Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Direct Growth of Nitrogen-Doped Graphene Films on Glass by Plasma-Assisted Hot Filament CVD for Enhanced Electricity Generation

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1) SEM surface images of graphene films deposited by plasma-assisted HFCVD with N_2 flows of 0 sccm and 20 sccm for 9 min.

Typically, the vertical graphene nanowalls, which are generated by the energetic plasma, are observed on the film surface. However, these nanowalls prepared by plasma-assisted HFCVD exhibit smaller size than those prepared by pure PECVD in literature,[1] and almost disappear under high N_2 flow condition with the same deposition time.

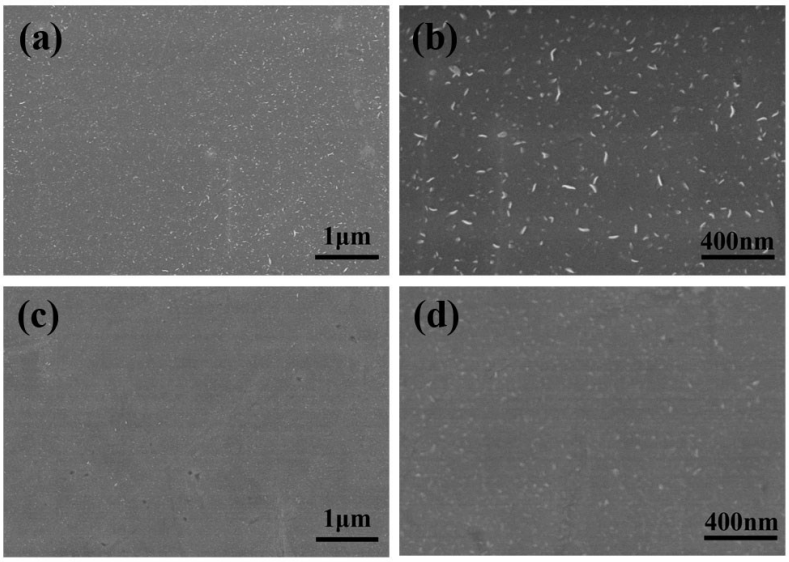

Figure S1. SEM surface images of graphene films deposited with different N_2 flows for 9 min: (a, b) 0 sccm; (c, d) 20 sccm.

2) HRTEM results of carbon films grown by PECVD with plasma power of 50 W and N_2 flow of 5 sccm for 9 min.

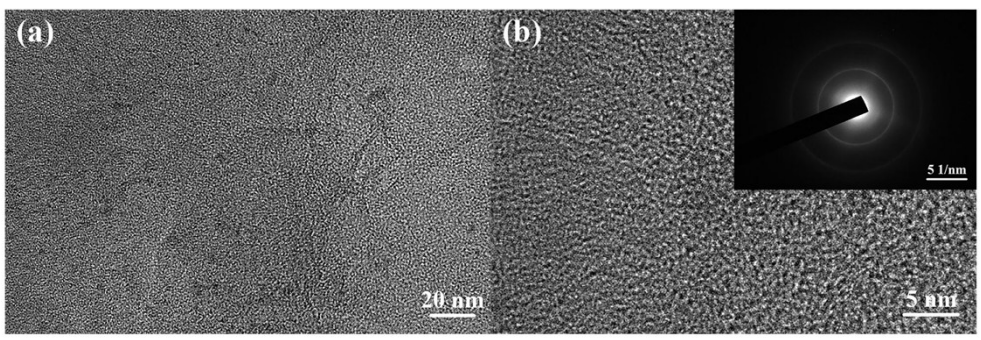

Figure S2. HRTEM images of carbon films grown by PECVD with plasma power of 50 W and N_2 flow of 5 sccm for 9 min. The disordered curves indicate the amorphous structure of carbon films. Inset of (b) shows the corresponding SAED pattern. The diffusive ring also indicates the amorphous structure of carbon films.

3) Raman spectra of graphene films grown by PECVD with plasma power of 130 W and N_2 flows of 5 sccm for 9 min. The comparison of Raman results of graphene films deposited with plasma powers of 50 W and 130 W is also provided.

