Supporting Information

Novel 2D porous C$_3$N$_2$ framework as promising anode material with ultra-high specific capacity for lithium-ion batteries

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Computational Details

The local structural relaxations and electronic properties calculations were performed in the framework of the density functional theory (DFT) within the generalized gradient approximation (GGA) parametrized as implemented in the VASP code.\textsuperscript{1} The 2\textit{s}2\textit{p}2, 2\textit{s}2\textit{p}3, and 3\textit{s}1 atomic orbitals were treated as valence states for C, N, and Li, respectively. The cut-off energy for the expansion of wavefunctions into plane waves was set to 500 eV in all the calculations. The vacuum region of 20 Å was inserted between adjacent images in z direction in order to avoid the interactions between neighboring layers. The convergence thresholds were set as 1.0 × 10\textsuperscript{−6} for total energy and 1 meV/Å for atomic force. The Brillouin zone was sampled with the resolution of 0.03 × 2\textpi\textsuperscript{−1} with \textit{k} points mesh. Van der Waals's interactions were taken into account using the semiempirical DFT-D2 and DFT-D3 approaches.

The cohesive energy of the PCGN monolayers was calculated by using the following formula:

$$E_{\text{coh}} = (E_{C_xN_y} - xE_C - yE_N) /(x + y)$$  \hspace{1cm} (1)

The adsorption energy ($E_{\text{ad}}$) of the Li atom on the $\alpha$-C\textsubscript{x}N\textsubscript{y} monolayer was obtained by

$$E_{\text{ad}} = (E_{Li_nC_xN_y} - nE_{Li} - E_{C_xN_y}) /n$$  \hspace{1cm} (2)

where $E_N$, $E_C$, $E_{Li}$, $E_{C_xN_y}$, and $E_{Li_nC_xN_y}$ are the total energies of a single N atom, a single C atom, a Li atom in body-centered cubic (bcc) structure, one unit cell of the $\alpha$-C\textsubscript{x}N\textsubscript{y} monolayer, and the lithiated monolayer, respectively. The specific capacity ($C$) was calculated following the formula

$$C = \frac{n \times F}{m \times M}$$  \hspace{1cm} (3)

where F, M, n, stand for the Faraday constant (26.8 Ah mol\textsuperscript{−1}) and the molar mass (e.g., 64 g mol\textsuperscript{−1} for $\alpha$-C\textsubscript{3}N\textsubscript{2}), and the number of Li-ion during the lithiation for (C\textsubscript{3}N\textsubscript{2})\textsubscript{n}Li\textsubscript{n}, respectively,
and \( m \) is 6 for the unit cell of \( \alpha\)-C\(_3\)N\(_2\).

Phonon dispersion calculations were carried out for the supercell with over 96 atoms (e.g., a 2 \( \times \) 2 supercell for \( \alpha\)-C\(_3\)N\(_2\)), which was based on the supercell approach as done in the Phonopy code.\(^2\) First-principles molecular dynamics (MD) simulations for three supercells were performed at different temperatures of 500, 750 and 1000 K. MD simulation in the NVT ensemble lasted for 12 ps with a time step of 2.0 fs. The temperature was controlled by using the Nosé-Hoover method. The climbing image nudged elastic band (CI-NEB) method was employed to calculate the diffusion barriers of the Li atoms.

**Supplementary Note 1:**

The low-energy 2D C-N structures by PSO structure search

The particle swarm optimization (PSO) method within the evolutionary algorithm as implemented in the Crystal structure AnaLYsis by Particle Swarm Optimization (PSO) code was employed to find the lowest energy structures of C\(_x\)N\(_y\) \((x,y = 1, 2, 3, 4, 5, \text{ and } 6)\) monolayers.\(^3,4\) Unit cells containing 1, 2, 3, 4, 5, and 6 formula units (f.u.) were considered. In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code \(^5\) were done with the conjugate gradients method and stopped when Gibbs free energy changes became smaller than \( 1 \times 10^{-5} \) eV per cell. After processing the first-generation structures, 60% of structures with lower Gibbs free energies are selected to construct the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. Structural searching for
each calculation was stopped after generating $1000 \sim 1200$ structures (e.g., about $20 \sim 30$ generations).
The above presents some low-energy structures at different stoichiometry ratios (including our predicted structures and the reported structures). (a) $\delta$-CN, (b) C$_4$N, (c) C$_5$N, (d) C$_6$N, (e) C$_7$N, (f) C$_3$N$_5$,$^6$ (g) g-C$_3$N$_4$,$^7, 8$ (h) s-g-C$_3$N$_4$,$^7, 9$ (i) C$_3$N$_3$,$^{10, 11}$ (j) $\beta$-CN,$^{10}$ (k) $\chi$-CN,$^{12}$ (l) $\alpha$-C$_4$N$_3$,$^{13}$ (m) C$_2$N,$^{14}$ (n) C$_3$N,$^{15}$ (o) $\beta$-C$_4$N,$^{16}$ (p) $\beta$-C$_5$N,$^{17}$ (q) $\alpha$-C$_6$N$_7$,$^{18}$ (r) pc-C$_3$N$_2$.$^{19}$ The black and blue balls represent C and N atoms, respectively.

**Supplementary Note 2:**

**The pore C-N skeletons by assembling organic units**

Through the analysis of low-energy porous C-N structures, such as $\alpha$-C$_3$N$_5$, $\alpha$-CN, C$_2$N, g-C$_3$N$_4$, and s-g-C$_3$N$_4$ monolayers, which also have been experimentally synthesized, we found that they mainly originate from symmetric N-rich organic units and few auxiliary C-rich organic units.

