Supporting Information for: Novel Two-Dimensional Silicon Dioxide with in-Plane Negative Poisson's Ratio

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Methodology

For 2D linear elastic solid materials, the mechanical properties of x–y plane such as Young's modulus E and Poisson's ratio ν can be expressed as following equations[6,48]

$$E_x = \frac{C_{11}C_{22} - C_{12}C_{21}}{C_{22}}, \quad E_y = \frac{C_{11}C_{22} - C_{12}C_{21}}{C_{11}}, \\ \nu_{xy} = \frac{C_{21}}{C_{22}}, \quad \nu_{yx} = \frac{C_{12}}{C_{11}}. \tag{1}$$

Table S1: Calculated values for elastic modulus tensor C_{ij} (in GPa) of α-2D silica, β-2D silica, γ-2D silica, and δ-2D silica, respectively. d (Å) in parentheses are the thicknesses of structures, and values without parentheses are 2D effective thicknesses.[1–3] Here, effective vdW thinkness is defined as the summation of the buckling distance and two vdW radii of the outmost surface atoms of structures.[1–3]

structures	C_{11}	C_{12}	C_{21}	C_{22}	C_{66}	d
α-2D silica	245.57	128.28	128.28	245.57	58.64	7.38 (4.34)
β-2D silica	97.28	-11.95	-11.95	248.27	38.82	6.55 (3.51)
γ-2D silica	137.72	-3.04	-3.04	137.72	13.20	6.88 (3.84)
δ-2D silica	350.05	-39.28	-39.28	350.05	41.12	4.75 (1.71)

Table S2: Relevant mechanical properties of 2D materials. BP is the abbreviation of monolayer black phosphorus. E_x and E_y are the in-plane Young's modulus. ν_{xy} and ν_{yx} are the Poisson's ratio in the x- and y-directions. Values in parentheses are the reported theoretical results for graphene[4,5] and BP[6,7] and numbers without parentheses are our results. For 2D silica, values in parentheses are the results using strain method, while numbers without parentheses are the results from elastic solid theory.[8]

structures	E_x (GPa)	E_y (GPa)	ν_{xy}	ν_{yx}
Graphene	1023 (1039)	1023 (1039)	0.170 (0.169)	0.170 (0.169)
BP	168 (166)	38 (44)	0.76 (0.62)	0.17 (0.17)
α-2D silica	178.56 (180.42)	178.56 (180.42)	0.522 (0.520)	0.522 (0.520)
β-2D silica	96.70 (100.62)	246.81 (241.59)	-0.048 (-0.049)	-0.123 (-0.124)
γ-2D silica	137.66 (131.84)	137.66 (131.84)	-0.022 (-0.021)	-0.022 (-0.021)
δ-2D silica	345.64 (331.80)	345.64 (331.80)	-0.112 (-0.120)	-0.112 (-0.120)

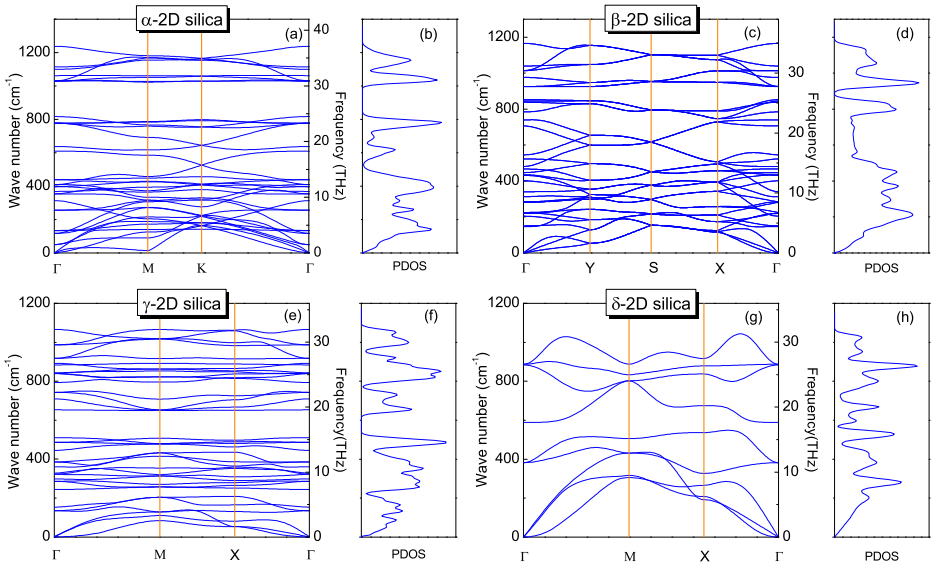

Figure S1: Phonon dispersions and phonon density of states (PDOS) of (a)(b) $P6/mmm$ Si_4O_8 (α-2D silica); (c)(d) $Pbcm$ Si_4O_8 (β-2D silica); (e)(f) P-$4m2$ Si_4O_8 (γ-2D silica) and (g)(h) P-$4m2$ SiO_2 (δ-2D silica). The relationship between wave number and frequency is: k=$1/\lambda$=v/c in which c is the speed of light. The unit of left y-axis is wave number (cm^{-1}) and the right is frequency (THz). All the structures of these 2D silica are free from imaginary frequencies in the first Brillouin zone, which means they are dynamically stable. The dispersion of α-2D-silica is in good agreement with the previous work.[9]

