

Supplementary Information

Role of Terminations and Coordination atoms on the pseudocapacitance of Ti₃CN monolayer

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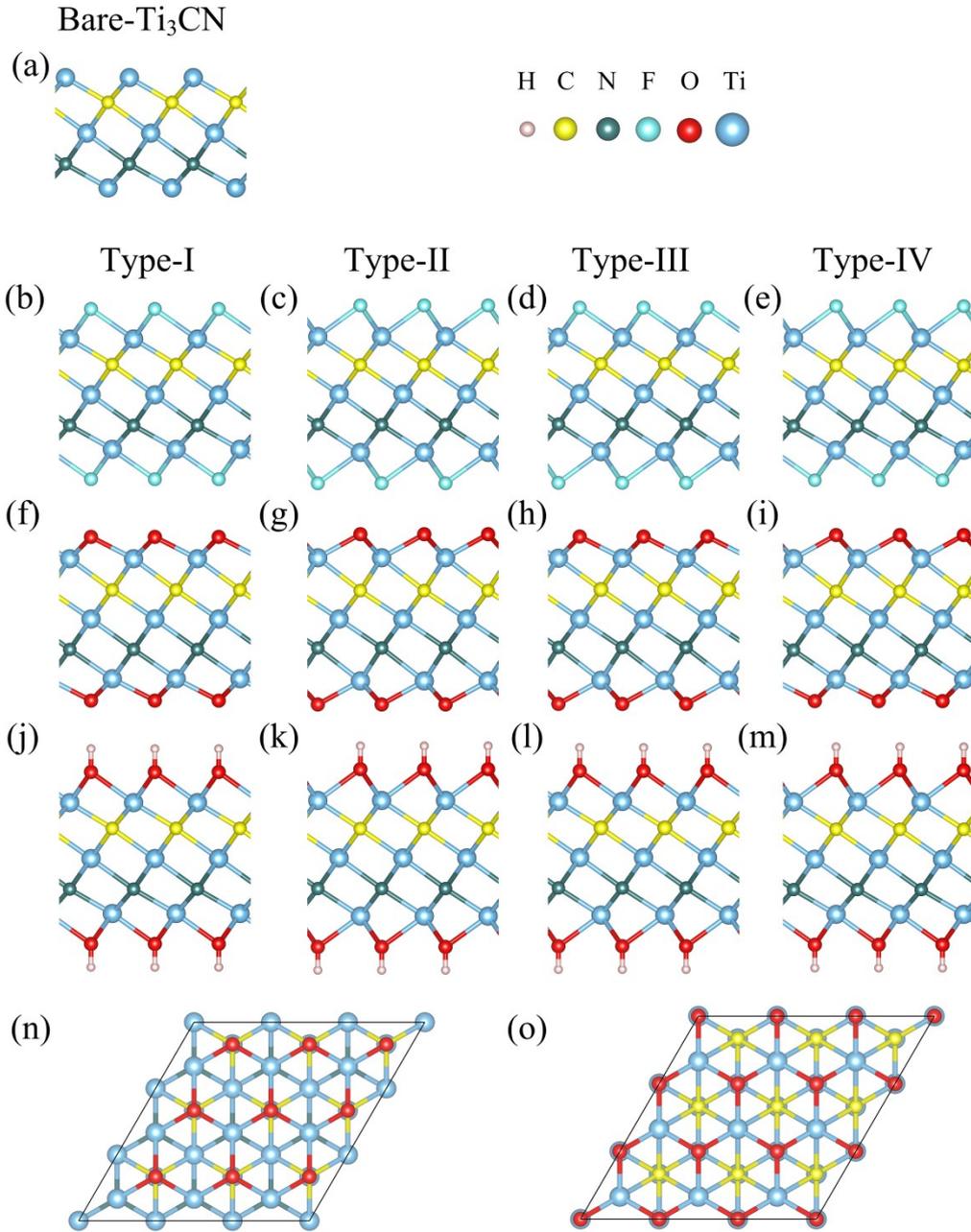


