## Support cooperative single atom on Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub> for efficient electrochemical CO<sub>2</sub> reduction: A DFT study

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Gibbs free energy of reaction for  $CO_2$  RR elementary steps involving (H<sup>+</sup> + e<sup>-</sup>) pair transfer was calculated using computational hydrogen electrode (CHE) model by Nørskov et al., defined as  $\Delta G_n(U) = \Delta G_n(U=0) + \text{neU}$ , where n is the number of (H<sup>+</sup> + e<sup>-</sup>) pairs transferred in CO<sub>2</sub> RR, e is the unit charge and U is the electrode potential versus the reversible hydrogen electrode (RHE). At U=0 V,  $\Delta G_n = \Delta E_n - T\Delta S + \Delta ZPE$  $+\Delta E_{sol} + \Delta G_{pH}$ , where  $\Delta E_n$  is DFT-calculated reaction energy in vacuum, T $\Delta S$  is the entropy contributions to the reaction at T=298K,  $\Delta ZPE$  is zero-point energy (ZPE) correction based on the calculated vibrational frequencies,  $\Delta E_{sol}$  represents the correction of  $H_2O$  solvation effect at the water-solid interface, and  $\Delta G_{pH}$  represents the correction of the free energy due to the variations in  $\mathrm{H^{+}}$  concentration, defined as  $\mathrm{G}_{\mathrm{pH}}$  $= -kT \ln[H^+] = kT \ln 10 \times pH$ , and the value of pH was set to 0 for strong acidic medium in this work and therefore, the calculated limiting potentials  $(U_L)$  were referenced to the RHE. Implicit model was used for treating  $H_2O$  solvation effect, where  $\Delta E_{sol}$  was accounted for depending on OH-containing species and their binding situations2: \*R-OH bound to M directly/indirectly through hydroxyl is stabilized by approximately 0.5eV/0.25eV, respectively, and those containing no hydroxyl (e.g., \*CO, \*CHO, \*CH<sub>2</sub>O, \*CH<sub>3</sub>O, CH<sub>x</sub>) were stabilized approximately by 0.1eV. The limiting potential  $(U_L)$  is obtained from the maximum free energy change ( $\Delta G_{max}$ ) among all elementary steps along the lowest-energy pathway by using the relation of  $U_L = -\Delta G_{max}/e$ .

The entropies of the gaseous molecules were taken from the NIST Chemistry WebBook [1] and the zero-point energy (ZPE) was calculated according to:

$$E_{ZPE} = \sum_{i=1}^{3N} \frac{hv_i}{2}$$

The entropy change for adsorbed intermediates was calculated within the harmonic approximation:

$$\Delta S_{ads}(0 \to T, P^0) = S_{vib} = \sum_{i=1}^{3N} \left[ \frac{N_A h v_i}{\frac{h v_i}{k_B T} - Rln(1 - e^{-h v_i} / k_B T)} \right]$$

Where vi is DFT-calculated normal-mode frequency for species of 3N degree of

freedom (N=number of atoms) adsorbed on M@MoS<sub>2</sub> SACs, N<sub>A</sub> is the Avogadro's constant ( $6.022 \times 10^{23}$  mol<sup>-1</sup>), h is the Planck's constant ( $6.626 \times 10^{-34}$ Js), and k<sub>B</sub> is the Boltzmann constant ( $1.38 \times 10^{-23}$  JK<sup>-1</sup>), R is the ideal gas constant (8.314 J K<sup>-1</sup>mol<sup>-1</sup>), and T is the system temperature, and T=298.15K in this work.

Table S1. Binding energy ( $E_b$ ), O-C-O angles, bond length and Bader charge of  $CO_2$  adsorbed on M@Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub> in the most stable configuration.