Herein, we present some typical organic units in the following (e.g. (a) hexaaminobenzene trihydrochloride,$^{14}$ (b) 2, 3, 6, 7, 10, 11-Hexaaminotriphenylene hexahydrochloride,$^{20-22}$ (c-f)Triazine,$^{23, 24}$ Heptazine,$^6, 25$ (h)1,4-piperazinedicarboxaldehyde,$^{26}$ (i)1,2,4,5-tetraaminobenzene,$^{20, 27, 28}$ (j)2,4,6-trichloro-1,3,5-triazine,$^{10, 29}$ (k) Phthalocyanine,$^{19}$ and (l) Pyrazine$^{28}$) and auxiliary C-rich organic units (e.g. (r)1,4-diformylbenzene$^{30}$, (s) benzene-1,3,5-tricarboxylic,$^{27}$ (f) hexaketocyclohexane octahydrate,$^{14, 20, 28}$ and (u) Benzene).
Assembling these organic units by various building block (e.g., knots, linkers) combinations, we can obtain various shapes, sizes, porous C-N skeletons as follows. Topology diagrams showing these pore C-N skeletons with trigon and hexagon uniform pores are given below.
1) Some synthesized porous C-N sheets:

(2) Design some new porous C-N sheets:
**Supplementary Note 3:**

The extracted pore C-N skeletons from COFs

Some COFs (e.g. C$_2$N, g-C$_3$N$_4$, and C$_3$N$_5$) can lose edge functional groups after being annealed at some temperature, leading to N-rich COFs. However, using such C-N skeletons to construct porous structures has not been attempted, which is a new method we used in this study.

Through our extensive survey, we obtained some porous C-N skeletons. Their optimized geometric structures and phonon spectra are given below. (a) $\beta$-C$_3$N, (b) $\alpha$-C$_5$N$_2$, (c) $\beta$-C$_5$N$_2$, and (d) $\beta$-C$_4$N from covalent triazine framework (CTF-0),$^{31}$ aza-fused $\pi$-Conjugated microporous polymers (Aza-CMPs),$^{32-34}$ iron phthalocyanine organometallic polymer (poly-FePc),$^{35}$ and aza-COF-2,$^{20-22}$ respectively.
Figure S1. (a-b) Top and side views, and electronic band structure of pristine $\alpha$-C$_3$N$_2$ monolayer. (c-l) Top and side views, and electronic band structures for $\alpha$-C$_3$N$_2$ monolayer with Li absorbed at different sites.
**Figure S2.** (a) Schematics of the diffusion paths I→II, II→III, III→III, and III→IV in the pristine $\alpha$-$\text{C}_3\text{N}_2$ framework (top view).

**Figure S3.** The schematics (a-e) for a configuration of three Li-ions surrounding on the $\alpha$-$\text{C}_3\text{N}_2$ framework and the diffusion of middle Li-ion from one pore to another along different paths (Path A, Path B, Path C) and (f) the calculated ion diffusion barriers.
Figure S4. (a) The different Li-adsorption sites in $\alpha$-C$_3$N$_2$ framework. The top (b) and side (c) views of all the possible Li adsorption sites and the multiple-layer Li atom adsorption on both sides of $\alpha$-C$_3$N$_2$ monolayer.
Figure S5. Top and side views of the optimized adsorption configurations at six different Li concentrations for the lithiated α-C₃N₂ monolayer. (a) (C₃N₂)₆Li₆, (b) (C₃N₂)₆Li₁₂, (c) (C₃N₂)₆Li₁₈, (d) (C₃N₂)₆Li₂₄, (e) (C₃N₂)₆Li₃₀, (f) (C₃N₂)₆Li₃₆, and (g) (C₃N₂)₆Li₄₀.
Figure S6. Snapshot after 12 ps MD simulations of Li$_{40}$(C$_3$N$_2$)$_6$ at the temperature of 300 K

Figure S7. 2D ELF map of lithiated $\alpha$-C$_3$N$_2$ framework with (a) two-layer and (b) three-layer Li atom adsorptions.
Figure S8. Lattice expansion degree (Δ) and lattice constant vary with the increase of absorbed Li-ions.
Figure S9. Phonon spectrum of the proposed $\alpha$-C$_3$N$_2$ monolayer.

Figure S10. Thermal stability of the $\alpha$-C$_3$N$_2$ monolayer. Snapshots of the final frame of $\alpha$-C$_3$N$_2$ monolayer at temperatures of (b) 500 K, (c) 750 K, and (d) 1000 K at the end of 12 ps MD simulations.

Figure S11. 2D C-N frameworks with different pore sizes and hierarchical porosity obtained by combining building blocks. (a) $\beta$-C$_3$N$_2$, (b) $\alpha$-C$_4$N$_3$, (c) $\alpha$-C$_5$N$_4$, (d) $\alpha$-C$_8$N$_5$, (e) $\beta$-C$_5$N$_3$, (f) $\alpha$-C$_5$N$_3$, and (g) $\alpha$-C$_7$N$_4$
Figure S12. Phonon spectra of the $\alpha$-C$_3$N$_2$ derivatives: (a) $\beta$-C$_3$N$_2$, (b) $\alpha$-C$_4$N$_3$, (c) $\alpha$-C$_5$N$_4$, (d) $\alpha$-C$_8$N$_5$, (e) $\beta$-C$_5$N$_3$, (f) $\alpha$-C$_3$N$_3$, and (g) $\alpha$-C$_7$N$_4$ monolayers.

Table S1. Structural information of $\alpha$-C$_3$N$_2$ and other porous C-N monolayers

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**References**


1542-1548.


