Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information (ESI)

Two-dimensional CaSi monolayer with quasi-planar pentacoordinate silicon

Yu Wang,[a] Man Qiao,[a] Yafei Li*[a] and Zhongfang Chen*[b]

[a]*Jiangsu Collaborative Innovation Centre of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China. Email: liyafei@njnu.edu.cn*

[b]*Department of Chemistry, Institute for Functional Nanomaterials, University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931, USA. Email: zhongfangchen@gmail.com*

Complete Reference 39:

Gaussian 03, Revision E.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O, Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hrarchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O, Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Savador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Pishorz, I. Kpmaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. AlLaham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Table S1 Lowest vibrational frequency (ν_{min}) and bond lengths ($d_{Si\text{-}Si}$, $d_{Si\text{-}Ca}$, and $d_{Ca\text{-}Ca}$) of $Ca_4Si_2^{2-}$

computed at different levels. The CCSD(T)/cc-pVTZ level is set as the benchmark. The uncertainties for bond lengths are in parentheses.

method	ν_{min} (cm^{-1})	$d_{Si\text{-}Si}$ (Å)	$d_{Si\text{-}Ca}$ (Å)	$d_{Ca\text{-}Ca}$ (Å)
VWN5/cc-pVTZ	16.9	2.26 (0.04%)	2.84 (6.27%), 2.88 (5.57%), 2.94 (8.97%)	3.56 (8.25%), 3.64 (6.67%)
PBEPBE/cc-pVTZ	22.5	2.28 (1.33%)	2.89 (4.62%), 2.94 (3.61%), 3.02 (6.50%)	3.67 (5.41%), 3.74 (4.10%)
B3LYP/cc-pVTZ	28.3	2.25 (0.00%)	2.92 (3.63%), 2.96 (2.95%), 3.09 (4.33%)	3.73 (3.86%), 3.79 (2.82%)
M06-2X/cc-pVTZ	34.2	2.22 (1.33%)	2.96 (2.31%), 2.99 (1.97%), 3.11 (3.72%)	3.74 (3.61%), 3.79 (2.82%)
CISD(full)/cc-pVTZ	40.3	2.21 (1.78%)	2.96 (2.31%), 3.00 (1.64%), 3.11 (3.72%)	3.75 (3.35%), 3.76 (3.59%)
CCSD(T)/cc-pVTZ	34.9	2.25	3.03, 3.05, 3.23	3.88,3.90

As revealed by Table S1, all these computations proved that the designed inspiring species, $Ca_4Si_2^{2-}$, is a local minimum. Compared with the CCSD(T) benchmark, VWN functional does not perform very well for this system, whereas the others, specially M06-2X functional, perform satisfactorily.

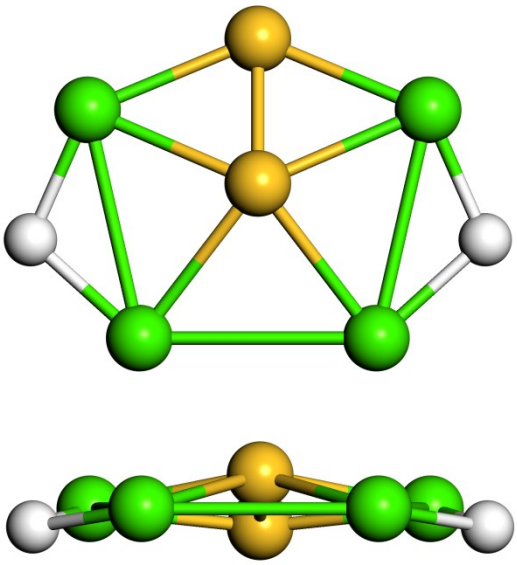

Fig. S1 Top (upper) and side (bottom) views of atomic configuration of $Ca_4Si_2H_2$ molecule computed at M06-2X/cc-pVTZ level.