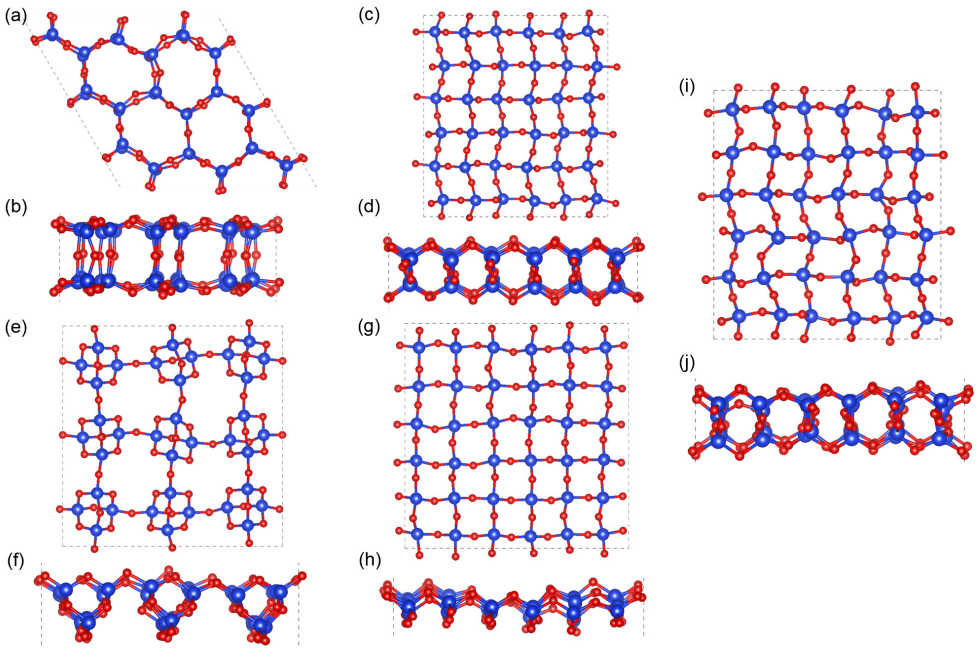

Figure S2: Snapshots of atomic configurations of (a)(b) (3×3) α-, (c)(d)(i)(j) (3×3) β-, (e)(f) (3×3) γ- and (g)(h) (6×6) δ-2D silica using canonical ensemble at the end of *ab initio* molecular dynamics simulations. Nose-Hoover thermostat is used for 10 ps with the time step of 1 fs in each structure at 1000 K except (i)(j) (3×3) β-2D slica for 2500 K. The result shows that these 2D silica are still robust as high as 1000 K, directly implying the dynamical stability of our 2D silica. Particularly, the lifetime of β-2D slica is more than 10 ps at 2500 K which is much higher than the melting point of quartz (1986 K).[10] This implies 2D silica can endure much higher temperature than bulk silica and can be retained from high temperature.

