Supporting Information

Scalable Salt-Templated Synthesis of Nitrogen-Doped Graphene Nanosheets toward Printable Energy Storage

Nan Wei[1,2†], Lianghao Yu[1†], Zhongti Sun[1†], Yingze Song[1†], Menglei Wang[1], Zhengnan Tian[1], Yu Xia[3], Jingsheng Cai[1], Ya-yun Li[3], Liang Zhao[1], Qiucheng Li[1], Mark H. Rümmeli[1], Jingyu Sun[1,2]*, and Zhongfan Liu[1,2,4]**

[1]College of Energy, Soochow Institute for Energy and Materials Innovations (SIEMIS), Jiangsu Provincial Key Laboratory for Advanced Carbon Materials and Wearable Energy Technologies, Soochow University, Suzhou 215006, P. R. China
[2]Beijing Graphene Institute (BGI), Beijing 100095, P. R. China
[3]Shenzhen Key Laboratory of Special Functional Materials & Shenzhen Engineering Laboratory for Advance Technology of Ceramics, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, P. R. China
[4]Center for Nanochemistry (CNC), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

*Corresponding authors: sunjy86@suda.edu.cn (J. Y. Sun); zfliu@pku.edu.cn (Z. F. Liu); kittyli@szu.edu.cn (Y. Y. Li)
†These authors contributed equally to this work.

- **Supporting Figures**

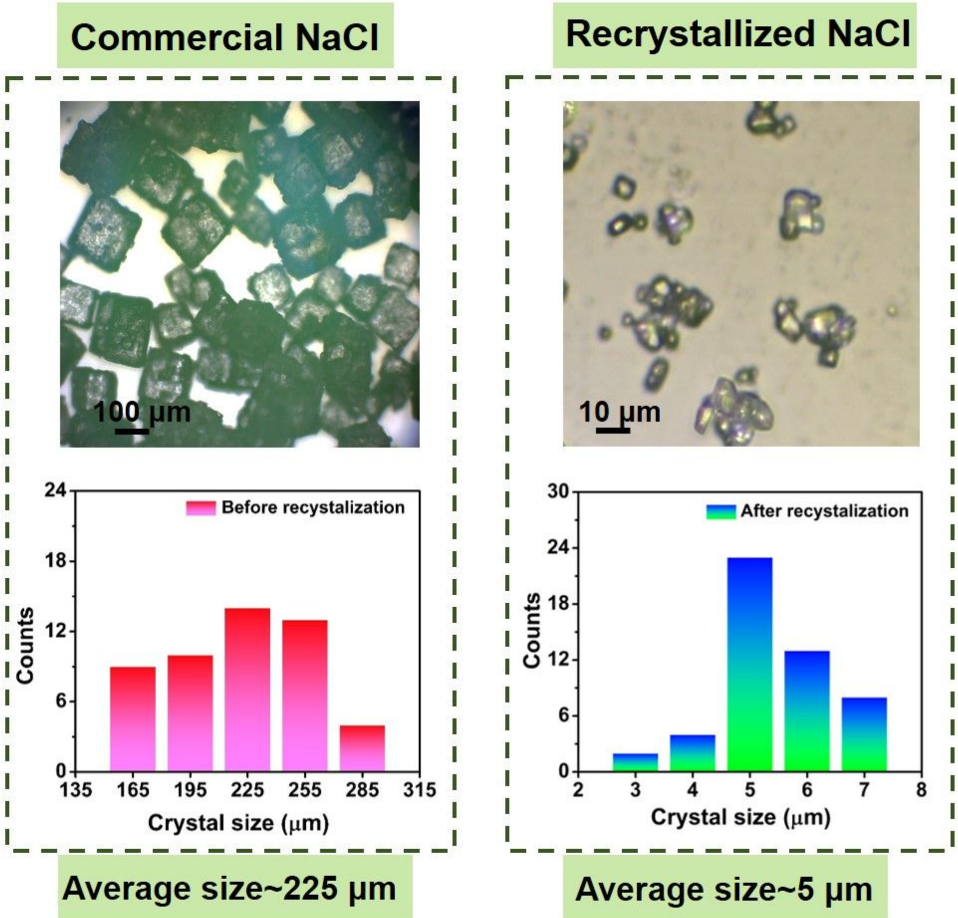

Figure S1. OM image and size distributions of commercial NaCl powder and recrystallized NaCl powder.

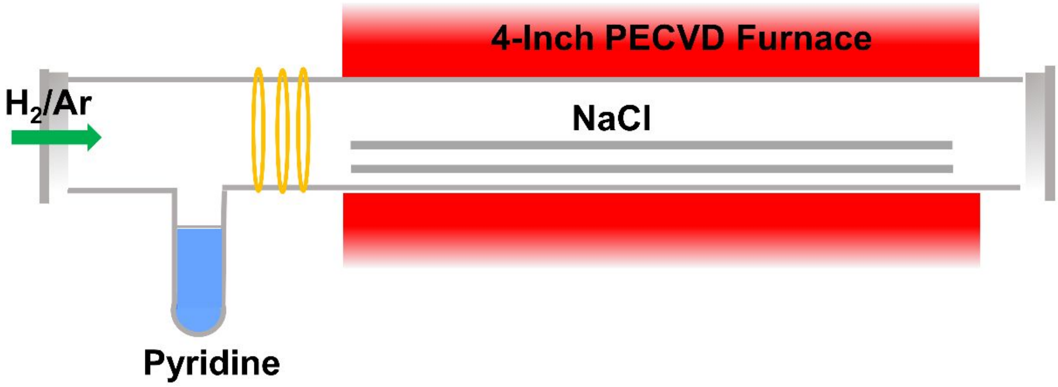

Figure S2. Schematic illustration of PECVD synthesis of NG directly on NaCl.