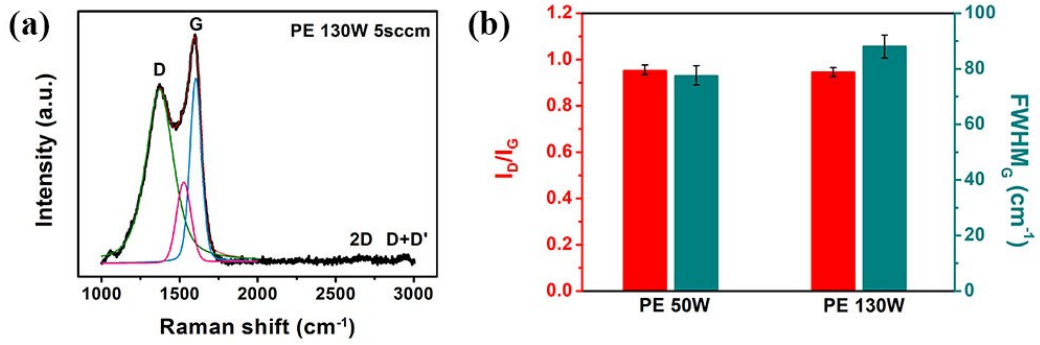

Figure S3. (a) Raman spectra of graphene films grown by PECVD with 5 sccm N_2 flow for 9 min. (b) Comparison of I_D/I_G and $FWHM_G$ of graphene films deposited with plasma powers of 50 W and 130 W.

4) XPS spectra of graphene films grown by plasma-assisted HFCVD and HFCVD for 9 min.

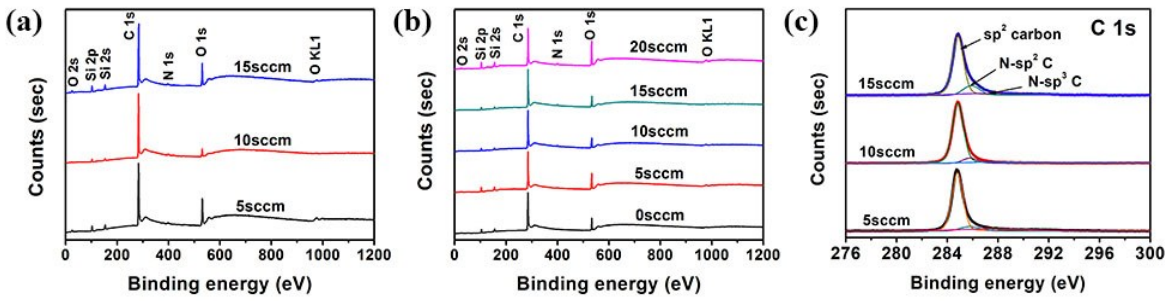

Figure S4. (a) XPS survey spectra of graphene films deposited by plasma-assisted HFCVD with N_2 flows

of 5 sccm, 10 sccm and 15 sccm for 9 min. (b) XPS survey spectra of graphene films deposited by HFCVD with the filament temperature of 2000 °C under different N_2 flows conditions for 9 min. (c) XPS C 1s spectra of graphene films grown by plasma-assisted HFCVD with N_2 flows of 5 sccm, 10 sccm and 15 sccm for 9 min.

5) Thickness of graphene films deposited by plasma-assisted HFCVD with different N_2 flows for 9 min.

