Supplementary Information (SI)

TiC_2: A New Two Dimensional Sheet beyond MXenes

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1. Candidate structures of C_2 containing TiC_2

By depositing C_2 dimers on the surface of a monolayer triangular Ti lattice, we obtain three candidate structures of the 2D TiC_2 sheet.

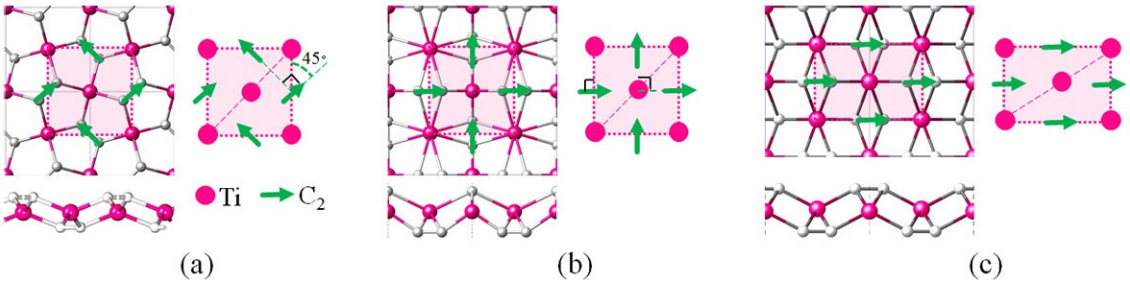

Fig. S1 C_2 dimers inserted at different positions and with different orientations on the surface of a triangular Ti lattice. (a) C_2 dimers bind to Ti atoms in EOC mode, and perpendicular to the nearest neighboring C_2 dimers; (b) C_2 dimers bind to Ti atoms in both SOC and EOC modes, and perpendicular to the near neighboring C_2 dimers; (c) C_2 dimers bind to Ti atoms in both SOC and EOC modes, but are all parallelly aligned.

2. Stability relative to the 2D TiC_2 isomeric structures

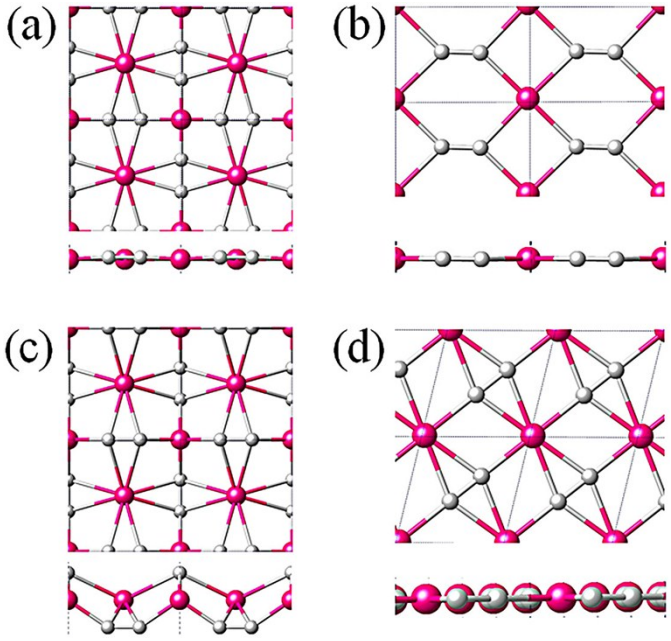

Fig. S2 Two energetically low-lying structural isomers of TiC_2 containing C_2 units. (a) and (b) are the initial structures; (c) and (d) are the corresponding optimized structures, respectively.

3. Stability relative to other Ti-C compounds

For comparison, we calculated the cohesive energy of TiC_2, Ti_3C_2 (MXene), bulk TiC, and some other Ti-C binary compounds. To gauge the relative stability of a compound with the composition of Ti_xC_{1-x}, using the method described by Zhang et al. [1], we define its molar formation energy δF as

$$\delta F\left(Ti_xC_{1-x}\right) = E_{coh}\left(Ti_xC_{1-x}\right) - x\mu_{Ti} - \left(1\text{-}x\right)\mu_C \quad \backslash^* \text{ MERGEFORMAT (1)}$$

where $E_{coh}(x)$ is the cohesive energy of the system, μ_{Ti} and μ_C are the chemical potentials of the Ti and C atoms, respectively. The relative stability of different Ti_xC_{1-x} structures can be gauged by comparing their δF: higher δF means inferior stability. We here set μ_C and μ_{Ti} as the cohesive

