

Electronic Supplementary Information

**Hybrid Multilayer Thin Film Supercapacitor of Graphene
Nanosheets with Polyaniline: Importance of Establishing Intimate
Electronic Contact through Nanoscale Blending**

*Taemin Lee, Taeyeong Yun, Byeongho Park, Bhawana Sharma, Hyun-Kon Song, and
Byeong-Su Kim**

Interdisciplinary School of Green Energy and KIER-UNIST Advanced Center for Energy,
Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Korea

bskim19@unist.ac.kr

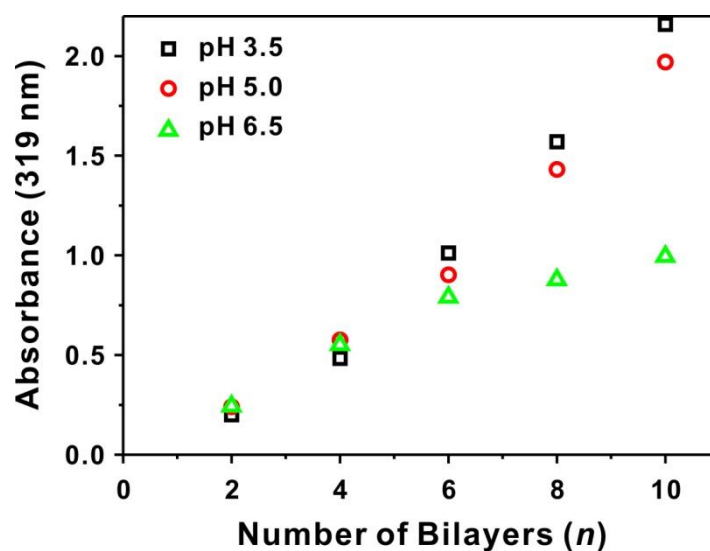


Fig. S1 Plot of the UV/vis absorption peak at 319 nm of PG_n multilayer film as a function of the number of bilayers constructed with varying pH of GO suspension at a fixed pH of PANi (pH 2.5).



Fig. S2 Representative photograph image of LbL-assembled hybrid electrodes of (left) PG_{10} (middle) $\text{PG}_{10}\text{-H}$, and (right) $\text{PG}_{10}\text{-HC}$.

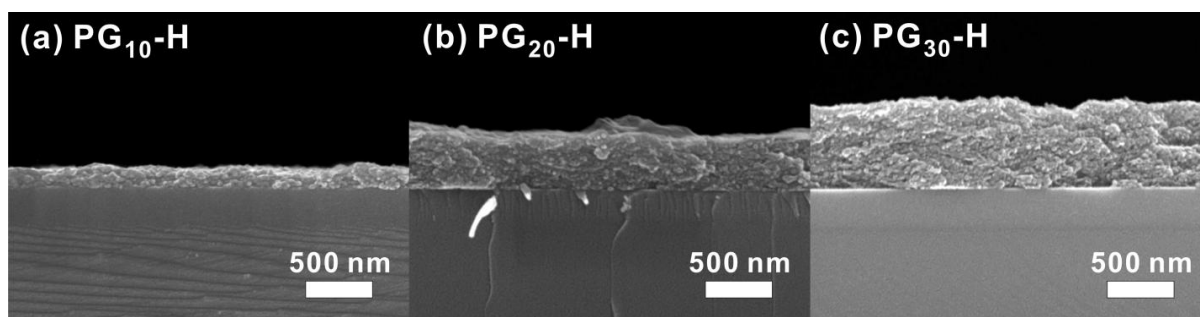


Fig. S3 Representative SEM images of $\text{PG}_n\text{-H}$ multilayer films of different number of bilayers. (a) $n = 10$, (b) $n = 20$, and (c) $n = 30$.

Table S1 XPS peak assignments of deconvoluted C1s and N1s composition with relative percentage of each peak.

