Support information

SynthesisandElectrochemicalPropertiesofTwo-Dimensional Hafnium Carbide

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Figure S1 The EDS results of (a) as-synthesized $Hf_3[Al(Si)]_4C_6$ powders (molar ratio of Hf:Al:Si:C approximate 3:3.89:0.14:5.85), and (b) the HF-etched powders (molar ration of Hf:C:O:F:Al approximate 3:2.2:1.33:0.34:1.29), both obtained from an area of about 2000 μ m², (c) EDS results of delaminated $Hf_3C_2T_z$ flakes shown in Figure 1d, insets are the aqueous suspension of delaminated $Hf_3C_2T_z$ flakes with laser beam showing the Tyndall scattering effect.



Figure S2 High-resolution XPS spectra of samples before and after etching treatment in the Hf 4f region.

As shown in Figure S2, the Hf 4f region for the as-prepared Hf₃[Al(Si)]₄C₆ powders was fit by three components: Hf-C bond (30.4% of Hf 4f photoemission; 14.2 eV, Hf 4f_{7/2}; 15.9 eV, Hf 4f_{5/2}), partially oxidized Hf-O bond (3.5% of Hf 4f photoemission; 15.3eV, Hf 4f_{7/2}; 17.0 eV, Hf 4f_{5/2}), Hf-O bond (66.1% of Hf 4f photoemission; 16.8eV, Hf 4f_{7/2}; 18.5 eV, Hf 4f_{5/2}), and which match previous work on HfC.^{1, 2} After HF treatment, the fitted results of XPS spectrum in the Hf 4f region consistently show the presence of mixed C-Hf-O_x-F_y bond (71.5% of Hf 4f photoemission; 16.9 eV, Hf 4f_{7/2}; 18.6 eV, Hf 4f_{5/2}),^{2, 3} C-Hf-T_z bond (23.4% of Hf 4f photoemission; 14.2eV, Hf 4f_{7/2}; 15.9 eV, Hf 4f_{5/2}),¹ and C-Hf-F_x bond (5.1% of Hf 4f photoemission; 18.2 eV, Hf 4f_{7/2}; 19.9 eV, Hf 4f_{5/2}) (Figure S2).^{1, 2, 4} In addition, the

corresponding fitted results in the O 1s region further confirm the presence of mixed C-Hf-F_x-O_y bond (81.6% of O 1s photoemission; 532.2 eV),^{2, 3} Hf-O bond (10.2% of O 1s photoemission; 530.0 eV),¹ and absorbed water molecular (Hf₃C₂OH-H₂O, 8.2% of O 1s photoemission; 533.8 eV)^{4, 5} in etched samples (Figure S3), which indicates the possible formation of Hf₃C₂ with mixed F, O, and OH surface termination.^{3, 4}



Figure S3 High-resolution XPS spectra of samples before and after etching treatment in the O 1s region.



Figure S4 High-resolution XPS spectra of samples before and after etching treatment in the C 1s region.

The C 1s region for samples before and after etching treatment, was fit by the components shown in Figure S4. Before treatment, this region was fit by components corresponding to C-Hf,¹ C-Al(Si),⁶ graphitic carbon (C-C),^{4, 7} CH_x,⁷ C-O,⁷ and a component arising from carboxyl groups.⁷ Among them, the content corresponding to C in Hf₃[Al(Si)]₄C₆ is about 27.9% (C-Hf

bond, 7.6% of C 1s photoemission, 281.4 eV; C-Al(Si) bond, 20.3% of C 1s photoemission, 283.8eV), and the other four peaks can be ascribed to possible adventitious contamination.^{3,4} In the case of the etched powders, the C 1s region was fit by the following seven components, a low-binding energy peak (4.4% of C 1s photoemission, 281.8 eV) that corresponds to C-Hf-T_z bond in Hf₃C₂T_z MXenes,¹ its energy is slightly higher than that of C in as-prepared $Hf_3[Al(Si)]_4C_6$ (281.4 eV) (Figure S2), this can possibly be attributed to defects introduced in the Hf-C layers due to the etching procedure,⁴ and similar results have been obtained in the case of Ti₃C₂T₂ MXenes.⁴ It followed by a peak (11.7% of C 1s photoemission, 283.9eV) corresponding to C-Al(Si) bond,⁶ and the fraction of C-Al(Si) bond, decrease from 20.29% to 11.74% after HF treatment, indicating the possibly selective etching of Al(Si)-C unit during the HF treatment. Then a large contribution to this region is graphitic C-C bond (39.7% of C 1s photoemission, 284.8 eV),⁷ which could be due to partially dissolution of Hf during the selective etching process and/or adventitious contamination.⁴ With another three peaks (CH_x bond, 6.72% of C 1s photoemission, 285.5 eV; C-O bond, 22.62% of C 1s photoemission, 286.5 eV; carboxyl groups, 6.7% of C 1s photoemission, 288.7 eV) corresponding to contamination of absorbed solvents used in the washing and drying processes.⁷ A high binding energy peak (C-F bond, 7.9% of C 1s photoemission, 292.2eV) can be attributed to the dissolution of plastic container and/or the contamination of PVDF membrane. In both cases, the relatively large amount of contamination and relative low intensity of the $Hf_3C_2T_z$ signal might be related to the lack of Ar etching.



