

Supplementary Material (ESI) for Chemical Communications

Functionalization of reduced graphene oxides by redox-active ionic liquids for energy storage

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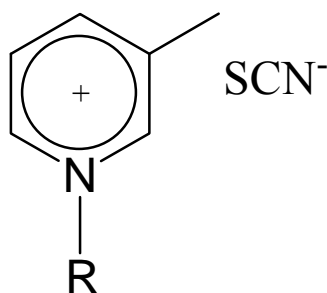
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Functionalization of reduced graphene oxides (RGOs) by pyridinium-based ionic liquids (ILs)

Graphene oxides (GOs) were synthesized through the acidification, oxidation, and exfoliation of natural graphite through the modified Hummers method.¹ The resultant GOs (5 mg) were fully exfoliated and dispersed in deionized (DI) water (10 mL). The GOs were reduced into reduced graphene oxide (RGO) by 10 μ L of hydrazine solution at 90 °C for 5 hours and then a homogenous black dispersion was washed with DI water at several times. The quality of RGO was confirmed in our previous reports.²

IL-functionalized RGOs were prepared by mixing RGOs (0.5 mg) with ILs (5 μ l) in agate mortar for 15 min. The resulting paste was rubbed onto a gold electrode and dried under vacuum at 80°C for 30 min to measure electrochemical properties of IL-functionalized RGOs. We used four ILs such as 1,3-dimethylpyridinium thiocyanate ([mmpy][SCN]), 1-butyl-3-methylpyridinium thiocyanate ([bmpy][SCN]), 1-hexyl-3-methylpyridinium thiocyanate [hmpy][SCN], and 1-octyl-3-methylpyridinium thiocyanate [ompy][SCN], as shown below.



[mmpy][SCN]: R=CH₃, [bmpy][SCN]: R=(CH₂)₃CH₃, [hmpy][SCN]: R=(CH₂)₅CH₃, [ompy][SCN]:
R=(CH₂)₇CH₃

Characterization

The Fourier transform infrared (FT-IR) spectra were collected on a JASCO FT-IR 470 plus. Each spectrum was recorded from 4000 to 650 cm^{-1} with using 30 scans. The UV spectra were collected from UV/vis/NIR spectrophotometer (V670, JASCO). Cyclic voltammetry was analyzed by a CHI 760D electrochemical workstation (CH Instruments) using Au as the working electrode, Ag/AgCl as the reference electrode, and Pt wire as the counter electrode, respectively. CV measurements were performed at different voltage scan rates in a range from 100 mV s^{-1} . Galvanostatic charge/discharge measurements were carried out using a Solartron 1260 at room temperature. Galvanostatic charge/discharge measurements were carried out at different specific current

from 1 to 30 A g⁻¹. The electrochemical impedance spectroscopy measurements were performed over a frequency range from 10⁶ to 10⁻³ Hz at the amplitude of the sinusoidal voltage of 10 mV and RT on supercapacitor devices using a Solartron 1260 impedance/gain-phase analyzer. The ionic conductivities of ILs were measured with a two-point probe cell. This apparatus was connected with a sealed cell with the cell constant of 1.0 cm⁻¹. The conductivity of the sample was obtained from complex impedance analysis. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity was obtained from the bulk resistance found in complex impedance diagram.

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1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. B. G. Choi, W. H. Hong, Y. M. Jung and H. S. Park, *Chem. Commun.*, 2011, **47**, 10293; B. G. Choi, J. Hong,
20 W. H. Hong, P. T. Hammond and H. S. Park, *ACS Nano*, 2011, **5**, 7205; B. G. Choi, H. S. Park, T. J. Park, M. H. Yang, J. S. Kim, S. Y. Jang, N. S. Heo, S. Y. Lee, K. Kong and W. H. Hong, *ACS Nano*, 2010, **4**, 2910.

Table S1 Ionic conductivities of [mmpy][SCN], [bmpy][SCN], [hmpy][SCN], and [ompy][SCN].