	Binding Energy (eV) / relative percentage (%)								
	C 1s						N 1s		
	C=C	C-C	C-N	C-O	C=O	O-C=O	=N-	-NH-	N ⁺
	284.37 (48.32)	285.1 (14.96)	285.8 (4.37)	286.63 (19.71)	287.95 (10.43)	289.89 (2.21)	398.21 (10.53)	399.37 (48.85)	401.09 (40.62)
PG ₁₀									
PG ₁₀ -H	284.38 (57.37)	285.08 (12.89)	285.84 (10.7)	286.67 (7.1)	287.87 (7.31)	289.23 (4.63)	398.22 (9.68)	399.5 (58.2)	401.09 (27.11)
PG ₁₀ -HC	284.45 (59.79)	285.16 (8.27)	285.83 (12.76)	286.63 (7.05)	287.87 (7.64)	289.36 (4.48)	398.21 (4.81)	399.57 (61.26)	401.07 (33.93)

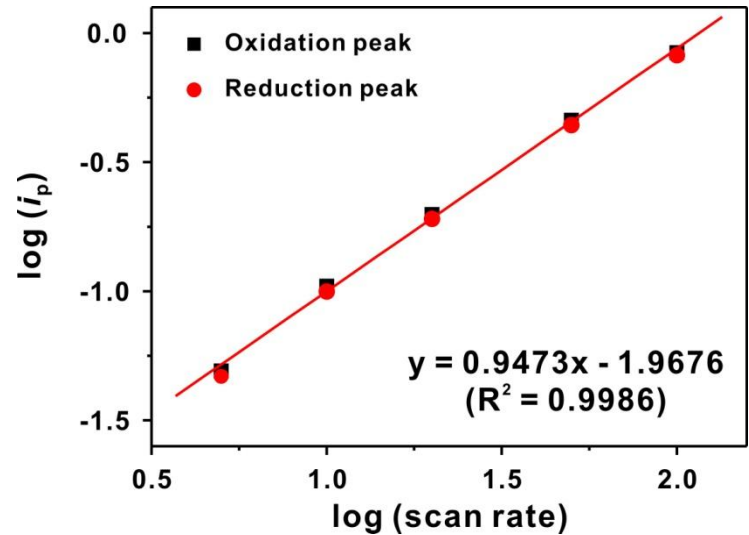


Fig. S4 Plot of the peak current density (mA cm^{-2}) vs potential scan rate (mV s^{-1}) of PG₁₀-H in an equi-span log-log scale. The slopes were estimated to be around 1.0 for both cases.

Table S2 Specific capacitance values of hybrid PG₁₀, PG₁₀-H, PG₁₀-HC, and GG₁₀-H electrodes obtained from cyclic voltammograms and galvanostat charge/discharge experiments.

	Specific capacitance (F g ⁻¹) (from cyclic voltammograms)				
	10 mV s ⁻¹	20 mV s ⁻¹	50 mV s ⁻¹	100 mV s ⁻¹	200 mV s ⁻¹
PG₁₀	402.48	326.17	269.18	241.54	219.35
PG₁₀-H	489.04	400.13	349.92	323.76	304.76
PG₁₀-HC	240.13	180.53	135.01	116.85	103.54
GG₁₀-H	24.62	19.08	15.3	12.84	10.94

	Specific capacitance (F g ⁻¹) (from charge/discharge curves)					
	0.5 A g ⁻¹	1 A g ⁻¹	1.5 A g ⁻¹	2.0 A g ⁻¹	2.5 A g ⁻¹	3.0 A g ⁻¹
PG₁₀	162.89	136.24	121.04	103.64	101.15	94.23
PG₁₀-H	375.15	218.43	163.92	129.92	124.65	116.46