Catalysts	E <sub>b</sub> (eV)	Angle(°)	C(O)-M (Å)	C-O (Å)	Bader(e <sup>-</sup> )
$Sc@Ti_{3-x}C_2O_y$	-0.89	130.6	2.36	1.22 1.31	-1.58
Y@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.69	180.0	2.48	1.16 1.19	-1.53
$Mn@Ti_{3-x}C_2O_y$	-2.10	124.4	1.90	1.20 1.46	-0.87
Fe@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.32	126.9	1.91	1.22 1.35	-0.56
Co@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.06	131.0	1.87	1.26 1.29	-0.41
Ni@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.74	132.9	1.93	1.22 1.30	-0.34
Cu@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.37	129.3	2.00	1.21 1.32	-0.34
Ru@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.37	127.8	2.02	1.20 1.40	-0.37
Rh@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.90	131.0	2.06	1.22 1.32	-0.07
$Pd@Ti_{3-x}C_2O_y$	-0.50	135.2	2.09	1.21 1.29	0.02
Ag@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.27	180.0	3.16	1.18 1.18	-0.05
Os@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.64	124.8	2.03	1.20 1.45	-0.38
Ir@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.09	127.5	2.08	1.21 1.34	0.02
Pt@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.71	129.1	2.10	1.21 1.33	0.22
Au@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.31	180	3.35	1.17 1.18	0.33

Table S2. Adsorption energy (in eV) of \*O on M@Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub>(M=Cr, V, Cu, Au).

Catalysts	*0
Cr@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-3.83
V@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-4.00
$Cu@Ti_{3-x}C_2O_y$	-2.92
$Au@Ti_{3-x}C_2O_y$	-2.78

Table S3. Adsorption energy (in eV) of \*CO, \*CHO, \*CH<sub>2</sub>O, \*HCOOH, \*CH<sub>3</sub>OH and \*H<sub>2</sub>O on  $M(N_X)@Ti_{3-x}C_2O_y$  SACs calculated using their corresponding gas-phase energy as the reference.

Catalysts	*CO	*CHO	*CH <sub>2</sub> O	*HCOOH	*CH <sub>3</sub> OH	*H <sub>2</sub> O
Sc@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.97	-3.41	-2.59	-1.76	-1.64	-1.27
Y@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.68	-2.86	-2.10	-2.98	-1.59	-1.52
Mn@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.55	-3.49	-2.65	-1.06	-1.44	-1.11

Fe@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.55	-3.52	-2.49	-1.46	-1.47	-1.03
Co@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.28	-3.14	-2.11	-1.24	-1.49	-1.16
Ni@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.75	-2.59	-1.64	-1.02	-1.49	-1.15
Cu@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.17	-2.27	-1.51	-1.05	-1.48	-1.14
Ru@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.76	-3.61	-2.70	-1.07	-1.43	-1.10
Rh@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.28	-3.02	-2.12	-1.10	-1.42	-1.10
$Pd@Ti_{3-x}C_2O_y$	-1.67	-2.51	-1.53	-0.96	-1.40	-1.08
Ag@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.94	-2.07	-1.37	-0.95	-1.33	-1.03
Os@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-3.17	-3.97	-2.94	-0.99	-1.38	-1.13
Ir@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.68	-3.39	-2.31	-1.00	-1.38	-1.10
Pt@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.07	-2.98	-1.76	-1.07	-1.36	-1.07
$Au@Ti_{3-x}C_2O_y$	-1.26	-2.63	-1.79	-0.82	-1.29	-1.02
FeN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.66	-3.51	-2.56	-1.50	-1.48	-1.10
CoN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.30	-3.04	-2.16	-1.26	-1.46	-1.13
NiN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-1.85	-2.65	-1.73	-1.19	-1.47	-1.13
$CuN@Ti_{3-x}C_2O_y$	-1.23	-2.51	-1.79	-1.27	-1.45	-0.11
$FeN_2$ $@Ti_{3-x}C_2O_y$	-2.71	-3.45	-2.55	-1.12	-1.47	-1.13
$CoN_2$ $@Ti_{3-x}C_2O_y$	-2.34	-3.13	-1.99	-1.19	-1.49	-1.15
NiN2@Ti3-xC2Oy	-1.91	-2.81	-1.88	-1.04	-1.48	-1.14
$CuN_2 @Ti_{3-x}C_2O_y$	-1.29	-2.65	-2.10	-1.09	-1.46	-1.13
FeN3@Ti3-xC2Oy	-2.71	-3.49	-2.59	-0.99	-1.49	-1.14
$CoN_3$ ( $a$ $Ti_{3-x}C_2O_y$	-2.34	-3.07	-2.06	-1.02	-1.46	-1.13
NiN3@Ti3-xC2Oy	-2.01	-2.88	-2.08	-1.07	-1.46	-1.12
$CuN_3@Ti_{3-x}C_2O_y$	-1.36	-2.75	-2.32	-1.11	-1.44	-1.10