Fig S1 A schematic showing the possible crystal structures of (a) Ti₃CN (b)-(e) type I-IV Ti₃CNF₂, (f)-(i) type I-IV Ti₃CNO₂, (j)-(m) type I-IV Ti₃CN(OH)₂ monolayer with side view. The top view of I-Ti₃CNO₂/ III-Ti₃CNO₂ (n) and II-Ti₃CNO₂/ IV-Ti₃CNO₂ (o) in which the O groups are located above the hollow sites pointing to the C/N and Ti(2) atoms, respectively. III-Ti₃CNO₂ and IV-Ti₃CNO₂ are assorted configurations of I-Ti₃CNO₂, and II-Ti₃CNO₂, in which the O groups are located above the hollow sites pointing to the C/N atoms on one side and the Ti(2) atoms on the other side. The top views of the Ti₃CNF₂ and Ti₃CN(OH)₂ monolayer are similar with that of the Ti₃CNO₂ monolayer.

In order to ascertain the stability of four different Ti_3CNT_2 configurations in the experiments, the formation energy, defined as the difference of total energy of the Ti_3CNT_2 monolayer and the sum of the total energy of the isolated Ti_3CN monolayer and the isolated T_2 gas, is calculated by the following equation ¹:

$$\Delta E = -[E_{tot}(Ti_3CNT_2) - E_{tot}(Ti_3CN) - E(T_2)]$$

Where $E_{tot}(Ti_3CNT_2)$, $E_{tot}(Ti_3CN)$ and $E(T_2)$ are the total energies of terminations adsorbed Ti_3CN , isolated bare Ti_3CN and the total energy of T_2 (T= F or O) gas, respectively. As for the $Ti_3CN(OH)_2$ monolayer, $E(T_2)$ is the sum of the total energy of O_2 and H_2 gas. The results of calculated formation energies are summarized in Table S1. According to the definition of the formation energy, the larger value is, the stronger interaction between the transition metal atom and the attached chemical group shows.

Table S1 The lengths of Ti(1)-C, Ti(2)-N, Ti(1)-T, Ti(2)-T (T = F, O or OH) bond in Ti_3CN , Ti_3CNF_2 , Ti_3CNO_2 , $Ti_3CN(OH)_2$ monolayer and relative formation energies. The units of distance and energy are angstrom (\AA) and eV, respectively.

System	Ti(1)-C/ \AA	Ti(2)-N/ \AA	Ti(1)-T/ \AA	Ti(2)-T/ \AA	$\Delta E/$ eV
Ti_3CN	2.06	2.04	---	---	---
I- Ti_3CNF_2	2.07	2.04	2.17	2.17	-10.62
II- Ti_3CNF_2	2.14	2.12	2.20	2.20	-10.04
III- Ti_3CNF_2	2.09	2.12	2.17	2.20	-10.34
IV- Ti_3CNF_2	2.12	2.04	2.21	2.17	-10.21
I- Ti_3CNO_2	2.20	2.16	1.99	1.99	-10.93

II-Ti ₃ CNO ₂	2.24	2.25	2.03	2.03	-9.45
III-Ti ₃ CNO ₂	2.20	2.24	1.99	2.03	-10.22
IV-Ti ₃ CNO ₂	2.24	2.16	2.03	1.99	-10.21
I-Ti ₃ CN(OH) ₂	2.08	2.05	2.19	2.19	-10.46
II-Ti ₃ CN(OH) ₂	2.13	2.12	2.20	2.20	-10.17
III-Ti ₃ CN(OH) ₂	2.09	2.10	2.19	2.20	-10.34
IV-Ti ₃ CN(OH) ₂	2.11	2.05	2.21	2.17	-10.21