energy of graphene and bulk *hcp* Ti. The results are summarized in Figure S3. A line connecting the cohesive energy of graphene and bulk Ti is used to estimate the stability of a Ti-C compound: a structure with cohesive energy below the line (δF<=0) is stable against discomposing into graphene and Ti; when δF>0, the structure becomes metastable or even unstable. The recently predicted single-layer t-TiC[1] has a positive δF and hence is metastable. In contrast, the TiC_2 structure in our work has a negative δF, -0.40 eV, indicating a thermodynamically stability. The experimentally identified bulk TiC and 2D MXene (Ti_3C_2 and Ti_2C) also have negative δF. One should note that some Ti-C clusters, even though with positive δF, have been experimentally synthesized.[2,3] Therefore, the single-layer TiC_2 is thermodynamically favorable and may be formed when suitable synthetic conditions are provided.

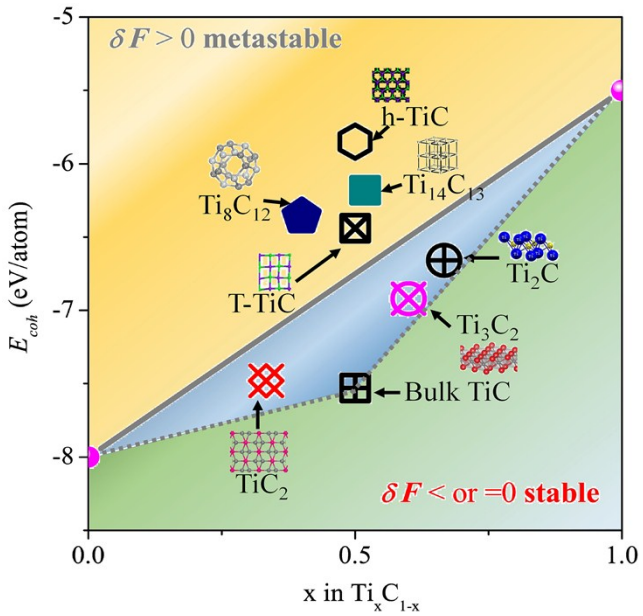

Fig. S3 Cohesive energy for binary compounds with composition Ti_xC_{1-x}. The solid line links cohesive energies of graphene (x =0) and bulk Ti (x=1). Formation energy δF is positive (negative) above (below) the solid line.

4. Stability relative to other isostructural metal carbides

We replace the Ti atoms in TiC_2 sheet with other 3d transition metal atoms forming a series of 2D MC_2 metal carbides. All structures are fully relaxed, and their cohesive energy are calculated as presented in Figure S4, which shows that TiC_2 has the largest cohesive energy, indicating Ti atoms bind most strongly with C_2 dimers in such structure.

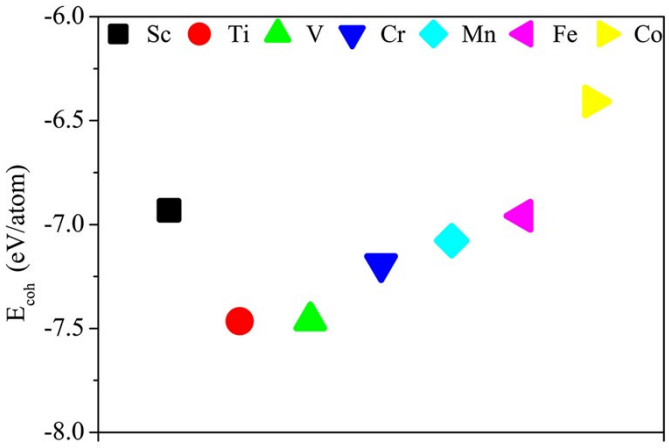

Fig. S4 Cohesive energy of 2D transition metal dicarbides MC_2 (M=Sc-Co) in the TiC_2 structure.

