaF (2 g) and HCl (40 mL) solution at 363 K for 72 h to obtain V<sub>2</sub>CT<sub>x</sub>. After etching, powders were separated from the solution by centrifugation, washed with deionized water and ethanol repeatedly. The obtained MXene powders were dried in vacuum at 353 K. Thereafter, MXene powders were collected for testing and were labeled as as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> or as-V<sub>2</sub>CT<sub>x</sub> in this paper.

As-prepared MXenes were further exfoliated by intercalation with dimethylsulfoxide (DMSO). 0.5 g MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> or V<sub>2</sub>CT<sub>x</sub>) powders were mixed with 10 mL DMSO and then magnetically stirred for 18 h at room temperature [37]. Thereafter, the samples were washed several times by deionized water and then dried in a vacuum oven at 353 K. The MXene after intercalation was labeled as int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> or int-V<sub>2</sub>CT<sub>x</sub> in this paper.

### 2.2 Characterization

X-ray diffraction (XRD) patterns of MAX (Ti<sub>3</sub>AlC<sub>2</sub>, V<sub>2</sub>AlC) and MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, V<sub>2</sub>CT<sub>x</sub>) powders were obtained with an X-ray diffractometer (Rigaku, Smartlab, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). All XRD samples were prepared by tiling powders on a flat sample holder. The morphology and microstructures of samples were observed by a field emission scanning electron microscopy (FE-SEM, Merlin Compact, Carl Zeiss NTS GmbH, Germany) and a transmission electron microscope (TEM, JEOLJEM-2010, Japan) with an accelerating voltage of 200 kV. TEM samples were prepared by ultrasonically dispersing MXene powders in ethylalcohol and then moving them to a copper grid. Raman spectrum was recorded with a confocal spectrometer (Horiba JobinYvon, LabRAM HR800, French), using the 514.5 nm excitation of the argon laser at room temperature. X-ray photoelectron spectroscopy (XPS) analyses were performed with a Surface Sciences Instruments spectrometer (PHI X-tool, Ulvac-Phi,

Japan) using a focused monochromatized Al K $\alpha$  radiation (1486.6 eV).

### 2.3 Adsorption test

Prior to all adsorption measurements, the samples were degassed in vacuum at 353 K for 2 h.

Nitrogen adsorption isotherms of MXenes were measured at 77 K (Quantachrome, Autosorb-iO-MP, USA). The obtained nitrogen adsorption–desorption isotherms were evaluated to give the pore parameters, including specific surface area, pore-size distribution, and total pore volume.

Adsorption of CO<sub>2</sub> was measured by high temperature and high pressure gas adsorption instrument (Gold APP, H-Sorb 2600, Beijing, China). Before adsorption, 0.4 g MXene powders were placed in a cylindrical container. Carbon dioxide isotherms of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and V<sub>2</sub>CT<sub>x</sub> were obtained at 298 K under 0–4 MPa.

## 3 Results and discussion

### 3.1 Characterization of samples

The X-ray diffraction (XRD) patterns of MAX phases, as-prepared MXenes, and intercalated MXenes are shown in Fig. 1. The values of lattice parameter *c* calculated from XRD patterns are listed in Table 1. Because cation and water molecules can enter the interlayer space, hydrate the intercalated cation, and expand the layers [38], *c* of MXene is changeable with process conditions. Larger *c* means larger interlayer

space. The intensity ratios of MAX’s (002) peak to MXene’s (002) peak,  $I_{MAX}/I_{MXene}$ , are also listed in Table 1, which represent the amount of residual MAX phase in the obtained MXene.