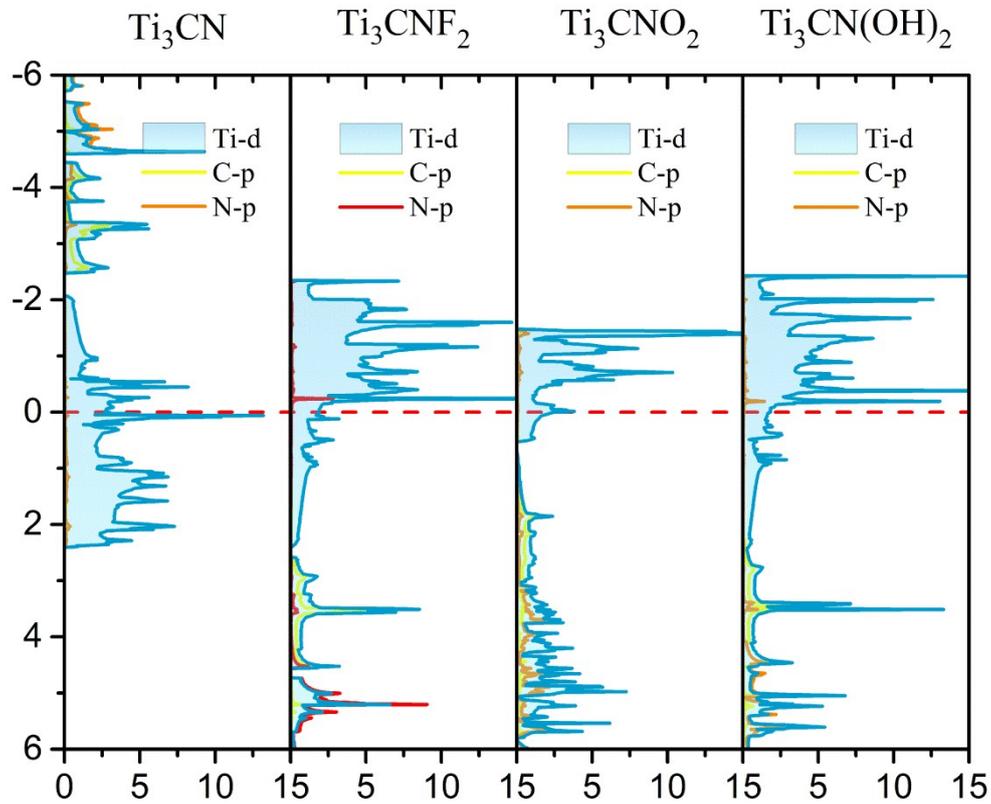


Fig S2 Calculated PDOS near the Fermi level 0 V (a) Ti₃CN, (b) Ti₃CNO₂, (c) Ti₃CNF₂ and (d) Ti₃CN(OH)₂.

