Supporting information

# Elucidation of Synergistic Effects of 3d Metal (M=Cu, Co, Ni) dopants and Terminations (T=-O- and -OH) of $Ti_3C_2T_x$ MXene for Urea Adsorption Ability via DFT Calculations and Experiments

Caihong Liang<sup>a, ‡</sup>, Zhihao Yen<sup>a, ‡</sup>, Teddy Salim<sup>b</sup>, Yeng Ming Lam,<sup>a, b,\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Nanyang Technological University, Singapore, 639798, Singapore

<sup>b</sup> Facility for Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore, 639798, Singapore

<sup>‡</sup> These authors contribute equally to this work.

\*Corresponding author:

E-mail: ymlam@ntu.edu.sg (YM. Lam)

### S1. Calculation and Experimental Methods.

#### **Details of Computational Models**

The basic model of  $Ti_3C_2T_x$  (T = -O- or -OH) is shown in Figure S1. The MXenes are 4 × 4 supercells with the *c* axes set as 30.1582 Å to ensure enough vacuum to avoid interactions between atoms within two neighbouring periods.

There are many studies on the possible termination groups on MXene and the choice of the slabs for this study is also essential.<sup>1-4</sup> It was found that LiF-HCl etching led to mostly oxygencovered MXene (5 at% OH, 22 at% F, and 73 at% O).<sup>3</sup> DFT results calculated by Meng et al.<sup>1</sup> found that the -F termination group has the lowest adsorption energy of urea amongst -OH, -O, and -F terminations, indicating the least favorable interactions. Therefore, -F termination is not considered in our calculation. Even though there is only 5 at% of -OH, the DFT calculations by Meng et al.<sup>1</sup> and Maleki et al.<sup>2</sup> indicated that this termination group has the best adsorption ability for urea. Based on the X-ray absorption fine structure (XAFS) studies, Bao et al.4 found that Cu single atom catalysts were connected with the O terminations on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> matrix. They also did calculations with the basic structure of Cu single atom anchored on O-atoms over  $Ti_3C_2T_x$  with OH terminations surrounding them. Thus, -OH and -O- are terminations found to be the most promising and hence will be used for DFT calculations in this work. As shown in Figure S1, there are four substitutional doping positions for single atom (SA), e.g., Cu atom, on Ti<sub>3</sub>C<sub>2</sub>(OH)<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub>, which include replacing the exposed Ti (blue rectangle) on the top Ti layer with Cu, replacing C (pink rectangle) with Cu and removing the right above termination, replacing one termination (-OH or -O-) (green rectangle) with Cu and anchoring a single atom (Cu) on terminations with -O-SA-O- structure (dashed yellow rectangle). Next, it is important to determine the best doping position for the single atom Cu on both Ti<sub>3</sub>C<sub>2</sub>(OH)<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub>, and subsequently this information can be extended to Co and Ni single atom calculations. Two configurations for the adsorbate are considered: vertical and parallel to the surface plane of MXene. Slabs after doping with SA are illustrated in Figure S2 and S5 in the sequence as described above.



**Figure S1**. The ball and stick model of  $Ti_3C_2(OH)_2$ : (a) side view; (b) top view; and the ball and stick model of  $Ti_3C_2O_2$ : (c) side view; (d) top view. The colourful rectangular areas represent the suggestive positions to locate SA (not the actual ones in the following calculations). Colour code: Ti, orange; C, grey; H, white; O, red.

#### Experiments for surface modification of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene

#### Materials

Lithium fluoride 300 mesh powder (LiF), Methanol HPLC  $\geq$  99.9% HPLC, Hydrochloric acid 37% (HCl), Copper (II) Chloride dihydrate ACS reagent  $\geq$  99.0% (CuCl<sub>2</sub>.2H<sub>2</sub>O), Cobalt (II) Nitrate Hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) ACS reagent grade  $\geq$  98%, Nickel (II) Nitrate Hexahydrate crystals (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O), Urea puriss. p.a., ACS reagent, reag. Ph. Eur.,  $\geq$ 99%, 3,4-Dihydroxy-L-phenylalanine  $\geq$  98% (TLC), Sodium Borohydride granular (NaBH<sub>4</sub>) 99.99% trace metal basis, were purchased from Sigma-Aldrich, Inc. 200 mesh Titanium Aluminum Carbide MAX phase powder (Ti<sub>3</sub>AlC<sub>2</sub>) purchased from ANR Technologies. QuantiChrom<sup>TM</sup> urea assay kit (DIUR-100) was purchased from BioAssay Systems.