5. Thermal stability of the TiC_2 sheet

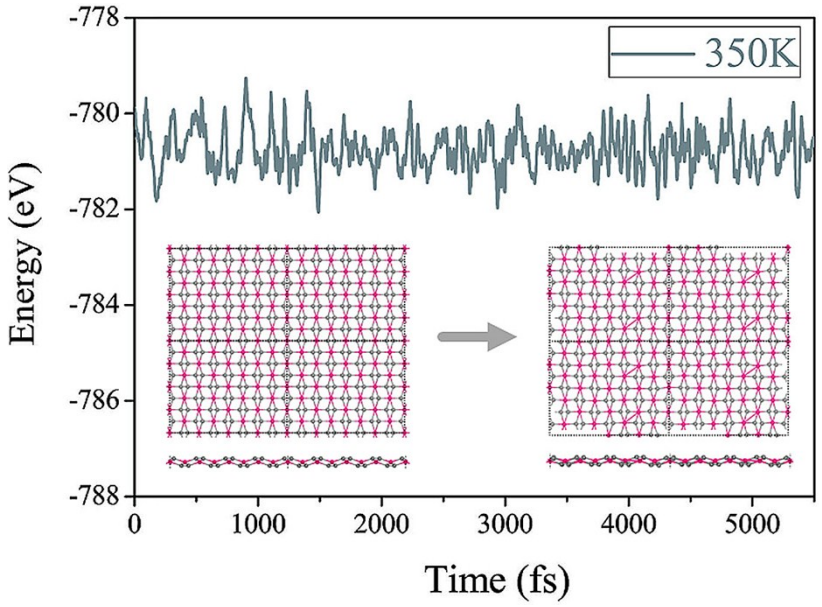

Fig. S5 Evolution of potential energy of TiC_2 during AIMD simulations at 350 K. 4×4×1 supercell is used to reduce the constraint of periodic condition in the axial direction. The insets show snapshots of atomic configurations at the beginning and the end of the simulations.

6. Electronic Properties of the TiC_2 sheet

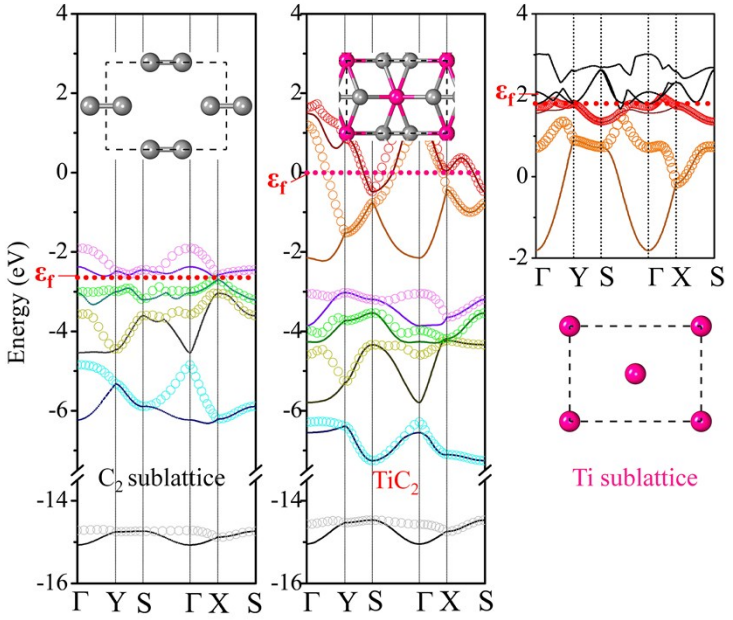

Fig. S6 Band structure of the TiC_2 sheet (center panel), the C_2 sublattice (left panel), and Ti sublattice (right panel). The high symmetric k point path is along Γ (0, 0, 0) → Y (0, 1/2, 0) →

S (1/2, 1/2, 0) → Γ (0, 0, 0) → X (1/2, 0, 0) → S (1/2, 1/2, 0), corresponding to the axial direction in the real space.

7. Application of the TiC_2 sheet as Li ion battery anode material

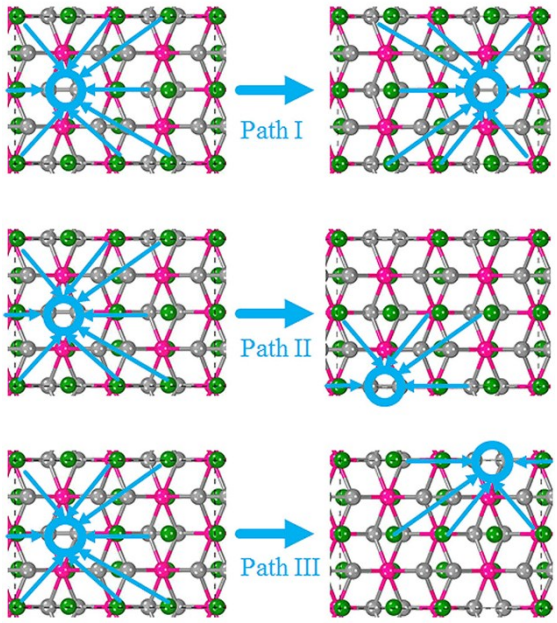

Fig. S7 Considered migration paths of a Li "monovacancy" on the TiC_2 sheet with the high coverage of TiC_2Li_2.