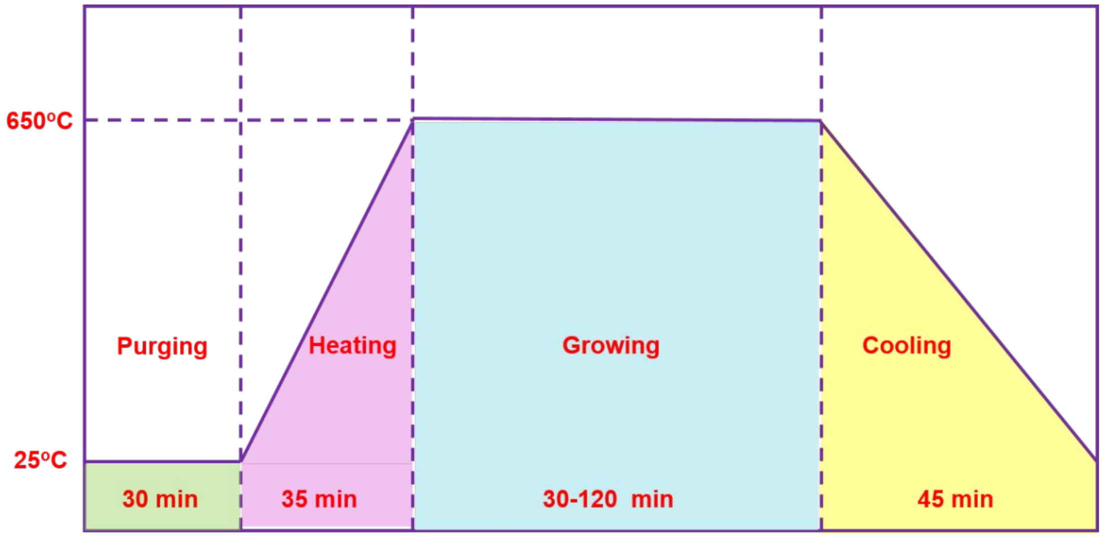

Figure S3. Experimental parameter setup for salt-templated PECVD growth of NG.

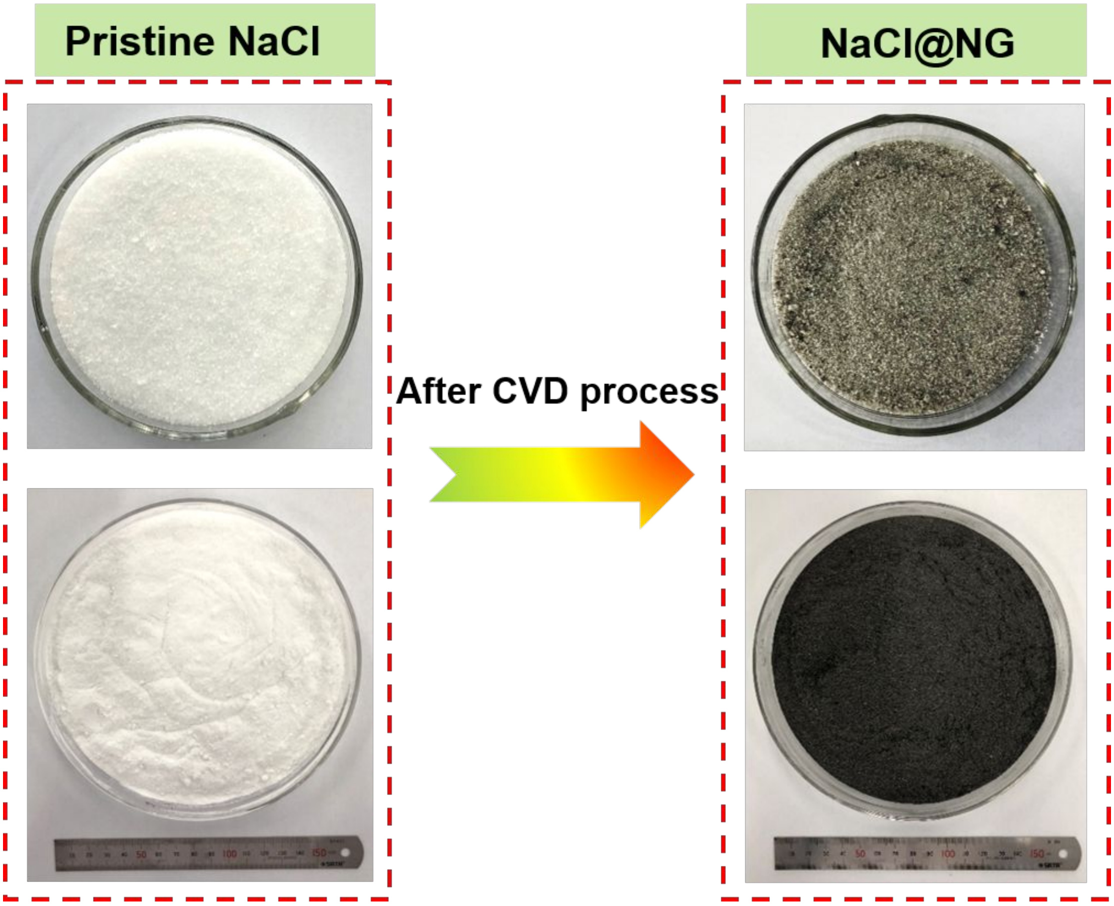

Figure S4. Photograph showing wheat-colored as-received (top) and recrystallized (bottom) NaCl powders and black-colored, NG-coated NaCl powders after PECVD process.