The reduction of Cu<sup>2+</sup> by MXene can be accomplished without additional reducing agent as reported<sup>4, 5</sup>. However, to deposit Co and Ni ions on MXenes, a reducing agent such as sodium borohydride (NaBH<sub>4</sub>) is required<sup>6</sup>.

#### Cu functionalization MXene

Method was adapted and modified from Bao et al<sup>7</sup>. DI water (250.0 mL) was added to a 500 mL round bottom flask containing MXene (250.0 mg). The mixture was sonicated for 10 min followed by magnetic stirring at 900 rpm for 10 min. To a 10 mL glass vial, CuCl<sub>2</sub>.2H<sub>2</sub>O (14.0 mg) was added along with DI water (14.0 mL) to obtain a solution concentration of 1 mg/dL. CuCl<sub>2</sub> solution (6.7 or 13.4 mL) was then added into the mixture dropwise and left to stir for 30 min, followed by sonication for 1 h. The mixture was poured into four centrifuge tubes and centrifuge at 10 000 rpm for 30 min. The supernatant was decanted, and the residue was resuspended with fresh DI water. The washing step was repeated twice and dried in a vacuum oven at 40 °C for 18 h. The product was obtained as a black solid.

#### Ni functionalization MXene

Method was adapted and modified from Chen et al<sup>8</sup>. DI water (250.0 mL) was added to a 500 mL round bottom flask containing MXene (250.0 mg). The mixture was sonicated for 10 min followed by magnetic stirring at 900 rpm for 10 min. To a 10 mL glass vial, Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (24.0 mg) was added along with DI water (24.0 mL) to obtain a solution concentration of 1 mg/dL. Ni(NO<sub>3</sub>)<sub>2</sub> solution (11.4 or 22.8 mL) was then added into the mixture dropwise and left

to stir for 30 min, followed by sonication for 1 h. NaBH<sub>4</sub> (75.6 mg) was added into a glass vial 20 of methanol:DI H<sub>2</sub>O (1:1) to obtain 0.1 M solution. The solution was added into the mixture dropwise and left to stir at rtp for 2 h. The mixture was poured into four centrifuge tubes and centrifuge at 10 000 rpm for 30 min. The supernatant was decanted, and the residue was resuspended with fresh DI water. The washing step was repeated twice and dried in a vacuum oven at 40 °C for 18 h. The product was obtained as a black solid.

#### **Co functionalization MXene**

Method was adapted and modified from Chen et al.<sup>8</sup> DI water (250.0 mL) was added to a 500 mL round bottom flask containing MXene (250.0 mg). The mixture was sonicated for 10 min followed by magnetic stirring at 900 rpm for 10 min. To a 10 mL glass vial,  $Co(NO_3)_2.6H_2O$  (24.0 mg) was added along with DI water (24.0 mL) to obtain a solution concentration of 1 mg/dL. The  $Co(NO_3)_2$  solution (11.4 or 22.8 mL) was then added into the mixture dropwise and left to stir for 30 min, followed by sonication for 1 h. NaBH<sub>4</sub> (75.6 mg) was added into a glass vial 20 of methanol:DI H<sub>2</sub>O (1:1) to obtain 0.1 M solution. The solution was added into the mixture dropwise and left to stir at rtp for 2 h. The mixture was poured into four centrifuge tubes and centrifuge at 10 000 rpm for 30 min. The supernatant was decanted, and the residue was resuspended with fresh DI water. The washing step was repeated twice and dried in a vacuum oven at 40 °C for 18 h. The product was obtained as a black solid.