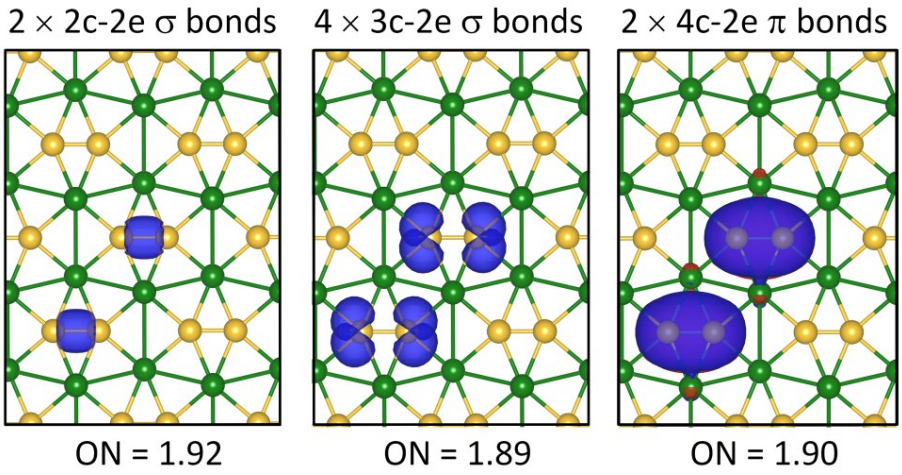

Fig. S2 SSAdNDP chemical bonding patterns of CaSi monolayer. ON is short for occupation number.

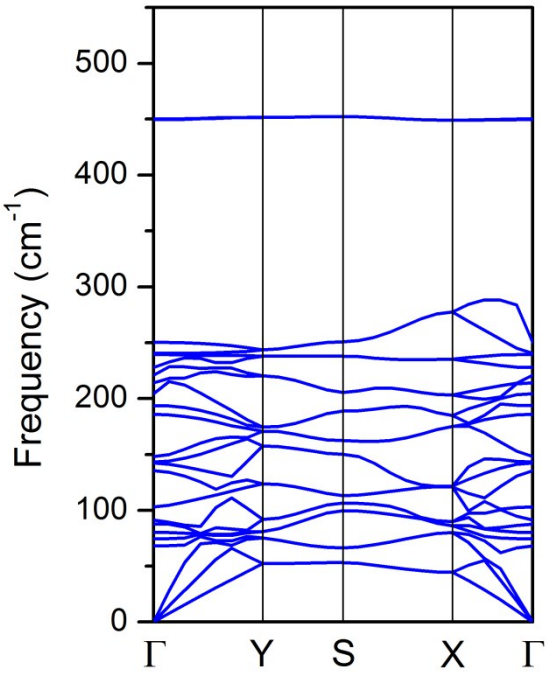

Fig. S3 Phonon spectrum of stretched planar CaSi monolayer (ε = 3.4%).

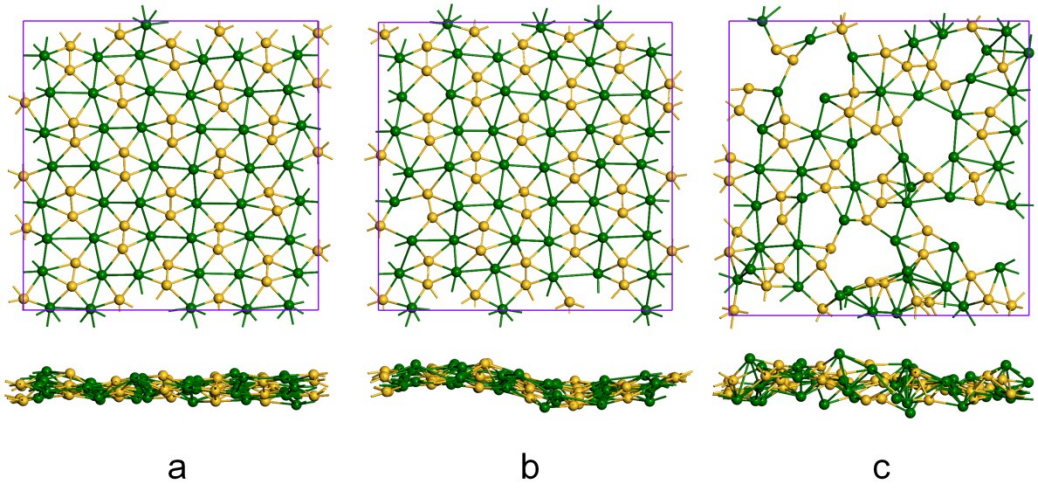

Fig. S4 A snapshot of the equilibrium structure of CaSi monolayer at (a) 1000 K, (b) 1500 K, and (c) 2000 K, respectively, at the end of 10 ps first-principles molecular dynamics simulation.