(1) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. From the XRD pattern of Fig. 1(a), it is evident that the (002) peak of Ti<sub>3</sub>AlC<sub>2</sub>, which is initially at  $2\theta \approx 9.5^\circ$ , is broadened and shifted to lower angle (7.53°) after exfoliation by NaF and HCl for 48 h at 333 K. The new peak belongs to Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene. The lattice parameter *c* of Ti<sub>3</sub>AlC<sub>2</sub> is calculated to be 18.6 Å and *c* of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is 23.4 Å. After intercalation, the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> was further exfoliated and *c* of intercalated Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) is 27.6 Å.  $I_{MAX}/I_{MXene}$  of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is ~0.036. This means there is residual Ti<sub>3</sub>AlC<sub>2</sub> in the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. However, the purity is enough for property characterization. After DMSO intercalation, the (002) peak of int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is shifted to low angle (6.41°) and *c* is increased from 23.4 to 27.6 Å.  $I_{MAX}/I_{MXene}$  of int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is ~0.037, similar with the value of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, which indicates that the purity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is almost unchangeable during the intercalation. Therefore, the intercalation can further exfoliate Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene and it is an effective way to obtain Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with larger interlayer space.

(2) V<sub>2</sub>CT<sub>x</sub>. In Fig. 1(b), (002) peak of V<sub>2</sub>AlC at 13.5° almost disappears after etching and a new peak at ~8.05° appears, which belongs to V<sub>2</sub>CT<sub>x</sub> MXene.  $I_{MAX}/I_{MXene}$  (Table 1) of as-V<sub>2</sub>CT<sub>x</sub> is ~0.092. This value is similar with the previous reported value in literature [17]. And V<sub>2</sub>CT<sub>x</sub> made by NaF+HCl etching is much purer than V<sub>2</sub>CT<sub>x</sub> made by HF etching, which has

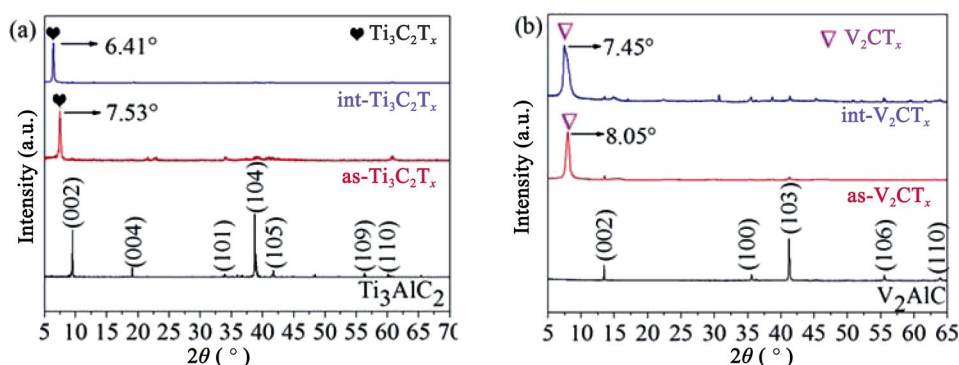


Fig. 1 XRD patterns of MAX phases, as-MXenes, and int-MXenes: (a) Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (b) V<sub>2</sub>AlC and V<sub>2</sub>CT<sub>x</sub>.

Table 1 XRD data of MAX phases and MXenes. Lattice parameter *c* was calculated from 2θ of (002) peak and  $I_{MAX}/I_{MXene}$  is intensity ratio of MAX’s (002) peak to MXene’s (002) peak

	Ti <sub>3</sub> AlC <sub>2</sub>	as-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	int-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	V <sub>2</sub> AlC	as-V <sub>2</sub> CT <sub>x</sub>	int-V <sub>2</sub> CT <sub>x</sub>
Lattice parameter <i>c</i> (Å)	18.6	23.4	27.6	13.1	21.9	23.7
$I_{MAX}/I_{MXene}$	—	0.036	0.037	—	0.092	0.093