**Figure S2**. The ball and stick model of Cu doped on  $Ti_3C_2(OH)_2$  in the way of replacing the exposed Ti on the top Ti layer ( $Ti_{3-x}Cu_xC_2(OH)_2$ : top view (a) and side view (b)), replacing C together with removing the right above termination ( $Ti_3C_{2-x}Cu_x(OH)_2$ : top view (c) and side view (d)), replacing one termination (-OH) ( $Ti_3C_2(OH)_{2-x}Cu_x$ : top view (e) and side view (f)) and anchoring single atom on the top of terminations with -O-SA-O- structure ( $Ti_3C_2(OH)_2Cu_x$ : top view (g) and side view (h)).



**Figure S3**. The local charge density difference (CDD) analysis between absorbed urea in parallel orientation on  $Ti_3C_2O_2$ ,  $Ti_3C_2(OH)_2$ , or Cu SA- $Ti_3C_2(OH)_2$  slabs (Isovalue = 0.001). The yellow part of iso-surface means the accumulation of electrons and the teal part of iso-surface means the depletion of electrons. Color code: Cu, deep blue; Ti, light blue; H, white; N, grey; O, red;C, brown.



**Figure S4**. The ball and stick model for urea adsorption on various Cu doped  $Ti_3C_2(OH)_2$  slabs: (a) perpendicular and (b) parallel configurations of urea on  $Ti_{3-x}Cu_xC_2(OH)_2$ ; (c) perpendicular and (d) parallel configurations of urea on  $Ti_3C_{2-x}Cu_x(OH)_2$ ; (e) perpendicular and (f) parallel configurations of urea on  $Ti_3C_2(OH)_{2-x}Cu_x$ ; and (g & h) perpendicular configuration of urea on  $Ti_3C_2(OH)_2Cu_x$ . The initial adsorption configuration of urea in (h) is parallel. However, it becomes vertical form after optimization.



**Figure S5**. The ball and stick model of Cu doped on  $Ti_3C_2O_2$  in the way of replacing the exposed Ti on the top Ti layer ( $Ti_{3-x}Cu_xC_2O_2$ : top view (a) and side view (b)), replacing C together with removing the right above termination ( $Ti_3C_{2-x}Cu_xO_2$ : top view (c) and side view (d)), replacing one termination (-OH) ( $Ti_3C_2O_{2-x}Cu_x$ : top view (e) and side view (f)) and anchoring single atom on the top of terminations with -O-SA-O- structure ( $Ti_3C_2O_2Cu_x$ : top view (g) and side view (h)).



**Figure S6**. The ball and stick model of urea adsorption on Cu doped  $Ti_3C_2O_2$ : (a) perpendicular and (b) parallel configurations of urea on  $Ti_{3-x}Cu_xC_2O_2$ ; (c) perpendicular and (d) parallel configurations of urea on  $Ti_3C_{2-x}Cu_xO_2$ ; (e) perpendicular and (f) parallel configurations of urea on  $Ti_3C_2O_{2-x}Cu_x$ ; and (g) perpendicular and (h) parallel configurations of urea on  $Ti_3C_2O_2Cu$ .



Figure S7. The density of states (DOS) spectra of metal doped  $Ti_3C_2O_2$ :  $Ti_3C_2O_2Cu$ ,  $Ti_3C_2O_2Co$ ,  $Ti_3C_2O_2Ni$ , and pure  $Ti_3C_2O_2$ .

## S3. Characterizations of XRD and XPS



**Figure S8.** XRD spectra of MAX phase, pristine MXene, and various 3d transition metal functionalized MXenes.





(b) (c) Figure S9. XPS spectra of pristine MXene (a) wide, (b) C 1s, (c) O 1s and (d) Ti 2p.<sup>9</sup>

TiO<sub>2</sub>



Figure S10. XPS spectra of Cu 39.3 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Cu 2p.<sup>10-12</sup>



Figure S11. XPS spectra of Cu 78.6 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Cu 2p. <sup>10-12</sup>



Figure S12. XPS spectra of Ni 39.3 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Ni 2p.<sup>13-14</sup>