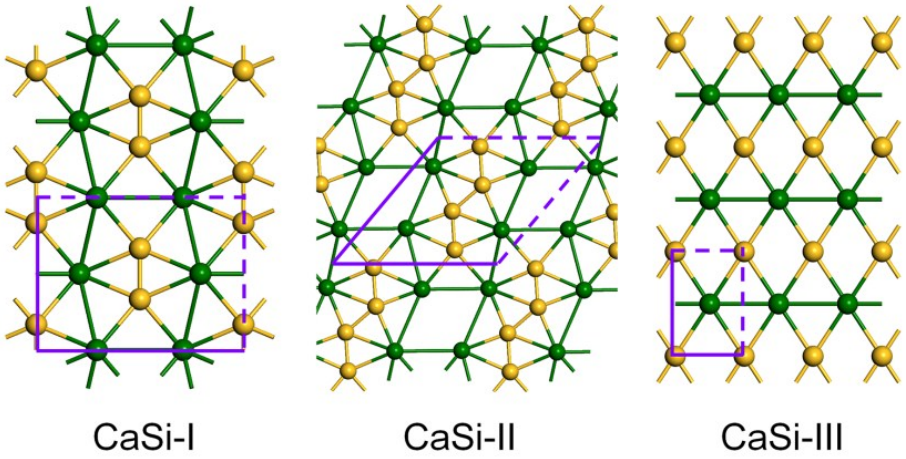

Fig. S5 Three low-energy isomers of 2D CaSi.

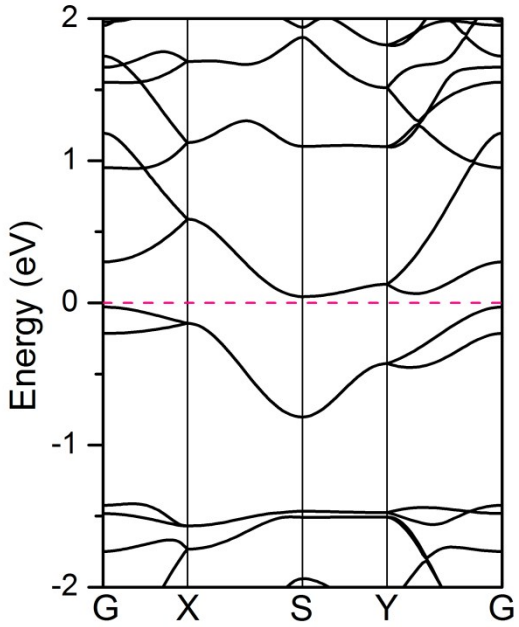

Fig.S6 Band structure of CaSi computed using PBE functional.

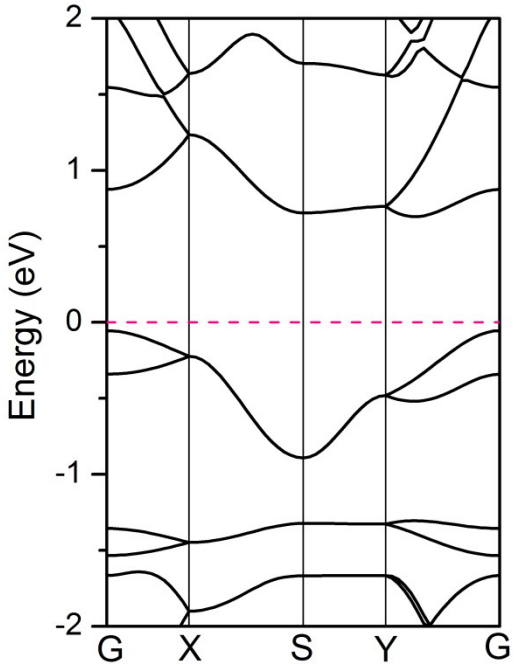

Fig.S7 HSE06 band Structure of entirely planar CaSi monolayer.

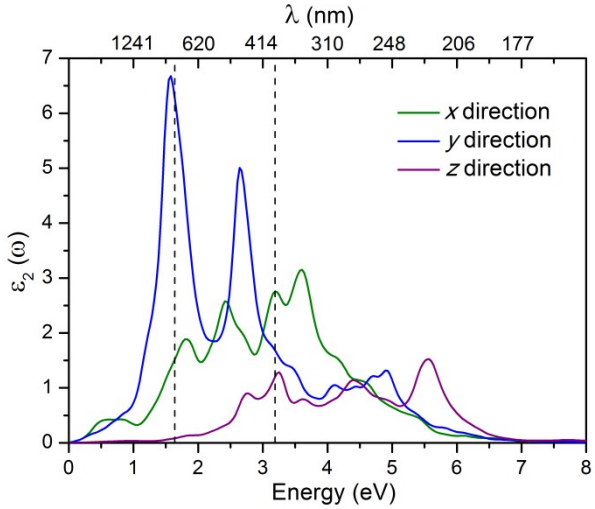

Fig.S8 Imaginary dielectric functions of CaSi monolayer along the *x*, *y* and *z* directions computed using PBE functional.