Figure S5 High-resolution XPS spectra of samples before and after etching treatment in the (a) Al 2p region, and (b) in the Si 2p region.

The Al 2p region and Si 2p region for samples before and after etching treatment, was fit by

the components shown in Figure S5a and S5b, respectively. Before HF treatment, the binding energies of 72.53eV and 74.31eV correspond to Al 2p region in Al-C and Al-O configurations.⁸ In the case of the etched sample, the Al 2p region was also fit by the Al-O (74.3eV) and Al-C (72.53eV) components,⁸ and the fraction of Al-C bond decreases from 26.14% to 15.31%. For Si 2p, two components with binding energy of 100.2eV and 102.6eV were fit in the as-prepared powder, respectively, indicating the presence of Si-C and Si-O_x bonds.^{8,9} After HF treatment, Si 2p region was fit by only one component corresponds to Si-O_x bond (102.6eV).⁹ The apparent decrease in the content of Al-C bond and the consumption of Si-C bond after HF treatment indicate the selective etching of Al(Si)-C bonds has occurred.

Given the focus on the oxidized state of hafnium, meanwhile, considering the very low content of O-Al and O-Si bonds and their overlap with that of O-Hf bond, it should be noted that we did not distinguish the components correspond to O-Al and O-Si bonds from the O 1s region in our current study.



Figure S6 The side-views of possible stacking types in multilayer $Hf_3C_2F_2$ configurations. (a) the fluorine groups point to the top-sites of surface hafnium atoms in the neighboring counterpart. (b) the fluorine groups arrange in a face-to-face manner. (c) the fluorine groups point to the top-sites of the nearest carbon atoms in the neighboring counterpart.

In order to answer the question why our obtained $Hf_3C_2T_z$ MXenes are inclined to delaminated configurations, the adhesive energy between the multilayer $Hf_3C_2F_2$ MXene is calculated since the synthesized MXenes are generally functionalized by F groups in the beginning.¹⁰ The corresponding value for the well-studied multilayer $Ti_3C_2F_2$ is also investigated for comparison. The adhesive energy is defined similar to that in equation (1) in the main text, as the energy difference between those of detached two monolayers and the multilayer MXene: $E_{adhesive} = (2E_{monolayer} - E_{multilayer})/2A$. The coefficient "2" before $E_{monolayer}$ means two monolayers, and the

second "2" in the denominator denotes two interface surfaces in a multilayered unit cell. The structures for monolayer $Ti_3C_2F_2$ and $Hf_3C_2F_2$ are determined by comparing the total energies of six different possible configurations (as shown in Figure S7), and the fluorine groups on the top-sites of the middle metal atoms are found to be stable. For multilayer MXenes, three possible stacking patterns as shown in Figure S6 are investigated. The most stable stacking patterns for both $Ti_3C_2F_2$ and $Hf_3C_2F_2$ are like that shown in Figure S6a, in which the fluorine groups point to the top-sites of the surface metal atoms in the neighboring counterpart. The stable multilayer $Ti_3C_2F_2$ was ascertained by Hu *et al.*, ¹¹ and the consistency between our work and the previous report testifies the reliability of our calculations. Based on the stable monolayer and multilayer MXenes, the adhesive energy in $Ti_3C_2F_2$ is calculated to be 1.36 meV/Å², but the corresponding value in $Hf_3C_2F_2$ is only 0.326 meV/Å². The relatively small adhesive energy implies that the multilayer $Hf_3C_2T_z$ can be readily to be delaminated in solution.