Figure S13. XPS spectra of Ni 78.6 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Ni 2p.<sup>13-14</sup>



Figure S14. XPS spectra of Co 39.3 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Co 2p.<sup>15-17</sup>



Figure S15. XPS spectra of Co 39.3 (a) wide, (b) C 1s, (c) O 1s, (d) Ti 2p and (e) Co 2p.<sup>15-17</sup>

#### References

- F. Meng, M. Seredych, C. Chen, V. Gura, S. Mikhalovsky, S. Sandeman, G. Ingavle, T. Ozulumba, L. Miao, B. Anasori, Y. Gogotsi, *ACS. Nano*, 2018, **12 (10)**, 10518-10528.
- 2 R. Maleki, A. Miri Jahromi, S. Mohaghegh, S. Rezvantalab, M. Khedri, L. Tayebi, *Appl. Surf. Sci.* 2021, **566**, 150629.
- 3 M. A. Hope, A. C. Forse, K. J. Griffith, M. R. Lukatskaya, M. Ghidiu, Y. Gogotsi, C.
  P. Grey, *Phys. Chem. Chem. Phys.* 2016, 18 (7), 5099-5102.
- 4 H. Bao, Y. Qiu, X. Peng, J.-a. Wang, Y. Mi, S. Zhao, X. Liu, Y. Liu, R. Cao, L. Zhuo, J. Ren, J. Sun, J. Luo, X. Sun, *Nat. Commun.* 2021, **12** (1), 238.
- 5 Y. H. Chen, M. Y. Qi, Y. H. Li, Z. R. Tang, T. Wang, J. Gong, Y. J. Xu, Cell Rep. Physical. Science, 2021, 2 (3), 100371.
- 6 X. Sheng, S. Li, H. Huang, Y. Zhao, Y. Chen, L. Zhang, D. Xie, J. Mater. Sci. 2021, 56 (6), 4212-4224.
- 7 R. J. Allan, Environ. pollut., Ser. B, Chem. phys. 1980, 1 (3), 217-231.
- 8 T. H. V. Kumar, A. K. Sundramoorthy, *J. Electrochem. Soc.* 2018, **165 (8)**, B3006-B3016.
- 9 J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, M. W. Barsoum, *Appl. Surf. Sci*, 2016, **362**, 406-417.
- 10H. Bao, Y. Qiu, X. Peng, J.-a. Wang, Y. Mi, S. Zhao, X. Liu, Y. Liu, R. Cao, L. Zhuo, J. Ren, J. Sun, J. Luo, X. Sun, *Nat. Commun.* 2021, **12** (1), 238.
- 11 Q. Zhao, C. Zhang, R. Hu, Z. Du, J. Gu, Y. Cui, X. Chen, W. Xu, Z. Cheng, S. Li, B. Li, Y. Liu, W. Chen, C. Liu, J. Shang, L. Song, S. Yang, ACS. Nano, 2021, 15 (3), 4927-4936.
- 12 L. Jin, S. You, Y. Yao, H. Chen, Y. Wang, Y. Liu, J. Mater. Chem. A, 2021, 9 (46), 25964-25973.
- 13 A. Meng, S. Wu, B. Cheng, J. Yu, J. Xu, J. Mater. Chem. A, 2018, 6 (11), 4729-4736.
- 14K. Q. Lu, Y. H. Li, F. Zhang, M. Y. Qi, X. Chen, Z. R. Tang, Y. M. A. Yamada, M. Anpo, M. Conte, Y. J. Xu, *Nat. Commun.* 2020, **11** (1), 5181.
- 15 F. Liang, L. Huang, L. Tian, J. Li, H. Zhang, S. Zhang, *CrystEngComm*, 2018, 20 (17), 2413-2420.
- 16D. Liu, T. Chen, W. Zhu, L. Cui, A. M. Asiri, Q. Lu, X. Sun, *Nanotechnol.* 2016, 27 (33), 33LT01.

17 X. Qiao, J. Jin, H. Fan, L. Cui, S. Ji, Y. Li, S. Liao, Catalysts, 2018, 8 (7), 275.