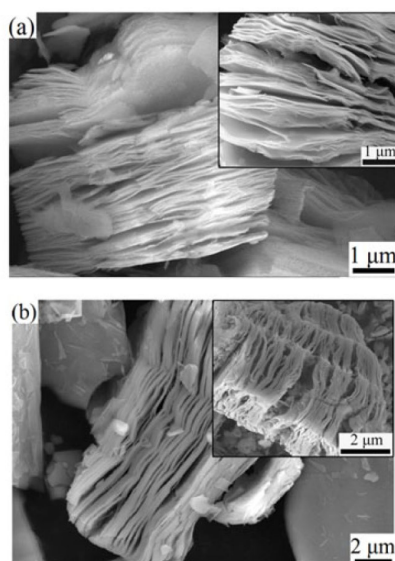
$I_{MAX}/I_{MXene}$  of  $\sim 1.06$  [39].  $I_{MAX}/I_{MXene}$  of int- $V_2CT_x$  is  $\sim 0.093$ , similar with the value of as- $V_2CT_x$ , which also indicates that the purity of  $V_2CT_x$  is almost unchangeable during the intercalation. As shown in Table 1,  $c$  of  $V_2AlC$  is  $13.1 \text{ \AA}$ . After exfoliation,  $c$  of as- $V_2CT_x$  is  $21.9 \text{ \AA}$ . After intercalation,  $c$  of int- $V_2CT_x$  increases to  $23.7 \text{ \AA}$ . Similar with  $Ti_3C_2T_x$ , after intercalation with DMSO,  $V_2CT_x$  is further exfoliated and space between MXene layers becomes larger.

The SEM image of as- $Ti_3C_2T_x$  is shown in Fig. 2(a); the inset is the SEM image of int- $Ti_3C_2T_x$ . The SEM image of as- $V_2CT_x$  is shown in Fig. 2(b); that of int- $V_2CT_x$  is shown in the inset of Fig. 2(b). The MXene samples in this paper have typical multi-layer stack morphology of MXene [7].

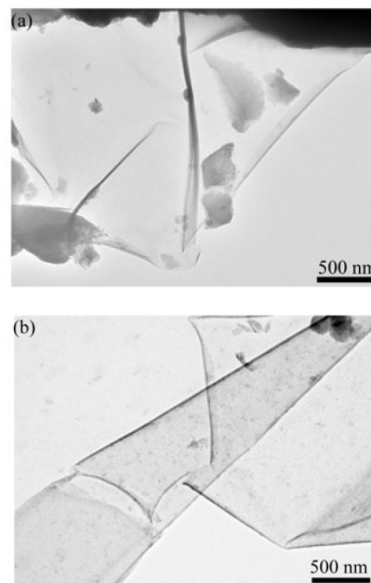
The TEM image of fully exfoliated  $Ti_3C_2T_x$  flakes is shown in Fig. 3(a) and that of  $V_2CT_x$  is shown in Fig. 3(b). From Fig. 3, the MXene sheets are quite thin and transparent to electrons [7,17]. The edge of the flake has significant curl, indicating that the  $V_2CT_x$  layer is very thin and has certain toughness.

Figure 4 is the Raman spectra of  $Ti_3C_2T_x$  and  $V_2CT_x$ . For  $Ti_3C_2T_x$ , the Raman spectrum is similar with previous report spectrum in literature [40]. The bands assigned to Al–Ti vibrations of precursor  $Ti_3AlC_2$  at  $185$  and  $272 \text{ cm}^{-1}$  are vanished. The bands at  $154$ ,  $204$ , and  $623 \text{ cm}^{-1}$  involve Ti–C vibrations [41]. From the Raman spectrum,  $Ti_3C_2T_x$  is successfully synthesized.

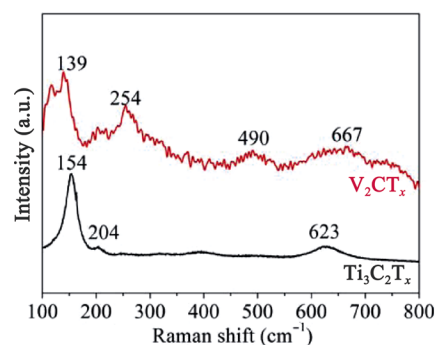
For  $V_2CT_x$ , the bands of  $V_2AlC$  at  $157$ ,  $239$ ,  $257$ , and  $364 \text{ cm}^{-1}$  [41] are vanished and new bands appear at  $139$ ,  $254$ ,  $490$ , and  $667 \text{ cm}^{-1}$ . This spectrum is similar



**Fig. 2** SEM images of (a)  $Ti_3C_2T_x$  and (b)  $V_2CT_x$ . The insets are int- $Ti_3C_2T_x$  and int- $V_2CT_x$ , respectively.