Additionally, we also studied the adhesive energies for multilayer oxygen and hydroxyl terminated $Hf_3C_2O_2$ and $Hf_3C_2(OH)_2$. In contrast, the stable stacking patterns for multilayer $Hf_3C_2T_2$ (T=O, OH) are different from that of fluorine terminated one, the functional groups point to the top-sites of the nearest carbon atoms like that shown in Figure S6c. The corresponding adhesive energies are determined to be 3.09 and 38.4 meV/ Å², respectively. Although multilayer $Hf_3C_2T_2$ (T=O, OH) MXenes show much larger adhesive energies than that in multilayer $Hf_3C_2F_2$ or even $Ti_3C_2F_2$, the morphology of the synthesized MXenes in solution may closely relate to the beginning fluorine groups.



Figure S7 (a) shows the electronic density distribution of the $Hf_3Al_4C_6$ monomer. (b) presents the $Hf_3Al_4C_6$ monomer with the Hf, C, Al atoms in the vicinity of the etching interface are labeled. (c) depicts the $Hf_3Al_4C_6$ monomer with a Al atom in the top layer replaced by a silicon, the corresponding atoms around the etching interface are also labeled.

In order to understand why introducing of silicon decreases the adhesive energy of the etching interface, the bond strengths in the vicinity of the etching interface are studied. According to Figure S7a, our Hf₃Al₄C₆ monomer is an ionic compound, where the carbon atoms gain, and both the aluminum and hafnium atoms lose electrons. Since the strength of an ionic bond is proportional to the atomic charge and reverse to the bond length for a giving bond,¹² thus the atomic charge for each atom and relevant bond lengths are studied. The pure Hf₃Al₄C₆ monomer and the silicon-doped Hf₃Al_{3.5}Si_{0.5t}C₆ are chosen and discussed in detail. The related atoms in the vicinity of the breaking interfaces are labeled as shown in Figure S7b and S7c. In Figure S7b, showing the structure of Hf₃Al₄C₆, the two labeled Hf atoms are equivalent to each other, and the same for C and Al atoms. However, after an Al atom is replaced by Si in Hf₃Al_{3.5}Si_{0.5t}C₆ as shown in Figure S7c, the preliminary equivalent atoms are differed due to their different chemical environment. The atomic charges of the labeled atoms and corresponding bond lengths are presented in Table S1. From this table, the atomic charges and bond lengths show evident changes after introducing silicon doping. For instance, the atomic charges of the Hf and C are 1.77 and -2.44 in Hf₃Al₄C₆, but which respectively reduce to 1.75 and -2.32 for Hf2 and C2 in Hf₃Al_{3.5}Si_{0.5t}C₆. Moreover, the bond length of Hf-C increases from 2.39 to 2.47 Å (Hf2-C2) after introducing the silicon atom. As a consequence, the bond strength of the Hf2-C2 is weakened. Based on the debilitated bond strength, the adhesive energy of the etching interface is generally decreased.



Figure S8 The side-views of six different models for Hf₃C₂T₂ (T=O, F, OH) MXenes.



Figure S9 X-ray diffraction patterns of $Hf_3[Al(Si)]_4C_6$ powders before and after treatment with concentrated HF solution with area corresponding to (0009) and (0015) planes.



Figure S10 Cycling performances of d-Hf₃C₂ T_z (bule) and Ti₃C₂ T_z (red) MXenes anodes at a current density of 200 mA g⁻¹ in LIBs (a) and SIBs (b), respectively.

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System	Atomic charge (e)				Bond length (Å)					
$Hf_3Al_4C_6$	Hf		С		Al		Hf-C		Al-C	
	1.77		-2.44		2.19		2.39		2.12	
$Hf_3Al_{3.5}Si_{0.5t}C_6$	Hf1	Hf2	C1	C2	Al	Si	Hfl-Cl	Hf2-C2	Si-C1	Al-C2
	1.77	1.75	-2.44	-2.32	2.18	2.36	2.41	2.47	1.99	2.14

Table S1. The atomic charges and corresponding bond lengths near the breaking bonds in $Hf_3Al_4C_6$ and $Hf_3Al_{3.5}Si_{0.5t}C_6$.

Table S2. The total energies of different models for $Hf_3C_2T_2$ (T=O,F,OH) MXenes.

