Text S1. Structure and stability of T-silica

The optimized single-layer silica sheet has the tetragonal symmetry (Layer group NO. 59, P-4m2) with a lattice constant of \(a = b = 2.84\ \text{Å}\), as shown in Fig. S1a. The layer thickness is 1.71 Å, which is larger than that of the \(h\alpha\) structure (0.86 Å),\(^1\) but smaller than that of the experimentally synthesized SiO\(_{2.5}\) phase (2.10 Å).\(^2,3\) All the Si-O bond lengths are 1.66 Å, which is between the maximum (1.70 Å) and the minimum (1.59 Å) values of that in bulk Stishovite. In addition, unlike the O-C-O angle (109°) in GDO,\(^4\) the O-Si-O bond angle is 118.12°, as shown in Fig. S1b, because of the imperfect \(sp^3\) hybridization of Si atoms. We note that this single-layer structure is identical to that of T-silica recently reported.\(^5\) Therefore, we also name it as T-silica.

Total energy calculations suggest that T-silica is energetically comparable to bulk Stishovite, since the energy difference \(E_{\text{T-silica}} - E_{\text{Stishovite}}\) is only 0.015 eV per formula unit (f.u.). While compared with the synthesized hexagonal bilayer silica (HBS), this new silica structure is about 0.6 eV/f.u. higher in energy, because the \(sp^3\) hybridized orbitals of Si atoms in T-silica have larger distortions than those in HBS. However, phonon spectrum calculated with a higher accuracy indicates that the
single-layer T-silica sheet can exist as a freestanding 2D crystal, as no imaginary modes exist in the entire Brillouin zone, as shown in Fig. S1c. We then performed *ab initio* molecular dynamics (AIMD) simulations at 300K to check the thermal stability. To minimize the constraint of the lattice, a $4 \times 4$ supercell containing 48 atoms is constructed to avoid the fake instability. The simulation was performed for 10 ps with a time step of 1 fs. We found that the geometry of T-silica remains nearly intact and its total energy keeps almost a constant during the simulations, confirming that T-silica is thermally stable at room temperature. We further elevate the heat bath temperature to 500 K, as shown in Fig. S1d, the fluctuation of the total energy with simulation time suggests that T-silica is still thermally stable at such high temperature, and this is further confirmed by checking the atomic configuration at the end of the AIMD simulations (see the inset image in Fig. S1d). Our results provide the support that T-silica is located at a local minimum on the potential energy surface.

**Fig. S1** (a) Top and (b) side views of the fully optimized T-silica sheet. Yellow and red balls represent the Si and O atoms, respectively. The square marked by green dashed lines denotes a unit cell. (c) Calculated phonon bands, and (d) total energy
fluctuation during AIMD simulations at 500 K of T-silica. The inset shows the atomic configuration at the end of the simulation.

**Text S2. Dynamical stability of 3- and 4-SNFs**

To check the dynamical stabilities of 3- and 4-SNFs, we calculated their phonon spectra by using density functional perturbation theory (DFPT). The results are presented in Fig. S2, which shows that all the vibrational modes are real in the Brillouin zone, indicating that both 3- and 4-SNFs are dynamically stable.

![Phonon spectra of (a) 3-SNF and (b) 4-SNF.](image)

**Fig. S2** Phonon spectra of (a) 3-SNF and (b) 4-SNF.

**Text S3. A Larger supercell simulation of the thermal exfoliation**

To reduce the effect of the unit cell protected high symmetry on the thermal exfoliation of Stishovite nanofilms, we performed additional AIMD simulations using a larger 3×3 supercell to mimic the thermal exfoliation. Here, we still use the 4-SNF nanofilm as an example. After heating for 500 femtoseconds at 300 K, the 4-SNF sheet is completely exfoliated into four individual T-silica single layers, which remain
separately without structure reconstruction during 10 ps simulations. Therefore, we confirmed that the thermal exfoliation can also be realized and no any structure reconstruction occurs after reducing the constraint of periodic boundary condition.

![Diagram](image1)

**Fig. S3** (a) Side views of the optimized 4-SNF with a 3×3 supercell, and (b) the exfoliated structure composed of the four single layers at the end of AIMD simulations at 300K with vdW correction.

**Text S4. Formation of a single layer T-GeO\(_2\) sheet**

We have demonstrated that T-silica can be exfoliated from Stishovite nanofilms by the thermal treatment. Following the same procedure, we explored the possibility of thermal exfoliation of a single-layer GeO\(_2\) sheet from rutile-type GeO\(_2\) nanofilms.

We first computationally cleaved GeO\(_2\) nanofilms from bulk GeO\(_2\) (001) surface. We take an ultrathin film containing four slab replicas of GeO\(_2\) as a test case. No surface reconstruction is observed after structural optimization, as shown in Fig. S4a. We then performed AIMD simulations at different temperatures, and found that a much higher temperature is needed to induce the thermal exfoliation due to the
enhanced bond strength of Ge-O as compared to that of Si-O. The exfoliation is observed when the simulation temperature is increased to 600 K and the ultrathin film completely decomposes into four individual GeO\textsubscript{2} layers within 500 fs during the simulations. The distance between two layers is more than 10 Å at the end of the simulation, indicating a small interaction between the GeO\textsubscript{2} layers.

![Diagram of GeO\textsubscript{2} nanofilm](image)

**Fig. S4** (a) Optimized structure of GeO\textsubscript{2} nanofilm with four slab replicas. (b) Atomic configuration of the GeO\textsubscript{2} nanofilm at 500 fs during the MD simulations at 600 K.

We then studied the structural and electronic properties of the T-GeO\textsubscript{2} sheet. The optimized structure also has the tetragonal symmetry with a lattice constant of a = b = 3.04 Å, as shown in Fig. S5a. The lattice constant of T-GeO\textsubscript{2} is larger than that of T-silica due to the bigger size of Ge. To confirm its dynamical stability, phonon spectrum was calculated using the density functional perturbation theory (DFPT). The results are plotted in Fig. S5b. The highest frequency of the T-GeO\textsubscript{2} sheet is about 24 THz, which is lower than that of T-silica. Throughout the entire Brillouin zone, no imaginary frequencies are observed, indicating that T-GeO\textsubscript{2} is dynamically stable.
The electronic band structure was calculated at the GGA/PBE level. Fig. S5c shows that the band gap of GeO$_2$ sheet is 2.82 eV, which is much larger than that of its bulk phase (0.97 eV). In addition, the valence band maximum (VBM) lies on the X point, while the conduction band minimum locates at the $\Gamma$ point, showing an indirect band gap character of T-GeO$_2$.

**Fig. S5** (a) Crystal structure, (b) phonon spectrum and (c) electronic band structure of the T-GeO$_2$ sheet.

**References**