Samples	[mmpy][SCN]	[bmpy][SCN]	[hmpy][SCN]	[ompy][SCN]
Ionic conductivity (S m ⁻¹)	0.03983	0.079639	0.063623	0.03179

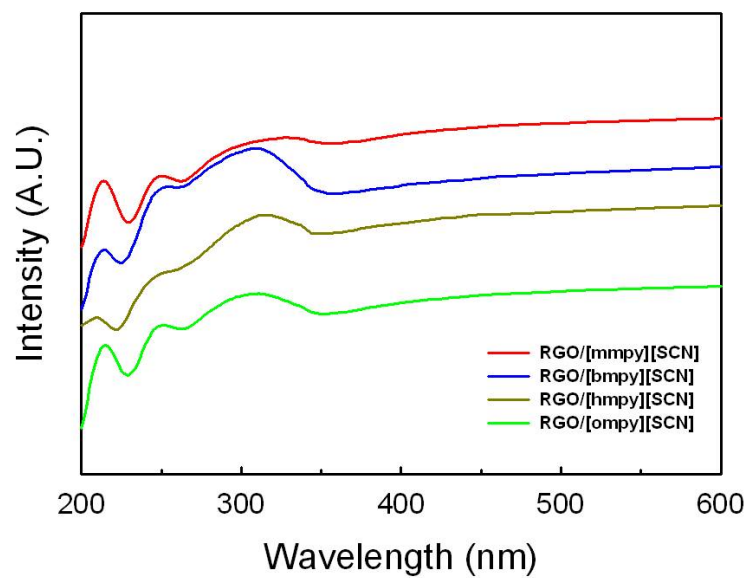


Fig. S1 UV-vis spectra of (a) RGO/[mmpy][SCN], (b) RGO/[bmpy][SCN], (c) RGO/[hmpy][SCN], and (d) RGO/[ompy][SCN].