**Fig. 3** TEM images of (a)  $Ti_3C_2T_x$  and (b)  $V_2CT_x$ .



**Fig. 4** Raman spectra of  $Ti_3C_2T_x$  and  $V_2CT_x$ .

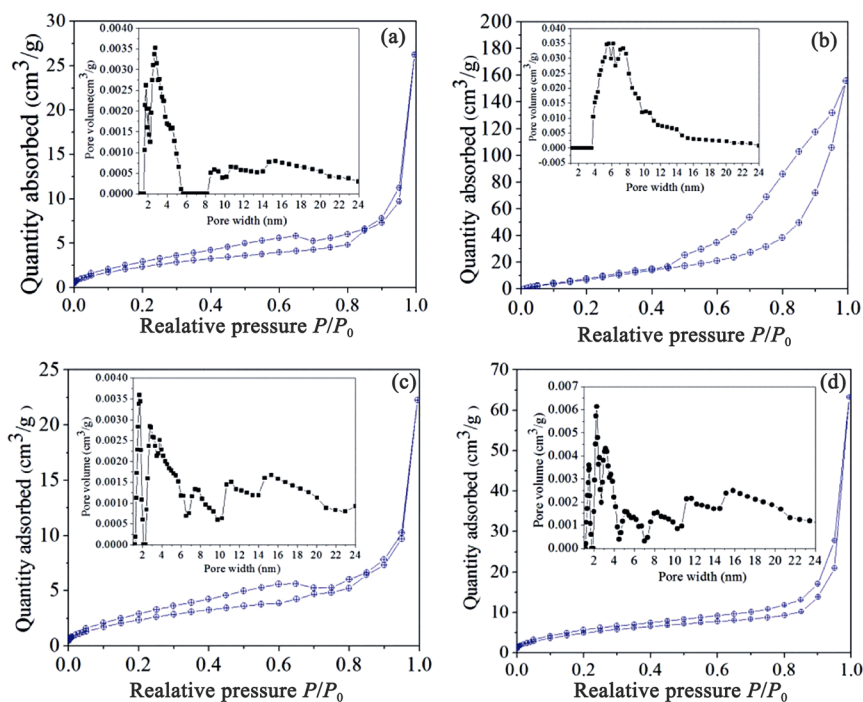
with the reported spectrum of  $V_2C$  MXene in a very recent literature [42]. Thus,  $V_2CT_x$  is successfully synthesized.

### 3.2 Surface area and porosity analysis of MXenes

The  $N_2$  adsorption–desorption isotherms at  $77 \text{ K}$  and pore size distribution of as-MXenes and int-MXenes are shown in Fig. 5. According to IUPAC (International Union of Pure and Applied Chemistry) classification, all  $N_2$  adsorption–desorption isotherms of MXenes are of type IV and exhibit a hysteresis loop, showing the existence of mesopores in MXenes. The corresponding pore size distributions of MXenes are calculated by BJH model and are shown in the insets of Fig. 5.

In Fig. 5(a), for as- $Ti_3C_2T_x$ , its SSA is calculated to be  $21 \text{ m}^2/\text{g}$ . The total pore volume of this  $Ti_3C_2T_x$  sample is obtained to be  $0.08 \text{ cm}^3/\text{g}$  at the relative pressure  $P/P_0 = 0.99$ . In Fig. 5(b), after intercalation, the SSA of int- $Ti_3C_2T_x$  is  $66 \text{ m}^2/\text{g}$  and the total pore





**Fig. 5** N<sub>2</sub> sorption isotherms and pore size distributions of MXenes: (a) as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (b) int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (c) as-V<sub>2</sub>CT<sub>x</sub>, (d) int-V<sub>2</sub>CT<sub>x</sub>.

volume is 0.25 cm<sup>3</sup>/g. The pore width of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is distributed in the range of 1.8–24 nm. After intercalation, the pore width of int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is distributed in the range of 3.9–24 nm. Additionally, the pore volume of int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is much larger than that of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. Thus, it can be concluded that the intercalation process really increases the distance between Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> layers, which, in turn, enlarges the interlayer space for gas adsorption.