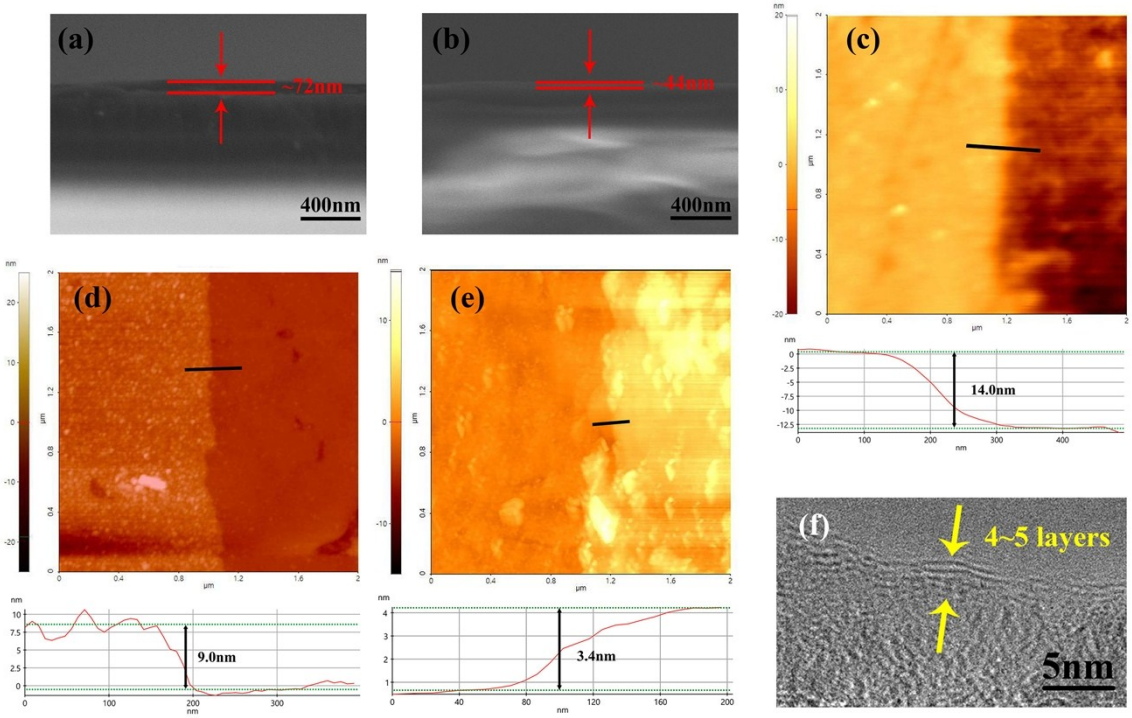

Figure S5. (a, b) SEM cross section images of graphene films grown with 0 sccm and 5 sccm N_2 flows, showing the thickness of ~72 nm and ~44 nm, respectively. (c, d, e) AFM images and height profiles of graphene films grown with 10 sccm, 15 sccm and 20 sccm N_2 flows, showing the thickness of ~14.0 nm, ~9.0 nm and ~3.4 nm, respectively. (f) HRTEM edge images of N-doped graphene films deposited with N_2 flow of 20 sccm, showing 4~5 graphene layers.

6) Raman spectra of graphene films deposited by plasma-assisted HFCVD with different transmittance under N_2 flows of 0 sccm and 20 sccm conditions. The graphene films with different transmittance are prepared by adjusting growth time.

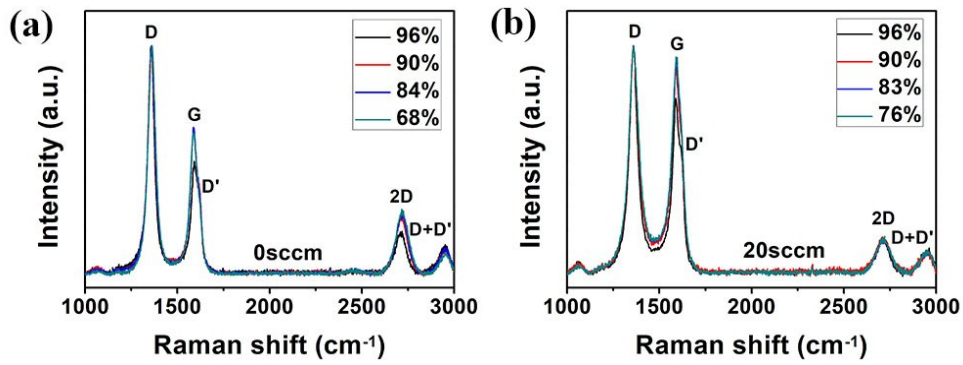

Figure S6. (a) Raman spectra of graphene films grown by plasma-assisted HFCVD with 0sccm N_2 flow for 5 min 30 s, 6 min, 6 min 40 s and 9 min. The corresponding transmittance is 96 %, 90 %, 84 % and 68 %, respectively. (b) Raman spectra of graphene films grown by plasma-assisted HFCVD with 20 sccm N_2 flow for 8 min 15 s, 9 min, 10 min 15 s and 12 min. The corresponding transmittance is 96 %, 90 %, 83 % and 76 %, respectively.

7) Arrhenius plots of resistance measurements of graphene films deposited by plasma-assisted HFCVD with different N_2 flows from 0 to 20 sccm for 9 min. The activation energy is obtained from the slope of fitting lines.

The change of resistivity ρ with respect to temperature T is described by the Arrhenius formula below:[2,3]

$$\frac{1}{\rho} = Ae^{-\frac{E_a}{k_B T}}, \rho = R\frac{s}{l}$$

where E_a is the conductive activation energy, k_B the Boltzmann constant (8.6174×10^{-5} eV·K^{-1}), A the pre-exponential constant, R the resistance, s the cross sectional area and l the length.