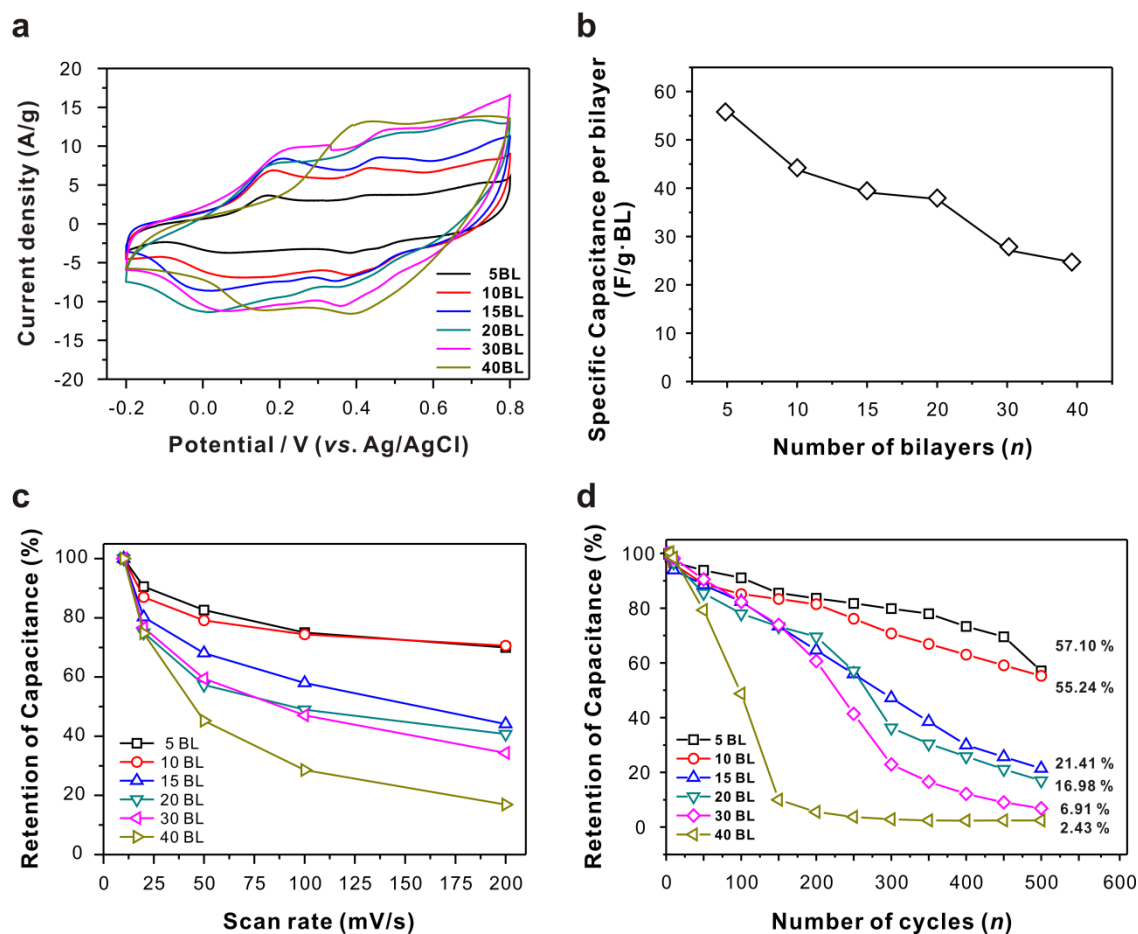


Fig. S5 Electrochemical performance of LbL-assembled PG_n -H multilayer films of different number of bilayers ($n = 5, 10, 15, 20, 30, 40$). (a) Cyclic voltammogram (CV) curves measured in a three-electrode system with a Ag/AgCl reference electrode in 1.0 M H_2SO_4 at a scan rate of 10 mV s^{-1} . (b) Plot of the specific capacitance per bilayer with respect to different numbers of bilayer. (c, d) Electrochemical stability of all PG_n -H multilayer films depending on (c) various scan rates from 10 to 200 mV s^{-1} and (d) number of cycles measured at a scan rate of 200 mV s^{-1} .