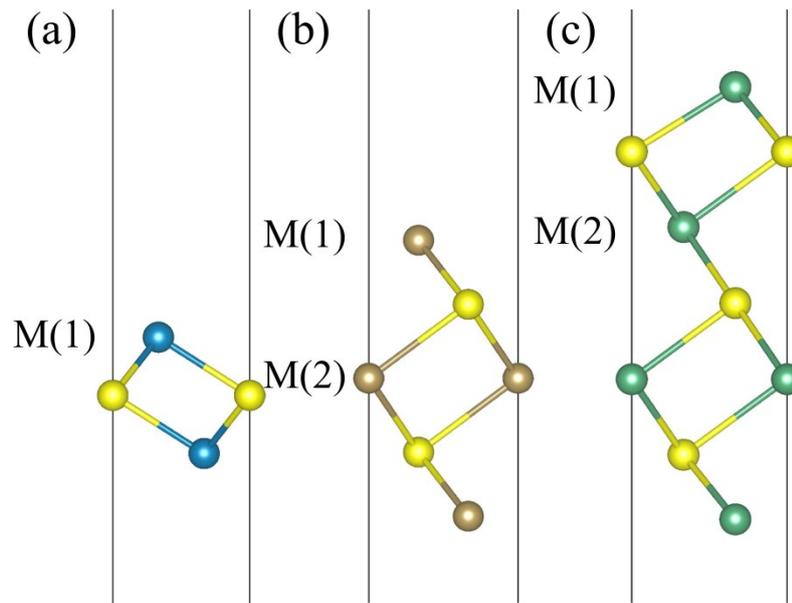


Figure S3: The atomic diagrams show the MXenes with three, five and seven layers: (a) Three-layer MXenes (Cr_2C and Cr_2N), (b) Five-layer MXenes (Ta_3C_2 , Ti_3C_2 and Ti_3N_2) and (c) Seven-layer MXenes (Ta_4C_3 , Nb_4C_3).