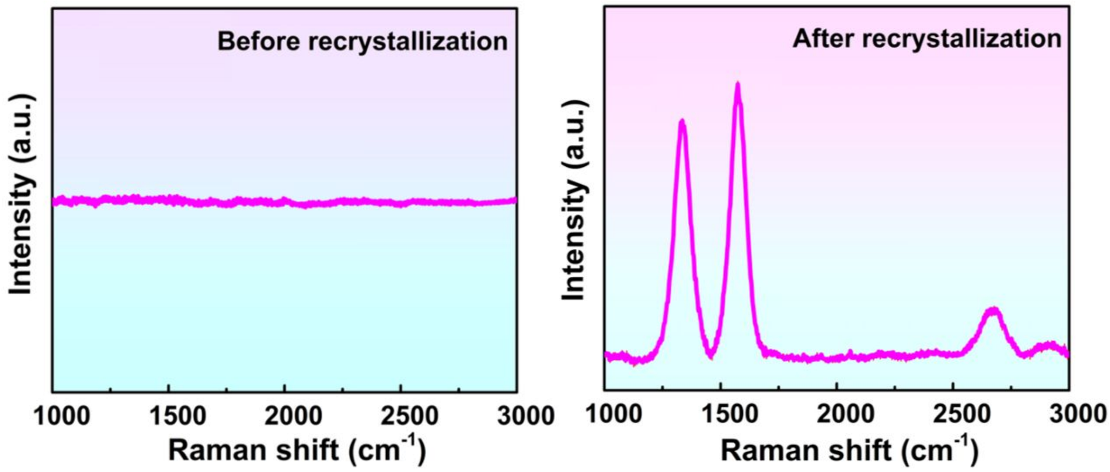

Figure S5. Raman spectra of commercial and recrystallized NaCl powders after CVD growth (growth condition: 700 ^{o}C, 200 sccm Ar, 60 sccm H_2, 80 W with a controlled pyridine vapor flow for 120 min).

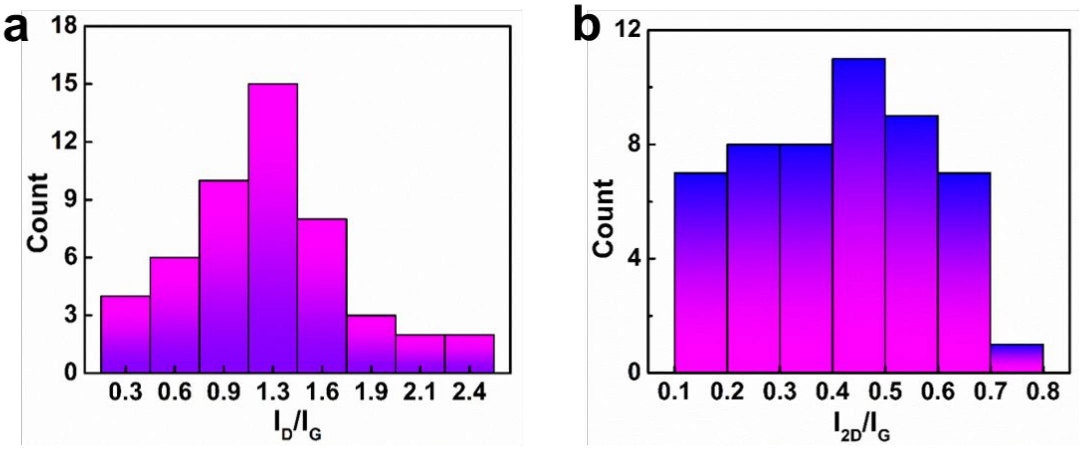

Figure S6. Raman statistics of I_D/I_G and I_{2D}/I_G ratios on NaCl@NG powder (growth condition: 700 ^oC, 200 sccm Ar, 60 sccm H_2, 80 W with a controlled pyridine vapor flow for 120 min).

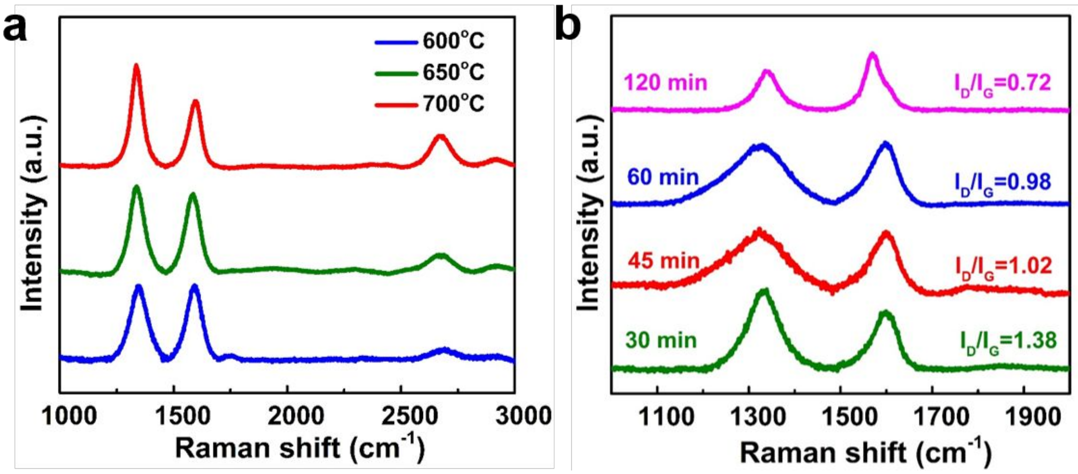

Figure S7. (a) Raman spectra of NG grown at 600, 650, and 700 ^{o}C for 60 min, respectively. (b) Raman spectra of NG grown at 700 ^{o}C for 30-120 min. Note that the other growth parameters were kept identical.