Table S3 Specific capacitance values of PG_{*n*}-H (*n* = 5, 10, 15, 20, 30, 40) multilayer films of various number of bilayers obtained from cyclic voltammograms.

	Specific capacitance (F g ⁻¹) (from cyclic voltammograms)				
BL	10 mV s ⁻¹	20 mV s ⁻¹	50 mV s ⁻¹	100 mV s ⁻¹	200 mV s ⁻¹
PG ₅ -H	280.14	253.63	231.54	210.14	196.03
PG ₁₀ -H	489.04	400.13	349.92	323.76	304.76
PG ₁₅ -H	587.22	471.13	399.84	340.49	259.04
PG ₂₀ -H	755.06	566.64	432.68	369.89	307.53
PG ₃₀ -H	816.90	626.36	486.07	384.52	280.71
PG ₄₀ -H	980.51	733.40	443.51	280.41	165.72

Table S4 List of electrochemical capacitance values of various PANi-GO hybrid electrodes from recent literatures.

System	Specific Capacitance	Measurement Condition	Reference
Simple mixing	210 F g ⁻¹	discharge current density at 0.3 A g ⁻¹	<i>G. Shi et al., ACS Nano (2010)</i> ¹
In situ polymerization	260 F g ⁻¹	discharge current density at 0.5 A g ⁻¹	<i>J. Wu et al., Chem. Mater. (2010)</i> ²
	555 F g ⁻¹	discharge current density at 0.2 A g ⁻¹	<i>Z. Wei et al., ACS Nano (2010)</i> ³
	746 F g ⁻¹	discharge current density at 0.2 A g ⁻¹	<i>X. Wang et al., ACS Appl. Mater. Interfaces (2010)</i> ⁴
	1046 F g ⁻¹	CV Scan rate at 1 mV s ⁻¹	<i>F. Wei et al., Carbon (2010)</i> ⁵
	286 F g ⁻¹	discharge current density at 0.3 A g ⁻¹	<i>G. D. Fu et al., Macromol. Rapid Commun. (2011)</i> ⁶
	250 F g ⁻¹	CV Scan rate at 100 mV s ⁻¹	<i>J.-B. Baek et al., ACS Nano (2012)</i> ⁷
In situ electropolymerization	233 F g ⁻¹	CV Scan rate at 20 mV s ⁻¹	<i>H.-M. Cheng et al., ACS Nano (2009)</i> ⁸
	640 F g ⁻¹	discharge current density at 0.1 A g ⁻¹	<i>W. Huang et al., Adv. Funct. Mater. (2011)</i> ⁹
	970 F g ⁻¹	discharge current density at 2.5 A g ⁻¹	<i>T. Cao et al., Adv. Funct. Mater. (2012)</i> ¹⁰