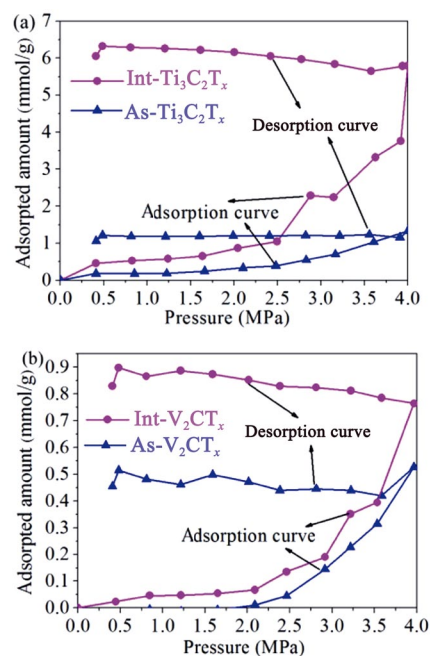
In Fig. 5(c), for as-V<sub>2</sub>CT<sub>x</sub>, the SSA is 9 m<sup>2</sup>/g and total pore volume is 0.04 cm<sup>3</sup>/g, both smaller than Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. It is because that the exfoliation of V<sub>2</sub>CT<sub>x</sub> is not as good as Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and there is not enough interlayer space in V<sub>2</sub>CT<sub>x</sub> MXene. In Fig. 5(d), after intercalation, the SSA of V<sub>2</sub>CT<sub>x</sub> is 19 m<sup>2</sup>/g and total pore volume is 0.09 cm<sup>3</sup>/g. The intercalation can increase the SSA and pore volume of V<sub>2</sub>CT<sub>x</sub>; however, the effect is less obvious than that for Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.

### 3.3 CO<sub>2</sub> adsorptive property of MXenes

CO<sub>2</sub> adsorption and desorption isotherms of as-MXenes and int-MXenes are shown in Fig. 6. According to theoretical calculation [31], only monolayer CO<sub>2</sub> molecules can be adsorbed on the surface of MXenes with O termination. Thus, Langmuir isotherm assumption is used to analyze the CO<sub>2</sub> adsorption of MXenes.

Figure 6(a) shows CO<sub>2</sub> adsorption and desorption curves of as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> under 0–4 MPa at

298 K. For as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, the CO<sub>2</sub> adsorbed amount is 1.33 mmol/g at 4 MPa; after intercalation with DMSO, the adsorbed amount is 5.79 mmol/g. The new value is 4.3 times of the previous adsorbed amount. It is obvious that intercalation can dramatically increase the adsorbed amount of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. As discussed in Section



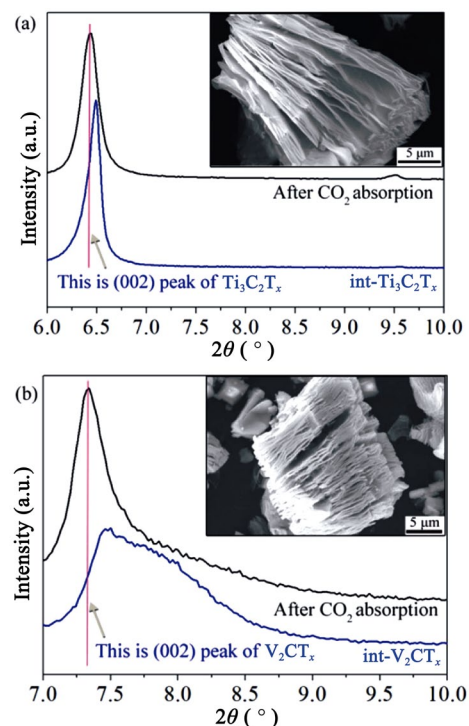
**Fig. 6** CO<sub>2</sub> adsorption and desorption curves of MXenes at 298 K under 0–4 MPa: (a) as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (b) as-V<sub>2</sub>CT<sub>x</sub> and int-V<sub>2</sub>CT<sub>x</sub>.

