

**ELECTRONIC SUPPLEMENTARY INFORMATION**

**Proposing prospects of Ti<sub>3</sub>CN transition metal carbides (MXenes) as  
anode in Li-ion battery: a DFT study**

Xingzhu Chen,<sup>a</sup> Zhouzhou Kong,<sup>a</sup> Neng Li,<sup>\*,a</sup> Xiujian Zhao,<sup>\*,a</sup> and Chenghua Sun<sup>\*,b</sup>

<sup>a</sup>State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology,  
Hubei, 430070, China

<sup>b</sup>ARC Centre of Excellence for Electromaterials Science (ACES), School of Chemistry, Faculty  
of Science, Monash University, Clayton, VIC 3800, Australia

\*Author to whom correspondence should be addressed:

NL & XZ: Tel: (+86) 27 87652553; Fax: (+86) 27 87883743; Email: [lineng@whut.edu.cn](mailto:lineng@whut.edu.cn),  
[opluse@whut.edu.cn](mailto:opluse@whut.edu.cn),

CS: Tel: (+61) 3 9902 9916; Fax: (+61) 3 9905 4597; E-mail: [Chenghua.Sun@monash.edu](mailto:Chenghua.Sun@monash.edu)

---

	Pages
<b>DFT-D2 METHOD DETAILS</b>	S1
<b>OPTIMIZED CARTESIAN COORDINATES</b>	S2
<b>TOTAL ENERGIES OF ADSORPTION SITES</b>	S3
<b>BADER CHARGE POPULATION ANALYSIS</b>	S4
<b>COMPUTATION OF DIFFUSION BARRIERS</b>	S5
<b>DENSITY OF STATE PROFILE</b>	S6

---

## 1. DFT-D2 METHOD DETAILS (The van der Waals (vdW) interactions correction)

The additional functional was introduced into standard DFT calculations, because DFT cannot deal with the van der Waals (vdW) interactions in weakly bonded systems such as atom adsorption on 2D MXene substrate considered in this work.

There are two types' methods for vdW correction in VASP: the vdW-DF and DFT-D approaches. The DFT-D method adds a semiempirical pairwise force field to conventional DFT calculations,<sup>1</sup> while the vdW-DF approach adds a nonlocal correlation functional that approximately account for dispersion interactions, which will complicate the calculation.<sup>2</sup>

On the one hand, as far as we know, there has no proof for which one between vdW-DF and DFT-D is more appropriate in the specific calculation. On the other hand, the DFT-D method (especially DFT-D2 and DFT-D3) is widely used in recent years. There are some latest literatures used DFT-D2 to describe the vdW force in MXene system, which is exactly the same with our case.<sup>3,4</sup> Thus, the DFT-D2 approach was used for our system in this work.

### REFERENCES

- 1 S. Grimme, *Journal of computational chemistry*, 2006, **27**, 1787-1799.
- 2 M. Dion, H. Rydberg, E. Schröder, D.C. Langreth, B.I. Lundqvist, *Physical review letters*, 2004, **92**, 246401.
- 3 Q. Tang, Z. Zhou and P. Shen, *Journal of the American Chemical Society*, 2012, **134**, 16909-16916.
- 4 X. Zhang, J. Lei, D. Wu, X. Zhao, Y. Jing and Z. Zhou, *Journal of Materials Chemistry A*, 2016, **4**, 4871-4876.

## 2. OPTIMIZED CARTESIAN COORDINATES

### The optimized atomic coordinates of Ti<sub>3</sub>CN (2×2×1 supercell)

1.0000000000

6.1308512688	0.0000000000	0.0000000000
-3.0636133053	5.3026007279	0.0000000000
0.0121473158	0.0176100747	26.8308134621