To obtain the activation energy, the curves of ln(1/*R*) versus 1000/*T* are plotted. The resistance *R* is measured from the I-V test. It is pointed out that despite the cross sectional area of graphene films is not a constant because of the different film thickness, the calculated activation energy is in fact not influenced by this parameter and therefore can be compared with each other.

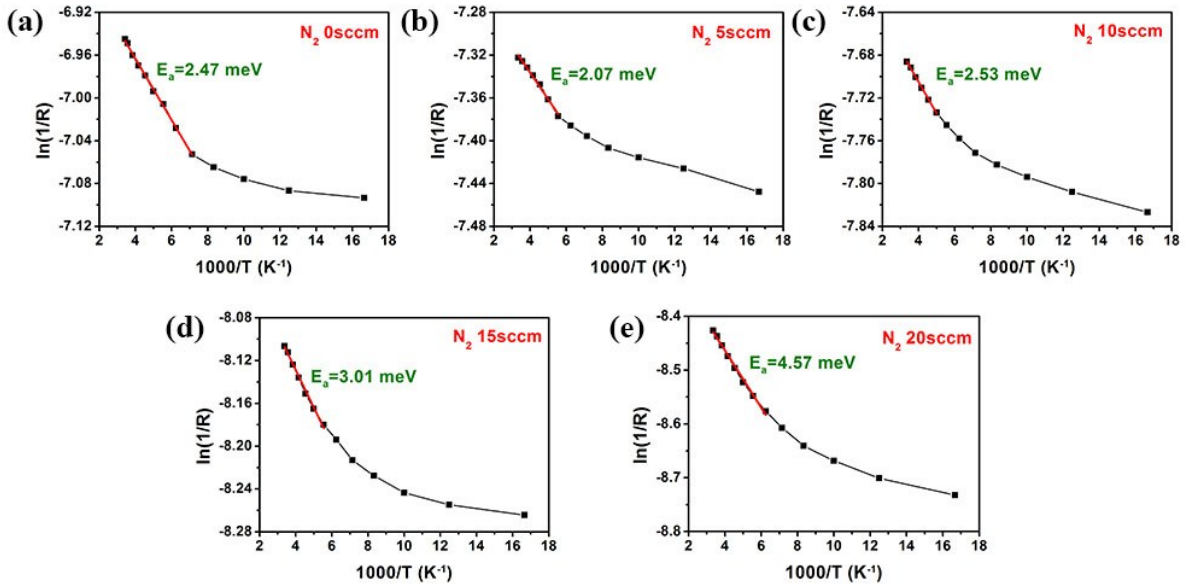

Figure S7. Arrhenius plots of resistance measurements for graphene films deposited by plasma-assisted HFCVD with different N_2 flows for 9 min: (a) 0 sccm; (b) 5 sccm; (c) 10 sccm; (d) 15 sccm; (e) 20 sccm. The red fitting lines and the corresponding activation energy are both marked.

8) Raman spectra of pristine and N-doped graphene glass fabricated by plasma-assisted HFCVD with different transmittance for electricity generation. The transmittance is adjusted by changing growth time.

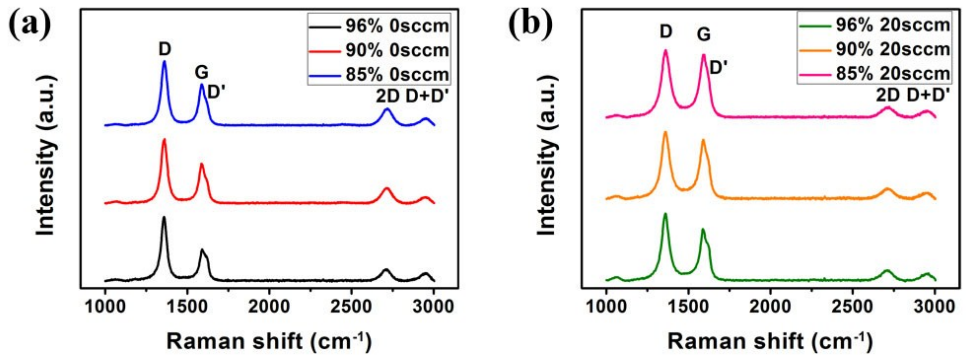

Figure S8. Raman spectra of pristine graphene glass (a) and N-doped graphene glass (b). Samples were fabricated by plasma-assisted HFCVD with transmittance of 96 %, 90 % and 85 %. The corresponding growth time for pristine graphene is 5 min 30 s, 6 min and 6 min 30 s, and for N-doped graphene is 8 min 15 s, 9 min and 10 min.