3.2, compared with as-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> has larger SSA, higher pore volume, and most pores have larger pore width. These factors are favorable for MXenes to adsorb CO<sub>2</sub>.

Figure 6(b) represents the CO<sub>2</sub> adsorption and desorption curves of as-V<sub>2</sub>CT<sub>x</sub> and int-V<sub>2</sub>CT<sub>x</sub> under 0–4 MPa at 298 K. Unlike Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, V<sub>2</sub>CT<sub>x</sub> has no adsorption capacity of CO<sub>2</sub> if the pressure is less than ~2 MPa. It is because V<sub>2</sub>CT<sub>x</sub> has smaller interlayer space for gas adsorption or the space is blocked by intercalation molecules, and some pressure is required to squeeze CO<sub>2</sub> into the pores. With the pressure increasing, CO<sub>2</sub> molecules begin to come into the interlayer space of V<sub>2</sub>CT<sub>x</sub> and the CO<sub>2</sub> adsorbed amount is 0.52 mmol/g at 4 MPa as shown in Fig. 6(b). After intercalation with DMSO, the CO<sub>2</sub> adsorbed amount is 0.77 mmol/g at 4 MPa.

From the results in Fig. 6, it can be concluded that the MXenes, no matter Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> or V<sub>2</sub>CT<sub>x</sub>, no matter as-prepared or intercalated, can adsorb CO<sub>2</sub>. From the desorption curves in Fig. 6, the adsorbed CO<sub>2</sub> cannot be released under atmospheric pressure. Therefore, MXenes can be used as sorbent to capture CO<sub>2</sub>. From the shape of adsorption curves in Fig. 6, the mesoporous in MXenes to adsorb CO<sub>2</sub> are slit-like. This agrees well with the morphology of MXene. The interlayer space in slit-like shape is the room to adsorb and storage gas molecules. This is obviously different with porous carbon, which has type I adsorption curve, corresponding to narrow micropores (< 1 nm) as shown in Ref. [43].

In order to verify whether there are microstructure and composition change of MXene after the adsorption, XRD patterns and SEM images of int-MXenes after CO<sub>2</sub> adsorption were obtained and are shown in Figs. 7(a) and 7(b). From the XRD patterns, after the adsorption, the (002) peaks of int-MXenes shift to small angle direction. This indicates that CO<sub>2</sub> enters the MXene layers and increases the distance between layers. In addition, there are no diffraction peaks of other substances. And from the SEM images, int-MXenes after CO<sub>2</sub> adsorption still maintain the two-dimensional layered structure without detectable change. These results indicate that adsorption of CO<sub>2</sub> by MXene has the characters of physical adsorption.



**Fig. 7** XRD patterns and SEM images of (a) int-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and (b) int-V<sub>2</sub>CT<sub>x</sub> after CO<sub>2</sub> absorption.

Theoretical calculation has similar conclusion. Based on the calculation [31], the adsorption energy of CO<sub>2</sub> on MXene with O termination is −0.14 eV and charge transfer is −0.007 eV. The adsorption is deemed as physical adsorption. However, this adsorption also has some chemical adsorption features, such as the unclosed hysteresis loop during desorption. Thus, the mechanism is not fully clear and more work is needed to clarify the mechanism.