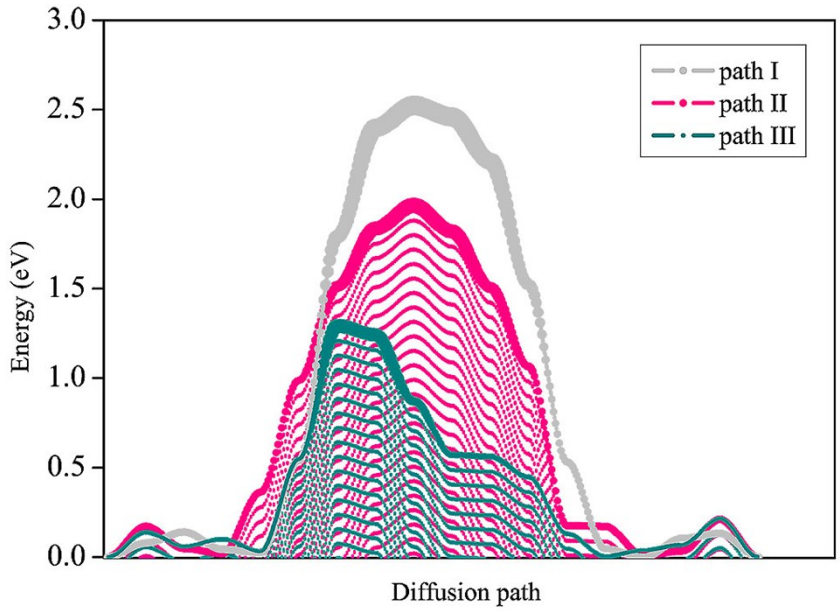

Fig. S8 The energy barrier profiles of Li diffusion on TiC_2 with the high coverage of TiC_2Li_2. The diffusion paths have been indicated in Figure S7.

Calculation Details: Estimation of the open circuit voltage (OCV)

Typically, the anode charge/discharge processes assume the following half-cell reaction that involves Li/Li^+:

$$TiC_2 + xLi^+ + xe^- \text{ Æ } TiC_2Li_x \qquad \text{* MERGEFORMAT (1)}$$

The (OCV) for an intercalation reaction involving x Li^+ ions is computed from the energy difference of the products and the reactants.

The electronic potential during this process can be written in the form of Gibbs free energy:

$$V = -\Delta G_f / zF \qquad \text{* MERGEFORMAT (2)}$$

where z and F are the number of valence electrons during the adatom process and the Faraday constant, respectively; ΔG_f is the change in Gibbs free energy during the adatom

process which is defined as:

$$\Delta G_f = \Delta E_f + P\Delta V_f - T\Delta S_f \quad \backslash* \text{ MERGEFORMAT (3)}$$

$P\Delta V_f$ is on the order of 10^{-5} eV and the term $T\Delta S_f$ is comparable to 26 meV at low temperature.[4,5] Thus, the entropy (thermal) effects and pressure terms are negligible, and will not be discussed further.ΔG_f is then approximately equal to the formation energy, ΔE_f, involved in the adsorption process, which is defined as:

$$\Delta E_f = E\left(TiC_2Li_x\right) - E\left(TiC_2\right) - xE\left(Li\right) \backslash* \text{ MERGEFORMAT (4)}$$

Here E (TiC_2) denotes the total energy of pristine TiC_2 monolayer, E (Li) and E (TiC_2Li_x) are the total energy of bulk bcc Li and the lithiated TiC_2 sheet (x Li atoms adsorbed in one supercell), respectively. The OCV is related to the formation energy by:

$$OCV = \Delta G_f / x \approx \Delta E_f / x = \left[E\left(TiC_2\right) + xE\left(Li\right) - E\left(TiC_2Li_x\right)\right] / x \ \backslash*$$

MERGEFORMAT (5)

References

1. Z. Zhang, X. Liu, B. I. Yakobson and W. Guo, *J. Am. Chem. Soc*., 2012, **134,** 19326- 19329.

2. B. C. Guo, K. P. Kerns and A. W. Castleman, *Science*, 1992, **255**, 1411-1413.

3. J.S.Pilgrim and M.A.Duncan, *J. Am. Chem. Soc*., 1993, **115**, 9724-9727.

4. M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho and J. Joannopoulos, *Phys. Rev. B*, 1997, **56**, 1354-1365.

5. A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse and J. Hafner, *Phys. Rev. B*, 1998, **58**, 2975-2987.