4 4 12

Cartesian

N	1.541329474	0.891884480	14.305761827
N	4.605746884	0.892153272	14.305736239
N	0.008700435	3.544468165	14.306423913
N	3.074855029	3.544005636	14.306220809
C	0.007256073	1.774827009	11.718509567
C	3.073139231	1.773552506	11.718279276
C	-1.524074076	4.425590976	11.718683084
C	1.540984318	4.425760952	11.718585531
Ti	-3.056545857	5.309836943	13.008646153
Ti	0.009156831	1.776402817	15.311497371
Ti	1.538509956	0.890835812	10.678390339
Ti	0.008415803	5.310095576	13.009273855
Ti	3.074107839	1.775837108	15.307221001
Ti	4.604133685	0.890722306	10.678448711
Ti	-1.525399202	2.659436183	13.008554196
Ti	-1.522209992	4.428731492	15.308383649
Ti	0.006314345	3.541908927	10.678748569
Ti	1.540871011	2.659110131	13.008257537
Ti	1.542130984	4.428225364	15.308206133
Ti	3.072147344	3.542136252	10.678385541

### 3. The Total energy of T (T= F, O, OH) @ Ti<sub>3</sub>CN with different sites

T group	C side (eV)			N side (eV)		
	C-top	FCC	Ti-top	N-top	FCC	Ti-top
F @ Ti <sub>3</sub> CN	-190.951	-191.382	-190.452	-190.847	-191.203	-190.253
O @ Ti <sub>3</sub> CN	-193.976	-194.548	-192.384	-193.878	-194.358	-192.381
OH @ Ti <sub>3</sub> CN	-197.173	-197.557	-196.299	-197.116	-197.417	-196.135

### 4. The Total energy of Li @ Ti<sub>3</sub>CNT<sub>2</sub> with different sites

	C side (eV)			N side (eV)		
	Titop	FCC	T-top	Titop	FCC	T-top
Li @ Ti <sub>3</sub> CNF <sub>2</sub>	-244.90	-245.08	-244.07	-244.74	-244.94	-243.98
Li @ Ti <sub>3</sub> CNO <sub>2</sub>	-268.88	-269.28	-268.22	-268.57	-268.92	-267.88
Li @ Ti <sub>3</sub> CN(OH) <sub>2</sub>	-291.73	-292.02	-291.05	-291.71	-291.92	-291.13
Li @ Ti <sub>3</sub> CN	-186.42	-186.56	-186.55	-186.61	-186.76	-186.75

## 5. Bader charge population analysis

1) Bader charge of single Li on  $\text{Ti}_3\text{CN}$  and  $\text{Ti}_3\text{CNT}_2$   $4\times 4\times 1$  supercells

	C-side ( $ e $ )	N-side ( $ e $ )
Li @ $\text{Ti}_3\text{CN}$	0.157	0.151
Li @ $\text{Ti}_3\text{CNF}_2$	0.104	0.103
Li @ $\text{Ti}_3\text{CNO}_2$	0.112	0.112
Li @ $\text{Ti}_3\text{CN}(\text{OH})_2$	0.282	0.282

2) Bader charge of T in  $\text{Ti}_3\text{CNT}_2$

	C-side ( $ e $ )	N-side ( $ e $ )
F ( $\text{Ti}_3\text{CNF}_2$ )	7.766	7.776
O ( $\text{Ti}_3\text{CNO}_2$ )	7.142	7.155
O ( $\text{Ti}_3\text{CN}(\text{OH})_2$ )	7.321	7.327

**6. The Li diffusion barriers on  $\text{Ti}_3\text{CN}$  and  $\text{Ti}_3\text{CNT}_2$  (T= F, O, OH) calculation with GGA and GGA+ $U$  method**

	GGA (eV)		GGA + U (eV)	
	C-side	N-side	C-side	N-side
$\text{Ti}_3\text{CN}$	0.016	0.030	0.024	0.026
$\text{Ti}_3\text{CNF}_2$	0.254	0.248	0.256	0.243
$\text{Ti}_3\text{CNO}_2$	0.317	0.262	0.301	0.263
$\text{Ti}_3\text{CN}(\text{OH})_2$	0.343	0.297	0.256	0.219

## 7. The calculated DOS of $\text{Ti}_3\text{CN}$ ( $\text{Ti}_3\text{CN-Li}_{0.25}$ ) and $\text{Ti}_3\text{CNT}_2$ ( $\text{Ti}_3\text{CNT}_2\text{-Li}_{0.25}$ )