9) Raman spectra of N-doped graphene glass fabricated by plasma-assisted HFCVD with N_2 flow of 20 sccm and transmittance of 96 % for the stability test of electricity generation.

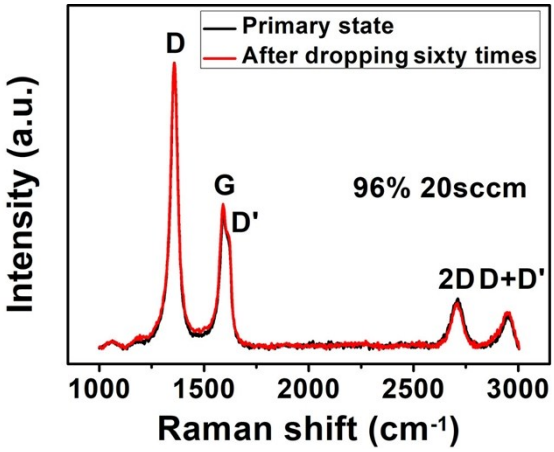

Figure S9. Raman spectra of N-doped graphene glass fabricated by plasma-assisted HFCVD with N_2 flow of 20 sccm and transmittance of 96 % for the stability test of electricity generation. The overlapping curves of primary state and final state after dropping NaCl droplets sixty times indicate the good stability of N-doped graphene glass for energy harvesting.

10) Contact angle images of pristine and N-doped graphene glass fabricated by plasma-assisted HFCVD with different transmittance. The transmittance is adjusted by changing growth time.

For the experiment of electricity generation, the volume of NaCl droplet is constant. The contact area between NaCl droplet and N-doped graphene glass is larger than that between the droplet and pristine graphene glass since the contact angles of N-doped graphene are all smaller than those of the pristine ones under the same transmittance. However, due to the small difference of contact angle here, the ratio difference of the droplet length *L* and the droplet width *W* between pristine and N-doped graphene glass is both small. The ratio difference of *L* and *W* is also small for the different transmittance conditions.

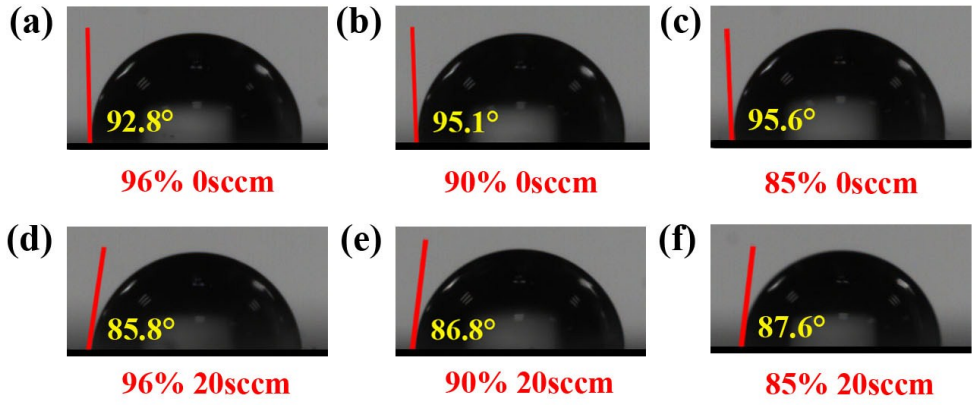

Figure S10. Contact angle images of pristine graphene glass (a, b, c) and N-doped graphene glass (d, e, f) fabricated by plasma-assisted HFCVD with transmittance of 96 %, 90 % and 85 %. The corresponding growth time for pristine graphene is 5 min 30 s, 6 min and 6 min 30 s, and for N-doped graphene is 8 min 15 s, 9 min and 10 min.

References

1 Y. Qi, B. Deng, X. Guo, S. Chen, J. Gao, T. Li, Z. Dou, H. Ci, J. Sun, Z. Chen, R. Wang, L. Cui, X.

Chen, K. Chen, H. Wang, S. Wang, P. Gao, M. H. Rummeli, H. Peng, Y. Zhang and Z. Liu, *Adv. Mater.*, 2018, 30, 1704839.

2 Z. Zhai, H. Shen, J. Chen, X. Li and Y. Jiang, *ACS Appl. Mater. Interfaces*, 2018, 10, 17427-17436.

3 W. J. McCarter, G. Starrs, T. M. Chrisp and P. F. G. Banfill, *J. Mater. Sci.*, 2007, 42, 2200-2203.