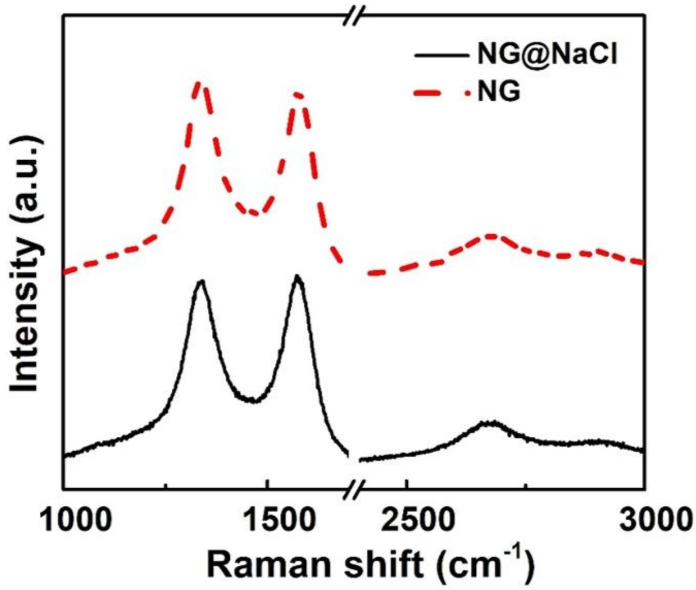

Figure S8. Raman spectra of obtained NG and NaCl@NG products, indicating that using water to remove the NaCl templates showed a slight influence on the product quality of NG (growth condition: 700 ^{o}C, 200 sccm Ar, 60 sccm H_2, 80 W with a controlled pyridine vapor flow for 120 min).

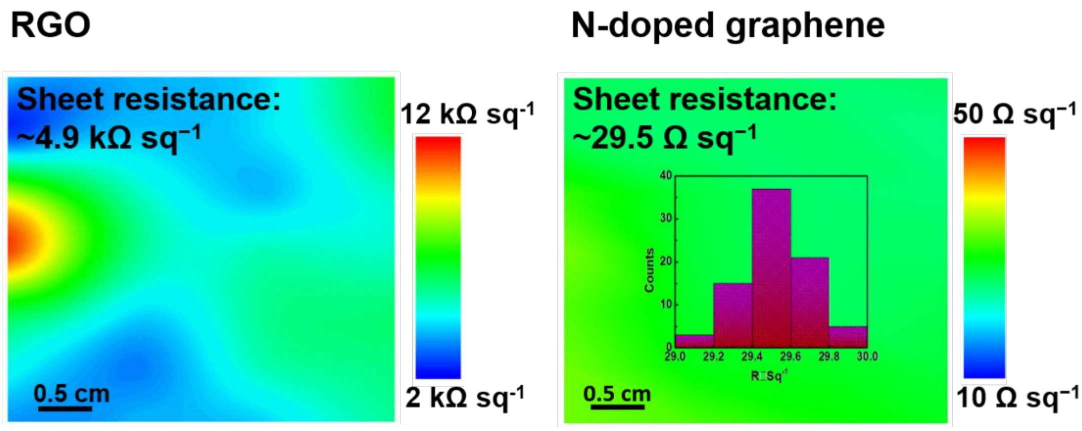

Figure S9. Comparison of sheet resistance mapping results between RGO and NG.

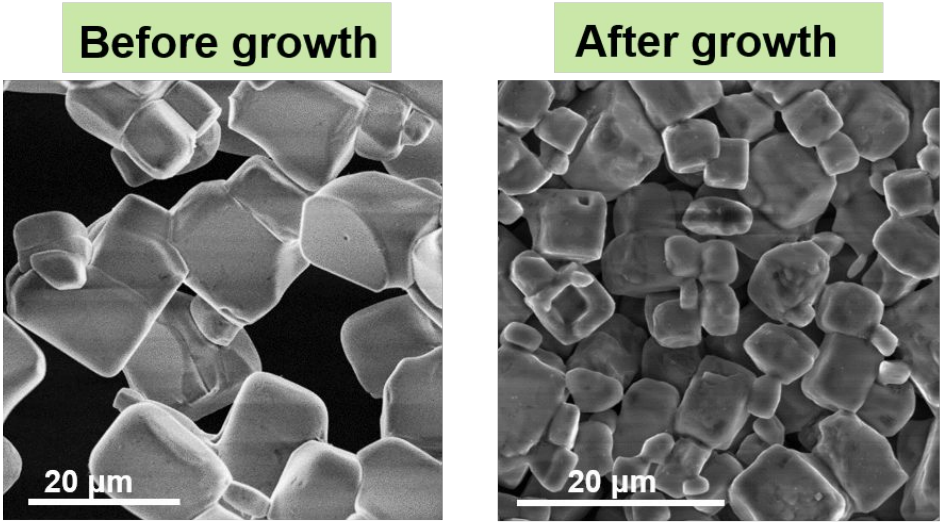

Figure S10. SEM images of NaCl powders (before CVD growth) and NaCl@NG (after growth).

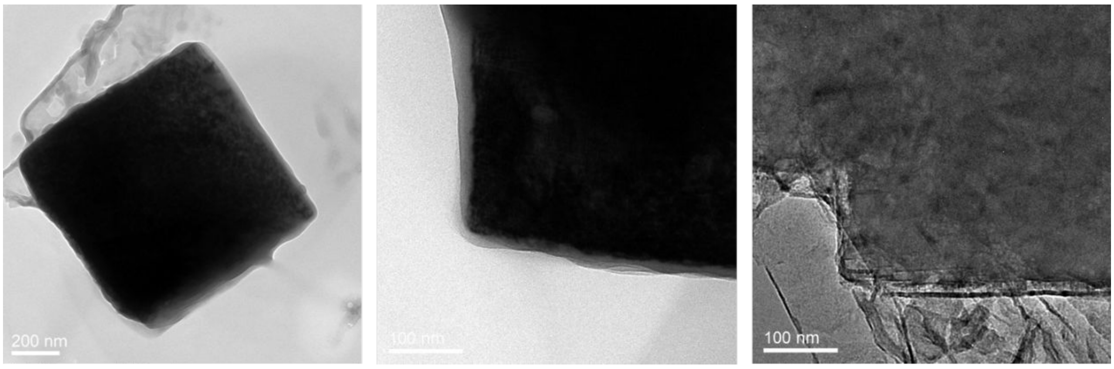

Figure S11. TEM images of as-grown NaCl@NG, showing the perfect wrapping of thin graphitic layers on cubic NaCl crystal.