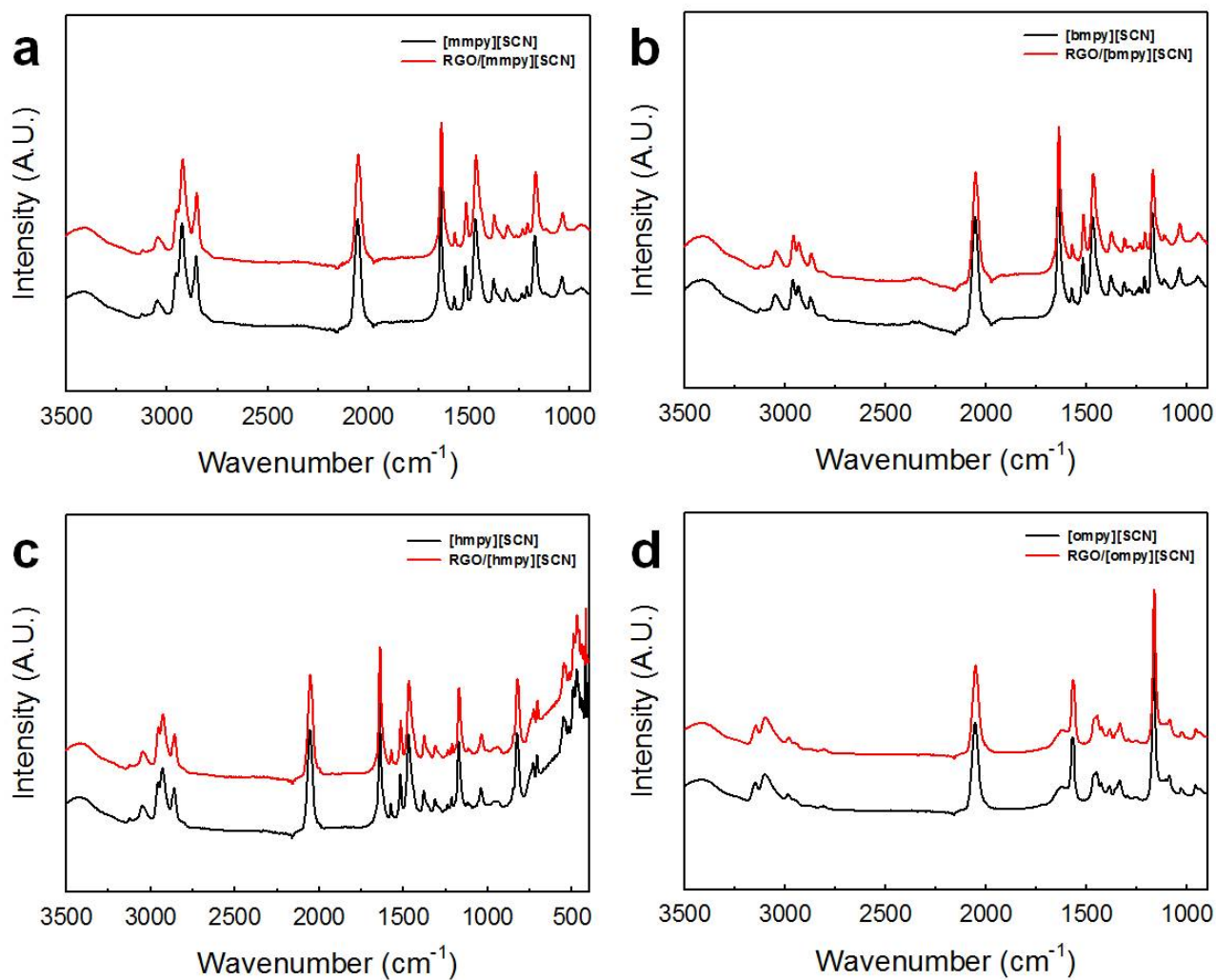


Fig. S2 FT-IR spectra of (a) [mppy][SCN] and RGO/[mppy][SCN], (b) [bppy][SCN] and RGO/[bppy][SCN], (c) [hmpy][SCN] and RGO/[hmpy][SCN], and (d) [ompy][SCN] and RGO/[ompy][SCN].