Because the surface of all MXenes is terminated by F/O/OH, the adsorption properties of MXene must be affected by the type and concentration of these termination groups, which can be estimated from the results of XPS. Table 2 lists the atomic concentrations obtained from XPS. As shown in Table 2, the main surface terminations of MXenes are O and F. For Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, the concentration of F is higher than that of O. For V<sub>2</sub>CT<sub>x</sub>, the concentration of O is higher than that of F. However, to fully understand the impact of termination, MXenes with the same chemical composition and different terminations should be made and tested,

**Table 2** Atomic concentration (%) estimated from XPS of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and V<sub>2</sub>CT<sub>x</sub>

Sample	Ti 2p	V 2p	C 1s	O 1s	F 1s	Na 1s	Al 2p	Cl 2p
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	13.23	—	35.59	18.24	29.19	0.18	3.04	0.53
V <sub>2</sub> CT <sub>x</sub>	—	9.54	41.99	35.58	6.88	0.29	4.82	0.9

which will be reported in the future.

It is noted that the adsorbed amount of  $\text{Ti}_3\text{C}_2\text{T}_x$  is much larger than that of  $\text{V}_2\text{CT}_x$ . This is a little surprise to us because  $\text{V}_2\text{CT}_x$  theoretically has higher SSA than  $\text{Ti}_3\text{C}_2\text{T}_x$ . Normally, higher SSA results in higher adsorbed amount. Thus,  $\text{V}_2\text{CT}_x$  has been supposed to have higher capacity than  $\text{Ti}_3\text{C}_2\text{T}_x$ . If totally exfoliated to single cell layers, every  $\text{V}_2\text{CT}_x$  layer has two V layers and one C layer while every  $\text{Ti}_3\text{C}_2\text{T}_x$  layer has three Ti layers and two C layers. The theoretical SSA of  $\text{V}_2\text{CO}_2$  is  $589 \text{ m}^2/\text{g}$ , while that of  $\text{Ti}_3\text{C}_2\text{O}_2$  is  $496 \text{ m}^2/\text{g}$ . The inconsistent relation between adsorbed amount and theoretical SSA can be explained by the exfoliation degree of the two MXenes. The exfoliation of  $\text{Ti}_3\text{C}_2\text{T}_x$  is very easy. It is the first MXene reported to be prepared [7]. Thus, higher exfoliation degree is easily to be achieved. In this paper, the SSA of int- $\text{Ti}_3\text{C}_2\text{T}_x$  is  $66 \text{ m}^2/\text{g}$ , 14% of theoretical SSA. However, the exfoliation of  $\text{V}_2\text{CT}_x$  is very difficult. High pure  $\text{V}_2\text{CT}_x$  MXene was first made in 2017 [17], 6 years later than the preparation of high pure  $\text{Ti}_3\text{C}_2\text{T}_x$ . Thus, the exfoliation degree of  $\text{V}_2\text{CT}_x$  is usually low. In this paper, the SSA of int- $\text{V}_2\text{CT}_x$  is  $19 \text{ m}^2/\text{g}$ , only 3.3% of theoretical SSA. Most  $\text{V}_2\text{CT}_x$  sheets should be multilayer rather than single layer. Therefore, although  $\text{V}_2\text{CT}_x$  has higher theoretical adsorbed amount, in this paper,  $\text{Ti}_3\text{C}_2\text{T}_x$  has higher capacity to adsorb  $\text{CO}_2$  because  $\text{Ti}_3\text{C}_2\text{T}_x$  is easily exfoliated. The achieved capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$  is  $5.79 \text{ mmol/g}$ . If  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene with theoretical SSA (100% exfoliated) can be made in the future, the theoretical capacity would be  $44.2 \text{ mmol/g}$ .