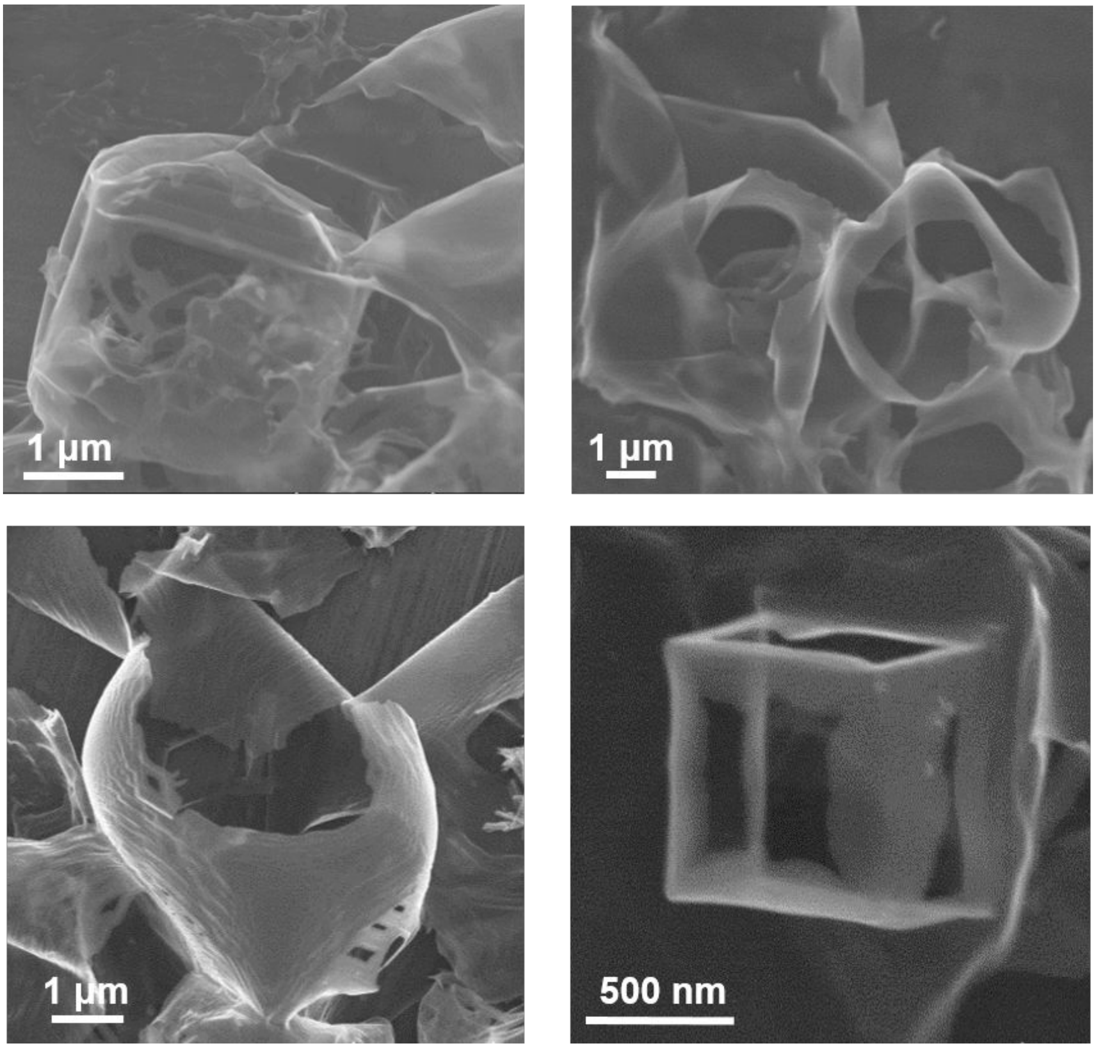

Figure S12. SEM images of NG cages.