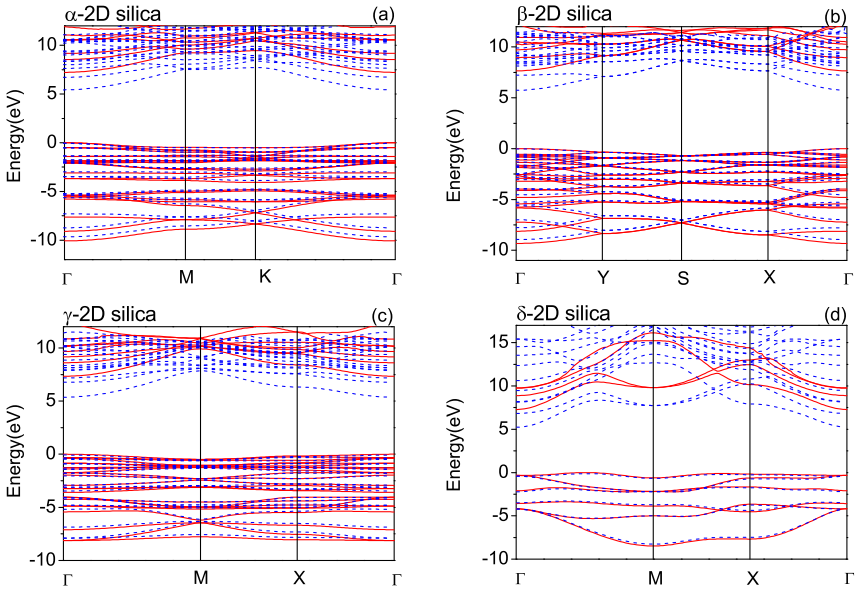

Figure S3: Electronic band structures of (a) $P6/mmm$ Si_4O_8 (α-2D silica), (b) $Pbcm$ Si_4O_8 (β-2D silica), (c) $P\text{-}4m2$ Si_4O_8 (γ-2D silica) and (d) $P\text{-}4m2$ SiO_2 (δ-2D silica) calculated by PBE in blue dashed line and HSE06 in red solid line. The fermi levels are set to zero. The band structure of α-2D-silica is in good agreement with the previous work.[9] The calculated HSE06 band gaps of α-2D silica, β-2D silica, γ-2D silica, and δ-2D silica are 7.31, 7.69, 7.40 and 7.34 eV. These 2D silica have the largest electronic band gaps in all known 2D materials, which means they are good insulators and absolute transparent. We believe that this favorable insulating property will have potential applications in energy storage of capacitors and nanoelectronics.[11]

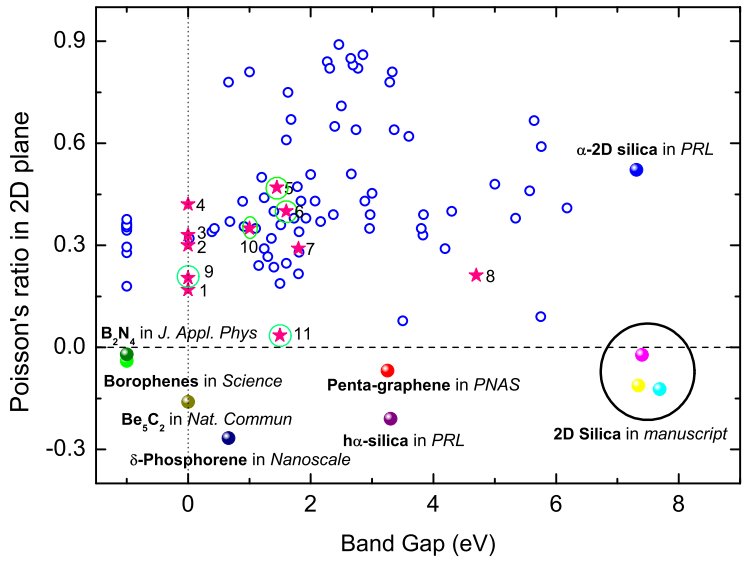

Figure S4: The relationship between band gaps and in-plane Poisson's ratios in monolayer 2D materials collected from the available published papers. 2D materials with in-plane Positive Poisson's ratio (PPR) use blue circles and pink pentacles. The pink pentacles with 1 to 11 are typical 2D materials (1:Graphene. 2:Silicene. 3:Germanene. 4:Stanene. 5:SnSe. 6:Phosphorene. 7:MoS_2. 8: h-BN. 9:Borophane. 10:Arsenic. 11:C_2F). Note: there are 5 2D materials with in-plane PPR but out-of-plane NPR denoted with green circles. In order to see clearly, the band gaps of metal are set to -1 to avoid confusion. There are 95 monolayer 2D materials with Poisson's ratios in available published papers altogether, in which only 6 (6/95=6.3%) has in-plane negative Poisson's ratio to the best of our knowledge. The references of in-plane PPR,[6,12–42] in-plane PPR but out-of-plane NPR,[24,25,43–46] and in-plane NPR are listed.[47–52]

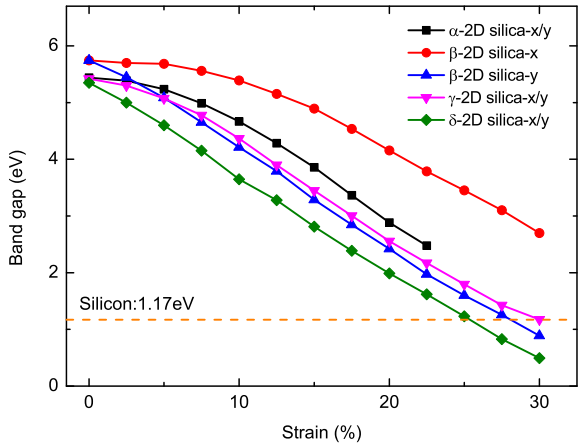

Figure S5: The effect uniaxial strain on band gap for $P6/mmm$ Si_4O_8 (α-2D silica), $Pbcm$ Si_4O_8 (β-2D silica), P-$4m2$ Si_4O_8 (γ-2D silica) and P-$4m2$ SiO_2 (δ-2D silica) calculated by the PBE method. The band gap of pure bulk silicon without strain in dashed line is set for comparison. It is observed that the band gap of these 2D silica is quite sensitive to the external strain by PBE calculations, i.e., the strain can decrease the band gap rapidly. It means that the external strain can tailor 2D silica from insulator to semiconductor and also can change the absorption edge and observed color, which implies a potential application in sensor materials.