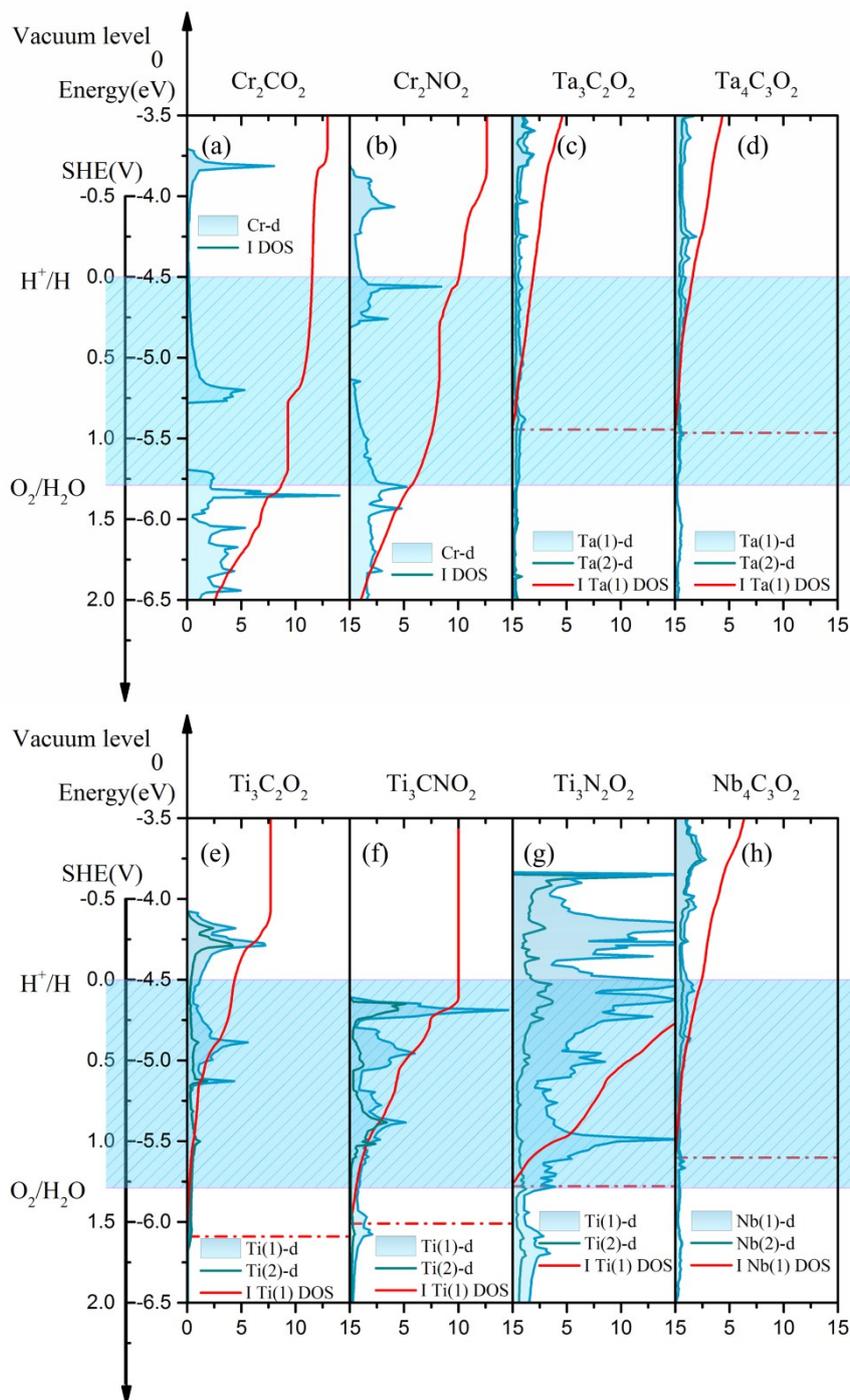


Figure S4: Relative PDOS and integral DOS of the *d*-orbitals of M (M = Cr, Ta, Ti or Nb) atoms referenced to SHE. The M(1) and M(2) are in the coordination environment of 3C/N-M(1)-3O and 3C/N-M(2)-3C/N, respectively. The blue region and cyan line represent the PDOS of M(1) and M(2), and the red line indicates the integral DOS of the *d*-orbitals of Ti(1) atoms aligned to SHE.

Table S2: The total energies of pure and different mixed Ti_3CN configurations. The I configuration represents the Ti_3CN monolayer with pure layers, while the II and III configurations indicate the C/N ratios of the mixed C/N layers are 1:3/3:1 and 2:2/2:2, respectively.

Configurations	I	II	III
Total energy(eV)	-176.88	-177.07	-177.13

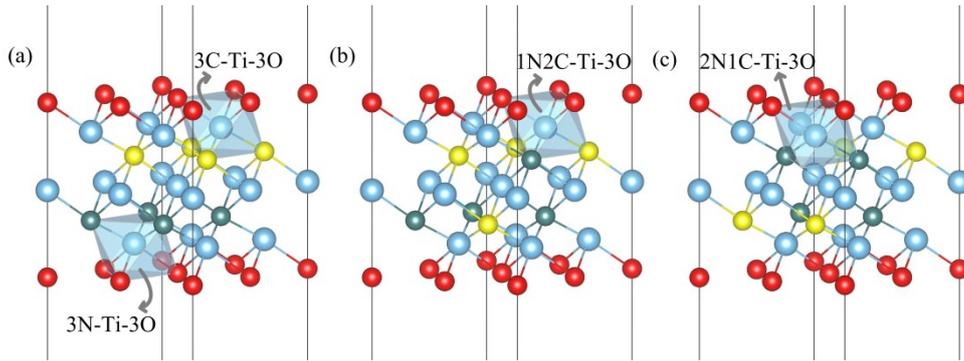


Figure S5 (a) The Ti_3CNO_2 monolayer with pure layers: the Ti atom is coordinated by 3 C atoms and 3 O atoms (3C-Ti-3O) or by 3 N atoms and 3 O atoms (3N-Ti-3O), (b) The Ti_3CNO_2 monolayer with mixed layers (C/N=1:3 or 3:1): the Ti atom is coordinated by 1 N atom, 2 C atoms and 3 O atoms (1N2C-Ti-3O), (c) The Ti_3CNO_2 monolayer with mixed layers (C/N=2:2): the Ti atom is coordinated by 2 N atoms, 1 C atom and 3 O atoms (2N1C-Ti-3O).