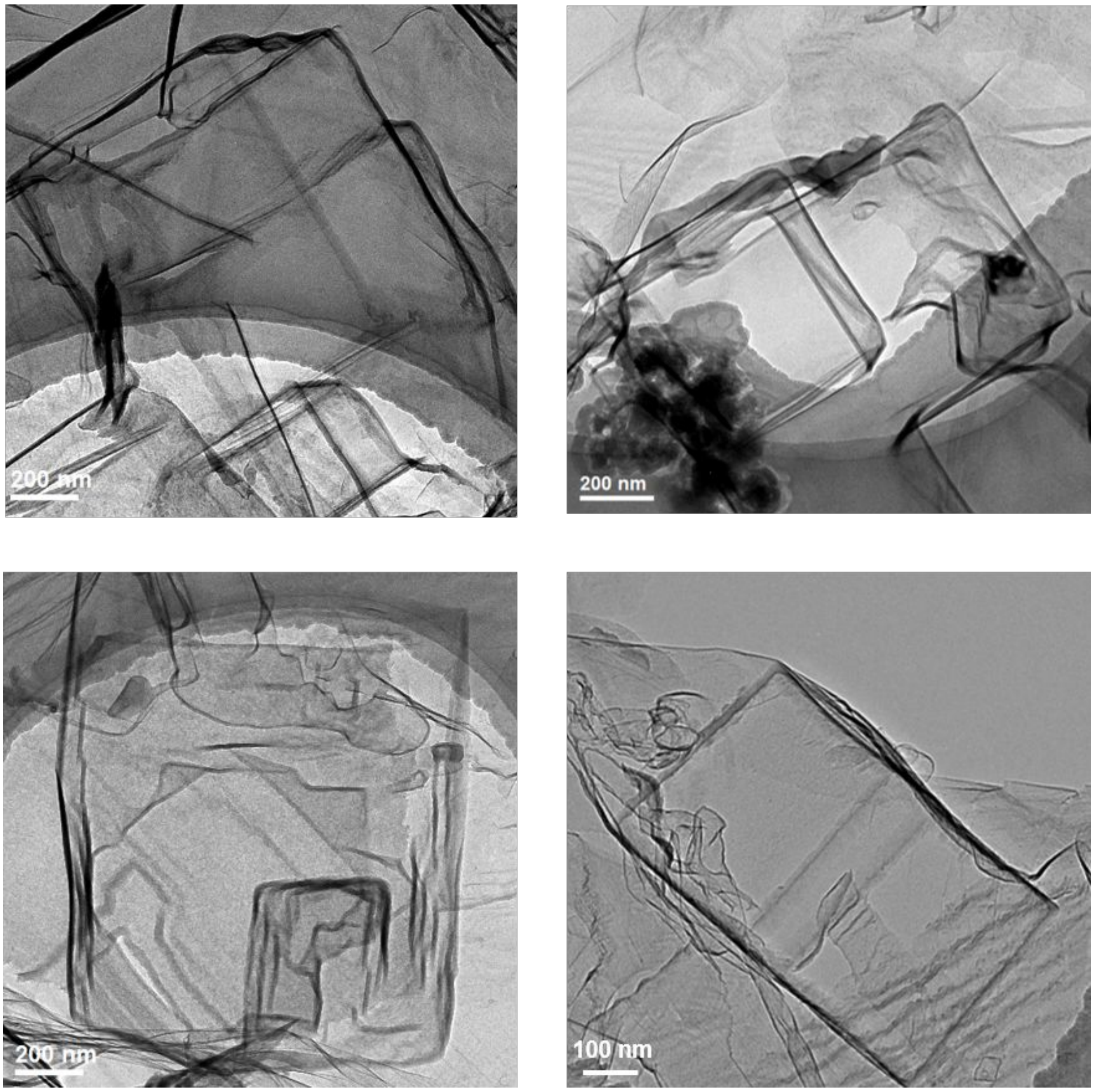

Figure S13. TEM images of NG cages.

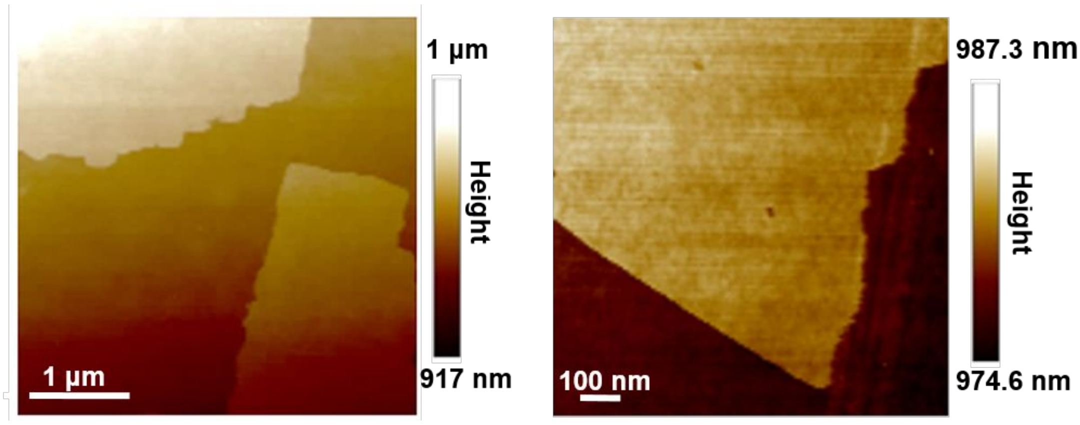

Figure S14. Representative AFM images of NG nanosheets deposited onto SiO_2/Si substrates for measurement.

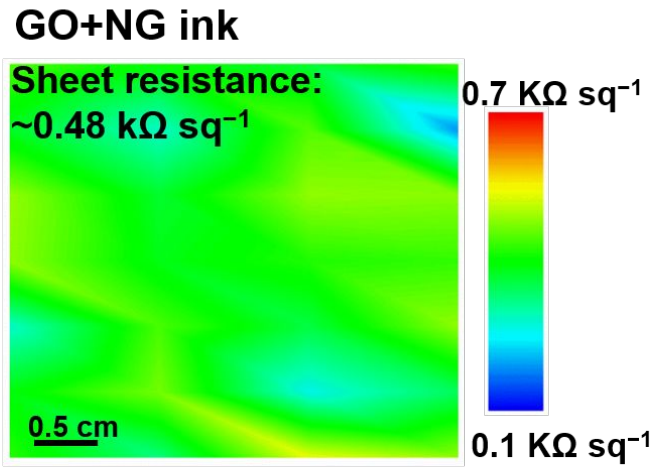

Figure S15. Sheet resistance mapping of NG-based composite ink. The ink film was printed on a flat glass substrate, followed by a GO reduction process. The average value of sheet resistance is *ca*. 480 Ω sq^{-1}, suggesting favorable electrical conductivity of such composite ink.