MXenes	Model I	Model II	Model III	Model IV	Model V	Model VI
$Hf_3C_2F_2$	-63.52	-65.24	-64.65	-64.03	-64.96	-64.41
$\mathrm{Hf}_{3}\mathrm{C}_{2}(\mathrm{OH})_{2}$	-75.21	-77.17	-76.73	-75.92	-76.98	-76.19
$Hf_3C_2O_2$	-64.39	-71.76	-69.90	-67.08	-70.82	-68.02

 Table S3. Exfoliation process parameters of Hf-Al-C composite powders.

Compound	HF conc. (wt. %)	Time (h)	Yield (wt. %)
Hf-Al-C	10	48	83
Hf-Al-C	25	48	75
Hf-Al-C	40	72	67
Hf-Al-C	50	72	60

References:

Rodenbücher, C.; Hildebrandt, E.; Szot, K.; Sharath, S. U.; Kurian, J.; Komissinskiy, P.; Breuer, U.; Waser, R.; Alff, L., Hafnium Carbide Formation in Oxygen Deficient Hafnium Oxide Thin Films. *Appl. Phys. Lett.* 2016, *108*, 252903.

(2) Baklanova, N. I.; Zima, T. M.; Boronin, A. I.; Kosheev, S. V.; Titov, A. T.; Isaeva, N. V.; Graschenkov, D. V.; Solntsev, S. S., Protective Ceramic Multilayer Coatings for Carbon Fibers. *Surf. Coat. Technol.* 2006, *201*, 2313-2319.

(3) Naguib, M.; Halim, J.; Lu, J.; Cook, K. M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W., New Two-Dimensional Niobium and Vanadium Carbides as Promising Materials for Li-Ion Batteries. *J. Am. Chem. Soc.* **2013**, *135*, 15966-15969.

(4) Halim, J.; Cook, K. M.; Naguib, M.; Eklund, P.; Gogotsi, Y.; Rosen, J.; Barsoum, M. W., X-Ray Photoelectron Spectroscopy of Select Multi-Layered Transition Metal Carbides (MXenes). *Appl. Surf. Sci.* **2016**, *362*, 406-417.

(5) Yamamoto, S.; Bluhm, H.; Andersson, K.; Ketteler, G.; Ogasawara, H.; Salmeron, M.; Nilsson, A., In Situ X-Ray Photoelectron Spectroscopy Studies of Water on Metals and Oxides at Ambient Conditions. *J. Phys.: Condens. Matter* **2008**, *20*, 184025.

(6) Maruyama, B.; Ohuchi, F. S., H₂O Catalysis of Aluminum Carbide Formation in the Aluminum-Silicon Carbide System. *J. Mater. Res.* **1991**, *6*, 1131-1134.

(7) Jayaweera, P. M.; Quah, E. L.; Idriss, H., Photoreaction of Ethanol on TiO₂ (110) Single-Crystal Surface. *J. Phys. Chem. C* **2007**, *111*, 1764-1769.

(8) Sun, Y.; Lu, C.; Cui, H.; Wang, J.; Ma, Y.; Wang, C., Room-Temperature Ferromagnetism of 2H-SiC-α-Al₂O₃ Solid Solution Nanowires and the Physical Origin. *Nanoscale* **2015**, *7*, 4912-4919.

(9) Avila, A.; Montero, I.; Galán, L.; Ripalda, J. M.; Levy, R., Behavior of Oxygen Doped SiC Thin Films: An X-Ray Photoelectron Spectroscopy Study. *J. Appl. Phys.* **2001**, *89*, 212-216.

(10) Xie, Y.; Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y.; Yu, X.; Nam, K.-W.; Yang, X.-Q.; Kolesnikov, A. I.; Kent, P. R. C., Role of Surface Structure on Li-Ion Energy Storage Capacity of Two-Dimensional Transition-Metal Carbides. *J. Am. Chem. Soc.* **2014**, *136*, 6385-6394.

(11) Hu, T.; Hu, M. M.; Li, Z. J.; Zhang, H.; Zhang, C.; Wang, J. Y.; Wang, X. H., Interlayer Coupling in Two-Dimensional Titanium Carbide Mxenes. *Phys. Chem. Chem. Phys.* **2016**, *18*, 20256-20260.

(12)Zio'lkowski, J., New Relation between Ionic Radii, Bond Length, and Bond Strength. *J. Solid State Chem.* **1985**, *57*, 269-290.