In order to evaluate the capacity of MXenes as  $\text{CO}_2$  sorbent under high pressure, we compared MXenes with other sorbents. Zeolite 13X has the capacity of  $7.38 \text{ mmol/g}$  [44] and porous polymers have the capacity of  $11.9 \text{ mmol/g}$  [45]. The first reported capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene ( $5.79 \text{ mmol/g}$ ) is close to the capacity of those common sorbents. And MXene's capacity can be improved with better exfoliation process to make MXene with higher SSA. This can be proved by the comparison the capacities of as- $\text{Ti}_3\text{C}_2\text{T}_x$  and int- $\text{Ti}_3\text{C}_2\text{T}_x$ . The theoretical capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$  is  $44.2 \text{ mmol/g}$ , which is already close to the capacity of MOF ( $54.4 \text{ mmol/g}$ ) [2]. Additionally, MXenes are not water sensitive. Water molecules can come into or come out of the interlayer space of MXenes and the pore structure of MXene will not be changed.

More importantly, the density of  $\text{Ti}_3\text{C}_2\text{O}_2$  is much higher than most common  $\text{CO}_2$  sorbents. For example, the packing density of polypyrrole-derived carbons is  $0.25\text{--}0.38 \text{ g/cm}^3$  [46]. The apparent density of  $\text{Ti}_3\text{C}_2\text{O}_2$

discs compacted under pressure of 10 MPa is  $3.87 \text{ g/cm}^3$ . If the unit of  $\text{CO}_2$  uptake is changed from gravimetric uptake (per g) to volumetric uptake (per  $\text{cm}^3$ ), which can be calculated by multiplying the adsorbed amount value in Fig. 6 by density of absorbent, the  $\text{CO}_2$  volumetric uptake can be as high as  $502 \text{ V}\cdot\text{v}^{-1}$  for int- $\text{Ti}_3\text{C}_2\text{T}_x$ . And for fully exfoliated  $\text{Ti}_3\text{C}_2\text{T}_x$ , the theoretic volumetric uptake can be  $3788 \text{ V}\cdot\text{v}^{-1}$ . These values are very high, compared with  $400 \text{ V}\cdot\text{v}^{-1}$  for polypyrrole-derived carbons with SSA of  $3934 \text{ m}^2/\text{g}$  and  $130 \text{ V}\cdot\text{v}^{-1}$  for MOF-210 with SSA of  $6240 \text{ m}^2/\text{g}$  [46]. Thus MXenes are very promising  $\text{CO}_2$  sorbent with excellent volumetric uptake capacity. The high volumetric capacity means  $\text{CO}_2$  can be stored in a tank with very small volume. This is important for the applications that require small dimensions, such as adsorption of gas from landfills, etc.

## 4 Conclusions

MXene powders ( $\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{V}_2\text{CT}_x$ ) were prepared by exfoliating MAX phases ( $\text{Ti}_3\text{AlC}_2$  and  $\text{V}_2\text{AlC}$ , respectively) powders in the solution of NaF and hydrochloric acid (HCl). XRD and Raman data show that MXenes were obtained successfully. As-prepared MXenes can be further exfoliated to increase SSA by intercalation with DMSO. Although  $\text{V}_2\text{CT}_x$  has higher theoretical SSA than  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$  made in this paper has better structure and higher SSA than  $\text{V}_2\text{CT}_x$  because  $\text{Ti}_3\text{C}_2\text{T}_x$  is easily exfoliated.

The  $\text{CO}_2$  adsorption properties of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene and  $\text{V}_2\text{CT}_x$  MXene were tested in this paper. It was found that MXenes are promising sorbent for  $\text{CO}_2$  capture. Intercalated MXenes have obviously higher adsorbed amount than as-prepared MXenes. Int- $\text{Ti}_3\text{C}_2\text{T}_x$  with the SSA of  $66 \text{ m}^2/\text{g}$  has the capacity of  $5.79 \text{ mmol/g}$ , which is close to the capacity of many common sorbents. The theoretical capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$  with the SSA of  $496 \text{ m}^2/\text{g}$  is  $44.2 \text{ mmol/g}$ , which is close to the capacity of MOF. Additionally, due to high pack density, MXenes have very high volume-uptake capacity. The capacity of int- $\text{Ti}_3\text{C}_2\text{T}_x$  measured in this paper is  $502 \text{ V}\cdot\text{v}^{-1}$ . This value is already higher than volume capacity of most known sorbents.

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