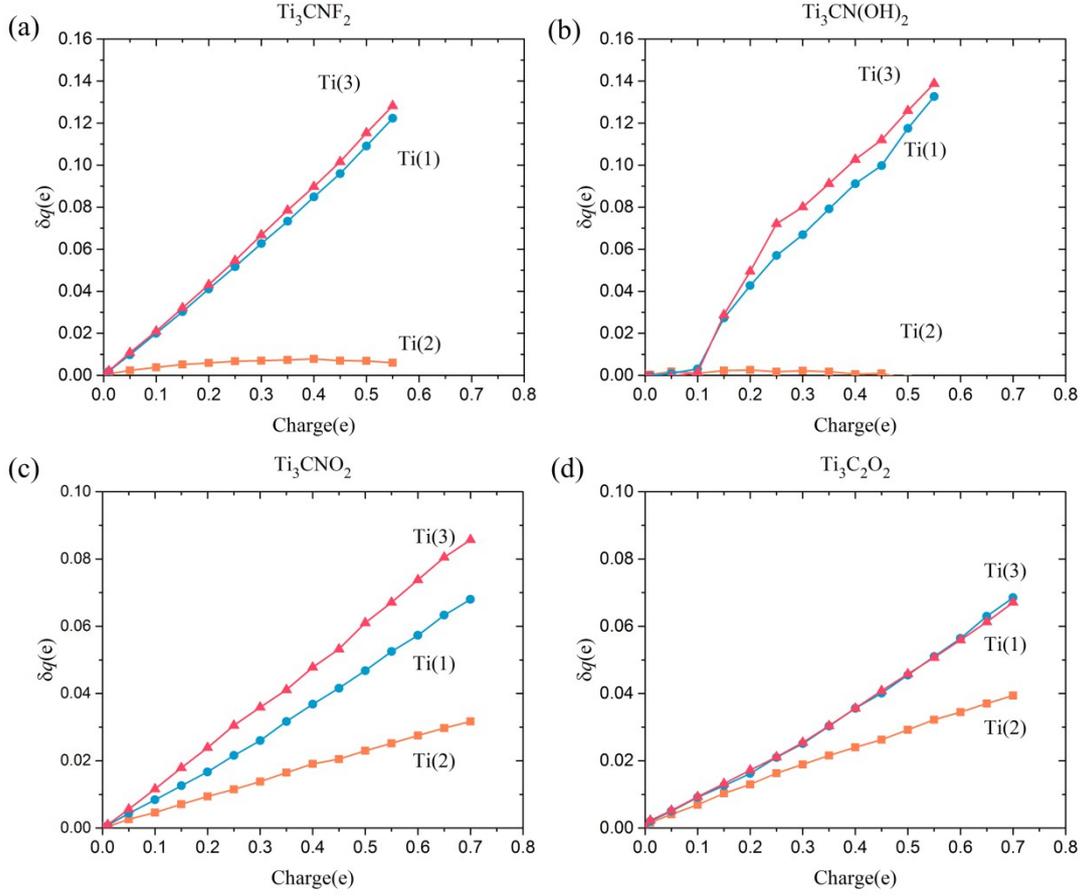


Figure S6 The accessory electrons of Ti atoms in (a) Ti₃CNF₂, (b) Ti₃CN(OH)₂, (c) Ti₃CNO₂ and (d) Ti₃C₂O₂ monolayer when charging the system with electrons.

The details of the relation of Fermi level and electron charge

Following the theoretical calculation,² the states-filling energy can be view as

$$W_{filling} = \int_{\varepsilon_{fermi}}^{\varepsilon'} \varepsilon D(\varepsilon) d\varepsilon ,$$

where ε is the Kohn-Sham (KS) energy, ε_{fermi} is the Fermi level and $D(\varepsilon)$ is the density of states. ε' satisfies the charge-conservation criterion:

$$\int_{\varepsilon_{fermi}}^{\varepsilon'} D(\varepsilon) d\varepsilon = \delta q ,$$

where δq is the charge electrons.

It can be indicated that when the Fermi level is higher, the $W_{filling}$ will become bigger, in other words, the electrons may become harder to charged. To evaluate the electron

charge, the similar Fermi level is needed.