Catalyst	$U_{L}(CO_{2}RR)$	U <sub>L</sub> (HER)	$U_{L}(CO_{2}RR)$
	(V)	(V)	- U <sub>L</sub> (HER)
Fe@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.42	-0.43	0.01
FeN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.53	-0.47	-0.06
FeN <sub>2</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.66	-0.45	-0.21
FeN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.61	-0.52	-0.09
Co@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.49	-0.27	-0.22
CoN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.62	-0.23	-0.39
CoN <sub>2</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.58	-0.25	-0.33
CoN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.63	-0.29	-0.34
Ni@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.51	-0.02	-0.49
NiN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.59	-0.06	-0.53
NiN <sub>2</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.42	-0.11	-0.31
NiN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.53	-0.23	-0.3
Cu@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.23	-0.12	-0.11
CuN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.35	-0.12	-0.23
CuN <sub>2</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.29	-0.14	-0.15
$CuN_3 @Ti_{3-x}C_2O_y$	-0.43	-0.29	-0.14

Table S4. The difference between the limiting potentials for the HER and CO<sub>2</sub>RR on  $M@Ti_{3-x}C_2O_y$ ,  $MN@Ti_{3-x}C_2O_y$ ,  $MN_2@Ti_{3-x}C_2O_y$  and  $MN_3@Ti_{3-x}C_2O_y$ .

Table S5. The data of \*CO and \*CHO adsorption energy, Bader charge analysis and d-band center.

Catalysts	*CO	*CHO	d-band center	Bader(e-)
Fe@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.55	-3.52	-1.50	-0.45
FeN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.66	-3.51	-1.33	-0.46
FeN2@Ti3-xC2Oy	-2.71	-3.45	-1.12	-0.40
FeN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-2.71	-3.49	-1.09	-0.44

Table S6. The adsorption energy of \*H and Bader charge analysis of nitrogen doping  $M@Ti_{3-x}C_2O_{y}$ .

Catalysts	*Н	Bader(e-)
Fe@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.75	-0.49
FeN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.80	-0.52
$FeN_2$ ( $i_{3-x}C_2O_y$	-0.77	-0.52
$FeN_3$ ( $aTi_{3-x}C_2O_y$	-0.85	-0.51
Co@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.60	-0.35
CoN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.56	-0.36
$CoN_2$ $@Ti_{3-x}C_2O_y$	-0.57	-0.35
$CoN_3$ @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.61	-0.39
$Ni@Ti_{3-x}C_2O_y$	-0.30	-0.28

NiN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.38	-0.30
NiN <sub>2</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.43	-0.32
NiN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.55	-0.35
Cu@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.19	-0.37
CuN@Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.43	-0.37
CuN2@Ti3-xC2Oy	-0.45	-0.42
CuN <sub>3</sub> @Ti <sub>3-x</sub> C <sub>2</sub> O <sub>y</sub>	-0.60	-0.45



Fig. S1 The side views of CO<sub>2</sub> adsorbed on  $Cr@Ti_{3-x}C_2O_y$ ,  $V@Ti_{3-x}C_2O_y$  and  $Cu@Ti_{3-x}C_2O_y$ .







Fig. S2. Free energy diagrams for the  $CO_2$  reduction reaction on  $M@Ti_{3-x}C_2O_y$  (M = Sc, Y, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au).



Fig. S3. Free energy diagram of the CO<sub>2</sub>RR on MN@Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub>, MN<sub>2</sub>@Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub> and MN<sub>3</sub>@Ti<sub>3-x</sub>C<sub>2</sub>O<sub>y</sub> (M=Fe, Co, Ni, Cu)



Fig. S4. Linear relationship among the binding energies of key intermediates \*CO, \*CHO, and \*COOH.