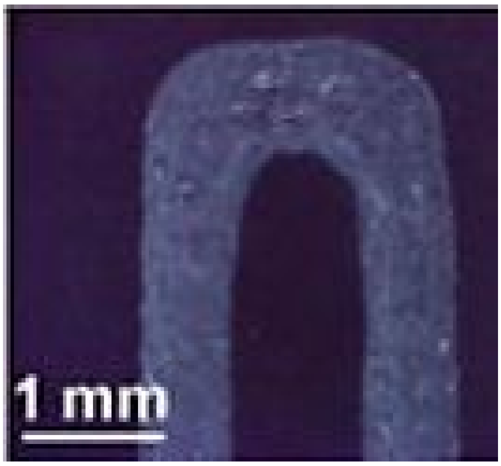

Figure S16. OM image showing the fine structure of printed patterns.

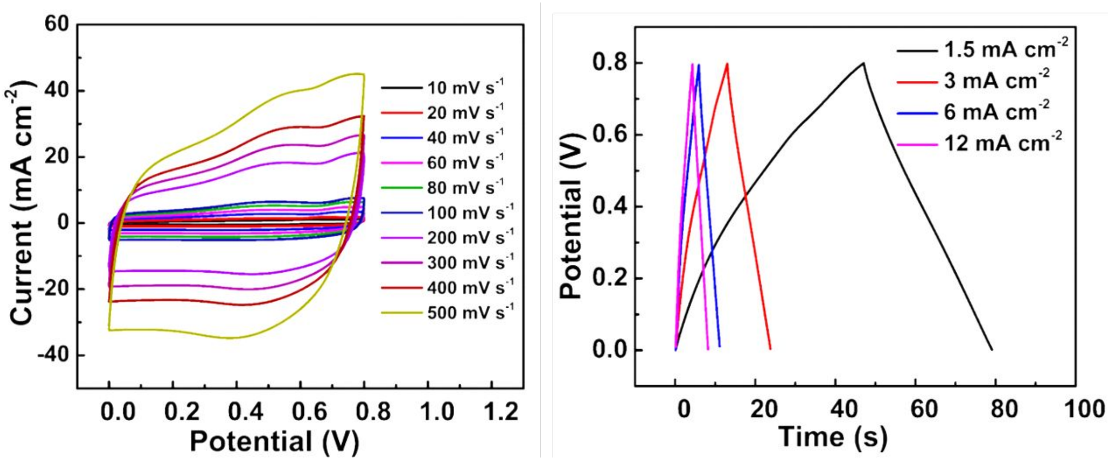

Figure S17. CV profiles of bare VN with different scan rates of 10-500 mV s^{-1}. (b) Galvanostatic charge-discharge curves of bare VN electrodes at various current densities of 1.5-12 mA cm^{-2}.

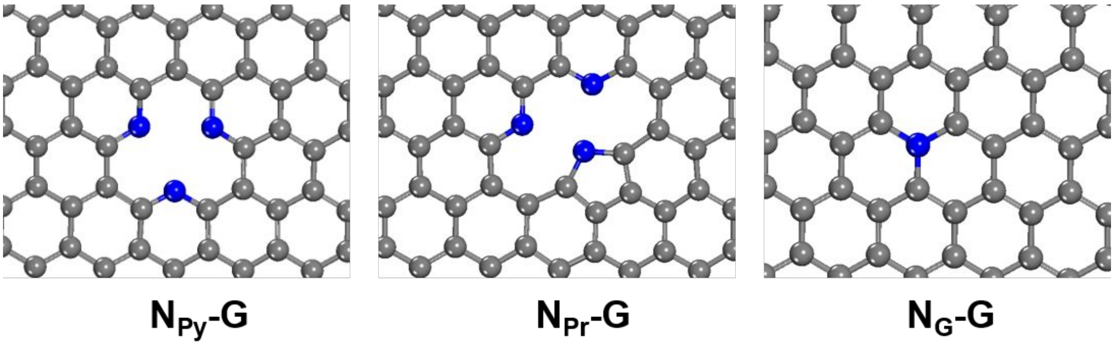

Figure S18. The configuration of nitrogen doping graphene (from left to right: N_{Py}-G, N_{Pr}-G and N_G-G). Carbon and nitrogen atom is in grey and blue color, respectively.