In the mixed system (Ti_3CNT_x), the O terminated Ti atoms would obtain electron easier than the F terminated Ti atoms since the Fermi level of Ti_3CNO_2 (-6.01 eV referenced to vacuum level) is lower than Ti_3CNF_2 (-4.91 eV referenced to vacuum level). When the Fermi level is higher than -4.5 eV,^{3, 4} the relative system may cannot obtain the electrons due to the redox reaction of H^+/H_2 . Thus, the $\text{Ti}_3\text{CN}(\text{OH})_2$ (-1.82 eV referenced to vacuum level) may cannot be charged in the mixed system. The similar Fermi levels of Ti_3CNO_2 (-6.01 eV referenced to vacuum level) and $\text{Ti}_3\text{C}_2\text{O}_2$ (-6.09 eV referenced to vacuum level) bring convenience to compare the charge storage of Ti atoms in Ti_3CNO_2 and $\text{Ti}_3\text{C}_2\text{O}_2$.

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The details of the relation of the dipole moments and work function

Following the theoretical method developed by Leung,⁵ the electron charge transfer [$\Delta\rho$] between the adsorbates and the substrate is defined as

$$\Delta\rho(z) = \rho(z) - [\rho_s(z) + \rho_t(z)],$$

where $\rho(z)$, $\rho_s(z)$ and $\rho_t(z)$ are the total charge densities of the functionalized system, the substrate, and the termination, respectively. Computationally, $\Delta\rho$ is generated from a total energy calculation of the substrate by removing the overlayer of terminations from the functionalized Ti_3CN without the structural optimization. Similarly, $\rho_t(z)$ is obtained from a total energy calculation of the termination layer by removing the substrate from the functionalized Ti_3CN . Thereby, the surface dipole moments induced by charge rearrangement can be expressed by

$$\Delta p(z) = \int_{z_0}^z z \Delta \rho(z) dz ,$$

where z_0 is the center of substrate (Ti₃CN monolayer). Then, we get

$$\Delta p = p - (p_s + p_t)$$

where p_s is the surface dipole density of the Ti₃CN substrate and p_t is the surface dipole density of the free-standing termination layer. Due to the symmetry of the charge density of the freestanding overlayer, ρ_t is equal to zero. Thereby, the change in the total dipole moment (ΔP) by functionalization can be expressed as

$$\Delta P = p - p_0 = \Delta p + p_s + p_t - p_0 ,$$

Then, the change of the work function induced by the terminations is given by the following expression:

$$\Delta \phi = -\frac{e}{\epsilon_0} \Delta P = -\frac{e}{\epsilon_0} [\Delta p + (p_s - p_0)] .$$

Therefore, $\Delta \phi$ is affected by the dipole moment of the transferred charges (Δp) between the substrate and the termination, and the change in the dipole moments due to substrate relaxation ($p_s - p_0$). The contribution of the structure relaxation is usually smaller than that of the charge rearrangement ⁵. However, in OH terminated MXenes, the contribution of the structure relaxation cannot be ignored ⁶.

References

1. M. Khazaei, M. Arai, T. Sasaki, C.-Y. Chung, N. S. Venkataramanan, M. Estili, Y. Sakka and Y. Kawazoe, *Advanced Functional Materials*, 2013, **23**, 2185-2192.
2. Y. Liu, Y. M. Wang, B. I. Yakobson and B. C. Wood, *Physical review letters*,

- 2014, **113**, 028304.
3. S. Morishita and K.-i. Suzuki, *Bulletin of the Chemical Society of Japan*, 1994, **67**, 843-846.
 4. S. Licht, A. J. Bard and M. Stratmann, Semiconductor electrodes and Photoelectrochemistry, *Encyclopedia of Electrochemistry*, vol. 6, 2002.
 5. T. C. Leung, C. L. Kao, W. S. Su, Y. J. Feng and C. T. Chan, *Physical Review B*, 2003, **68**.
 6. W. Li, Y. Yang, G. Zhang and Y. W. Zhang, *Nano Lett*, 2015, **15**, 1691-1697.