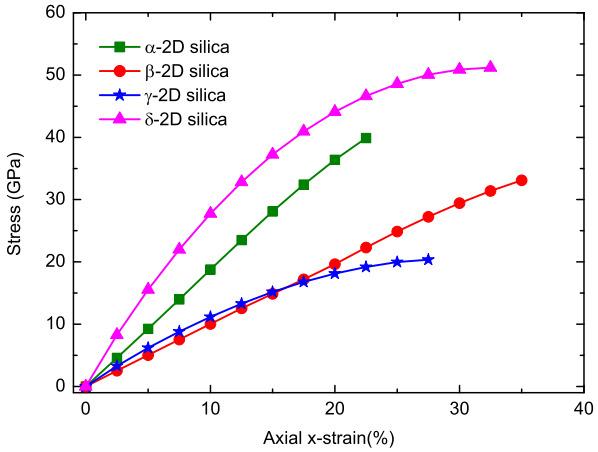

Figure S6: The relationship between stress and strain in the x direction for $P6/mmm$ Si_4O_8 (α-2D silica), $Pbcm$ Si_4O_8 (β-2D silica), P-$4m2$ Si_4O_8 (γ-2D silica) and P-$4m2$ SiO_2 (δ-2D silica) calculated by the PBE method.

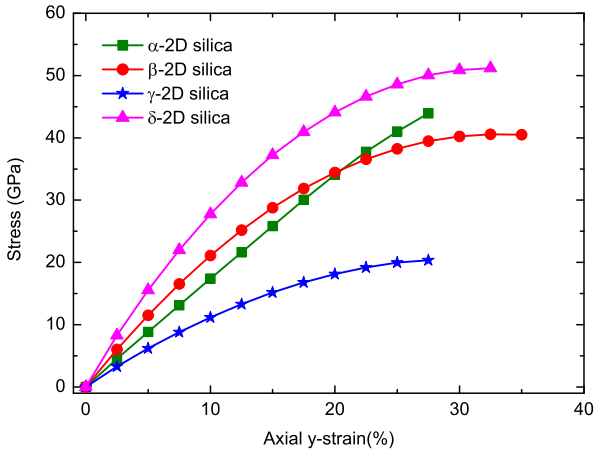

Figure S7: The relationship between stress and strain in the y direction for $P6/mmm$ Si_4O_8 (α-2D silica), $Pbcm$ Si_4O_8 (β-2D silica), P-$4m2$ Si_4O_8 (γ-2D silica) and P-$4m2$ SiO_2 (δ-2D silica) calculated by the PBE method.

where C_{11}, C_{12}, C_{21}, C_{22} and C_{66} are the components of the elastic modulus tensor shown in Table S1. We calculated the Young's modulus E and Poisson's ratio ν for our 2D silicon dioxide according to the eq. (1). The result is shown in Table S2. In order to check the correctness of our computational methods and results, we choose graphene and black phosphorus as references (Table S2). Our results are in good agreement with the published results.[4–7]

In our calculations of uniaxial strain (for example, in the x direction), the lattice constant of x-direction was manually set and fixed a value L_x, and then via optimizing structure which corresponds the lowest total erengy of whole system to get the lattice constant L_y and stress.[53,54] Therefore, Young's modulus E and Poisson's ratio ν can be obtained in each strain percentage.

Stress–strain curves of x- and y-directions are depicted in Figure S6 and Figure S7. In theory, Young's mudulus E is the slope of stress–strain curve and can be obtained by dividing the tensile stress by the extensional strain in the elastic region of the stress–strain curve. Young's mudulus convey the hardness of a material. A material whose Young's modulus is high can be regarded as rigid. Obviously, δ-2D silica has a much bigger slope (346 GPa) than

α-2D silica, β-2D silica and γ-2D silica in the stress–strain curve, which is more than triple of that of α-quartz (100 GPa)[55–57] and is comparable to that of single-layer boron nitride (BN) (366 GPa).[58] More interestingly, β-2D silica, like single-layer black phosphorus,[24] display a strong anisotropic mechanical property compared to α-2D silica, γ-2D silica, and δ-2D silica. These exotic mechanical properties are expected to have great potential applications in nanomechanics and nanoelectronics.

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