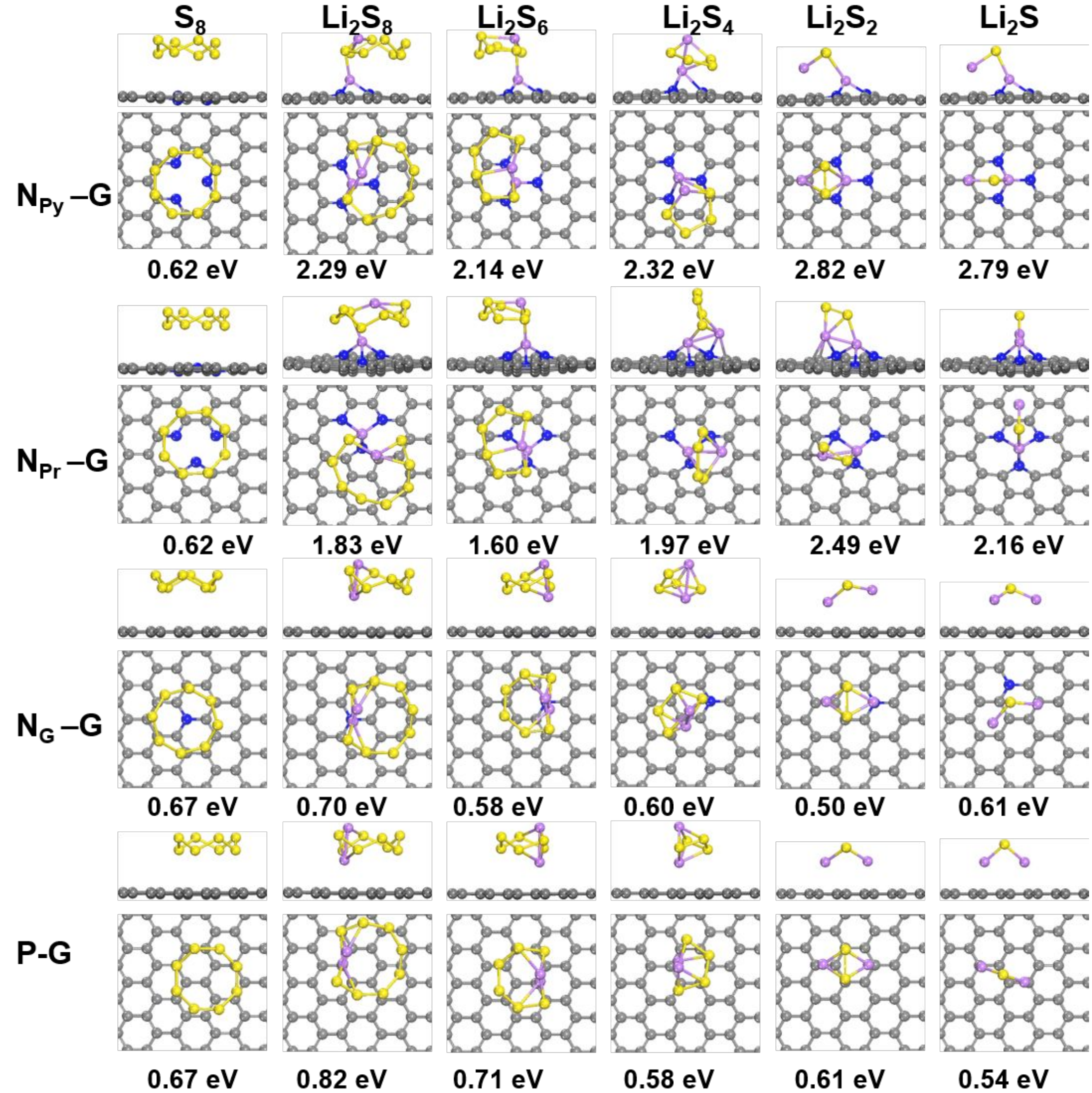

Figure S19. Calculated adsorption configurations and binding energies of polysulfides on the pyridinic-, pyrrolic-, graphitic-nitrogen doping graphene and pristine graphene (N_{Py}-G, N_{Pr}-G, N_G-G and P-G). Carbon, nitrogen, lithium and sulfur atom is in grey, blue, purple and yellow color, respectively.

● Supporting Notes

Notes to Figure 1c:

Evaluation symbol: environmental friendliness (E), quality (Q), cost aspect (C), scalability (S), and purity (P).

RGO: The production process is normally involved with hazardous materials such as acid and $KMnO_4$, which is not environmentally friendly. The obtained RGO is of low quality because of the presence of extrinsic defects (O and H-containing groups) and of low purity. Nevertheless, this production method allows the employment of bulk quantities with high yield, which would be scalable. Owing to the combination of low-cost precursor and high-cost processing/cleansing fee, the cost aspect for RGO is at a mediocre level.[1-2]

LPEG: In liquid-phase exfoliation, graphite particles are first dispersed in a solvent to reduce the strength of the van der Waals attraction between the graphene layers. Afterwards, an external driving force such as ultrasonication, electric field or shearing is used to induce the exfoliation of graphite into good quality graphene sheets. Even though the use of large amount of organic solvent would pose a negative impact on the environmental benignancy of production, this material is normally of high scalability and marginal costs.[3-4]

CVD derived G on silica: In CVD grown graphene on silica powder, graphene has a high crystallinity with ordered sp^2 carbon structure, which benefits from the high-temperature (>1000 °C) synthesis. Graphene flakes can be obtained via the HF etching of silica template, followed by washing and drying. It is noted that the such wet-chemical etching process is inevitably involved to remove the substrates, which is tedious and environmentally unfriendly. The production route also makes it difficult to meet the demand for graphene production in a scalable manner.[4-5]

CVD grown graphene on NaCl: The PECVD process gives rise to relatively low quality of graphene as compared to the graphene directly grown on silica. But the NaCl template can be easily removed by dissolving in water without any contamination. This low-temperature synthesis might offer a facile way for manufacturing NG on a large scale.

● Supporting References

1. Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G., Processable Aqueous Dispersions of Graphene Nanosheets. *Nat. Nanotechnol.* **2008,** *3*, 101-105.

2. Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S., The Chemistry of Graphene Oxide. *Chem. Soc. Rev.* **2010,** *39*, 228-240.

3. Paton, K. R.; Varrla, E.; Backes, C.; Smith, R. J.; Khan, U.; O'Neill, A.; Boland, C.; Lotya, M.; Istrate, O. M.; King, P.; Higgins, T.; Barwich, S.; May, P.; Puczkarski, P.; Ahmed, I.; Moebius, M.; Pettersson, H.; Long, E.; Coelho, J.; O'Brien, S. E., *et al*., Scalable Production of Large Quantities of Defect-Free Few-Layer Graphene by Shear Exfoliation in Liquids. *Nat. Mater.* **2014,** *13*, 624-630.

4. Tour, J. M., Layered Materials: Scaling Up Exfoliation. *Nat. Mater.* **2014,** *13*, 545-546.

5. Chen, K.; Li, C.; Shi, L. R.; Gao, T.; Song, X. J.; Bachmatiuk, A.; Zou, Z. Y.; Deng, B.; Ji, Q. Q.; Ma, D. L.; Peng, H. L.; Du, Z. L.; Rummeli, M. H.; Zhang, Y. F.; Liu, Z. L., Growing Three-Dimensional Biomorphic Graphene Powders Using Naturally Abundant Diatomite Templates Towards High Solution Processability. *Nat. Commun.* **2016,** *7*, 13440.