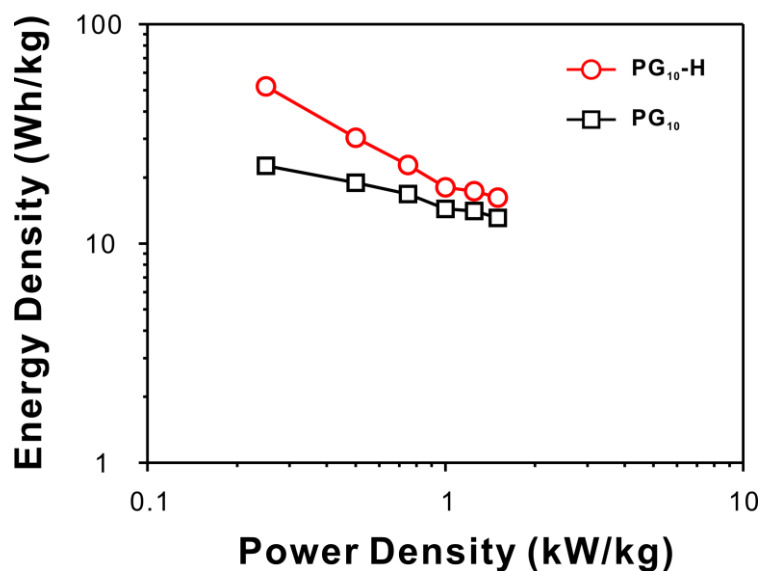


Fig. S6 Ragone plot of the LbL-assembled hybrid PG₁₀ (black-line) and PG₁₀-H (red-line) supercapacitor electrodes measured at different discharge current density from 0.5 to 3 A g⁻¹.

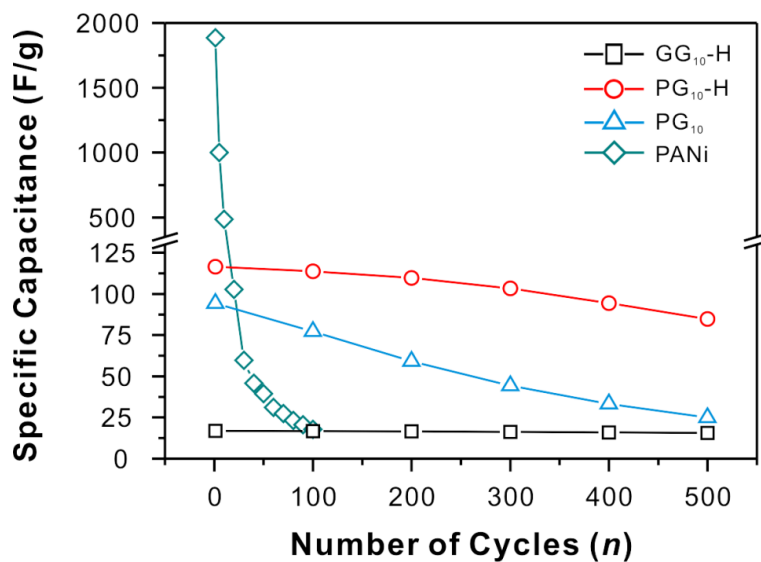


Fig. S7 Comparison of cycling stability of all samples at a high discharge current density of 3 A g⁻¹. Electropolymerized pure PANi film was used for comparison.

References

1. Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, *ACS Nano*, 2010, **4**, 1963-1970.
2. K. Zhang, L. L. Zhang, X. S. Zhao, J. Wu, *Chem. Mater.*, 2010, **22**, 1392-1401.
3. J. Xu, K. Wang, S.-Z. Zu, B.-H. Han, Z. Wei, *ACS Nano*, 2010, **4**, 5019-5026.
4. H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, *ACS Appl. Mater. Interfaces*, 2010, **2**, 821-828.
5. J. Yan, T. Wei, B. Shao, Z. J. Fan, W. Z. Qian, M. L. Zhang, F. Wei, *Carbon*, 2010, **48**, 487-493.
6. L. Q. Xu, Y. L. Liu, K.-G. Neoh, E.-T. Kang, G. D. Fu, *Macromol. Rapid Commun.*, 2011, **32**, 684-688.
7. N. A. Kumar, H.-J. Choi, Y. R. Shin, D. W. Chang, L. Dai, J.-B. Baek, *ACS Nano*, 2012, **6**, 1715-1723.
8. D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G. Q. Lu, H.-M. Cheng, *ACS Nano*, 2009, **3**, 1745-1752.
9. X. M. Feng, R. M. Li, Y. W. Ma, R. F. Chen, N. E. Shi, Q. L. Fan, W. Huang, *Adv. Funct. Mater.* 2011, **21**, 2989-2996.
10. M. Xue, F. Li, J. Zhu, H. Song, M. Zhang, T. Cao, *Adv. Funct. Mater.* 2012, **22**, 1284-1290.