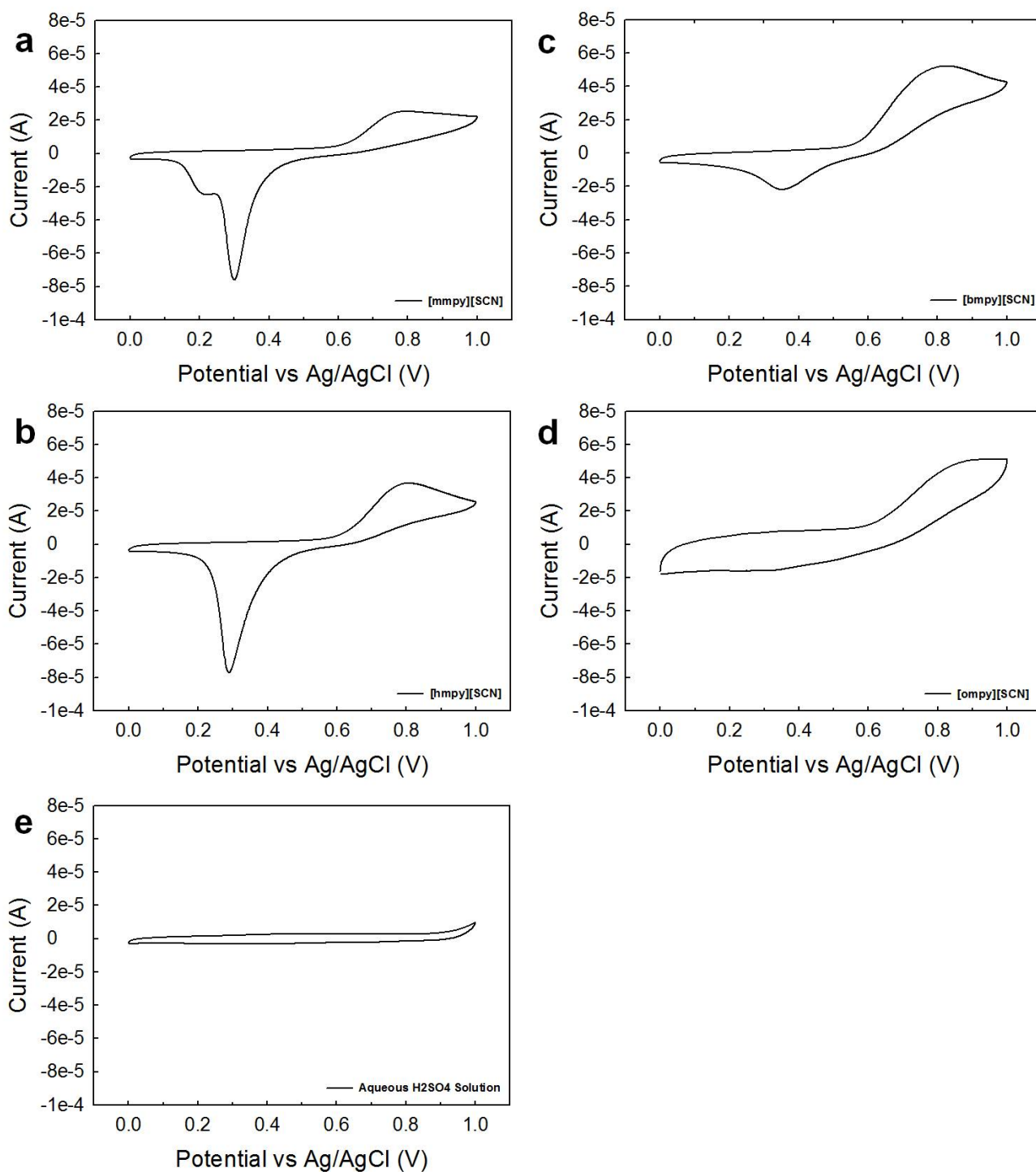


Fig. S3 CVs curves of (a) [mmpy][SCN], (b) [bmpy][SCN], (c) [hmpy][SCN], and (d) [ompy][SCN] in 1M aqueous H₂SO₄ solution (concentration of IL: 20 wt%) and (e) 1M aqueous H₂SO₄ solution at the scan rate of 100 mV s⁻¹.

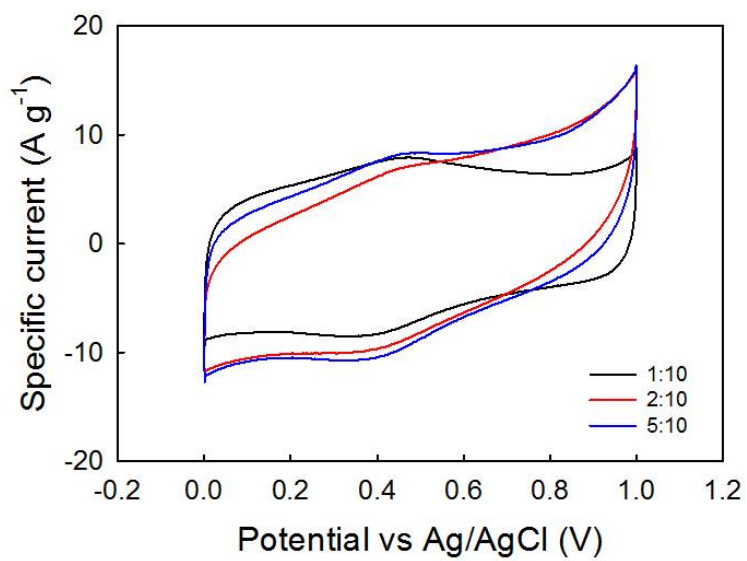


Fig. S4 CV plots of RGO/[bmpy][SCN] hybrids as a function of the weight ratio of [bmpy][SCN] to RGO of 1 to 10, 2 to 10, 5 to 10 at the scan rate of 100 mV s⁻¹.

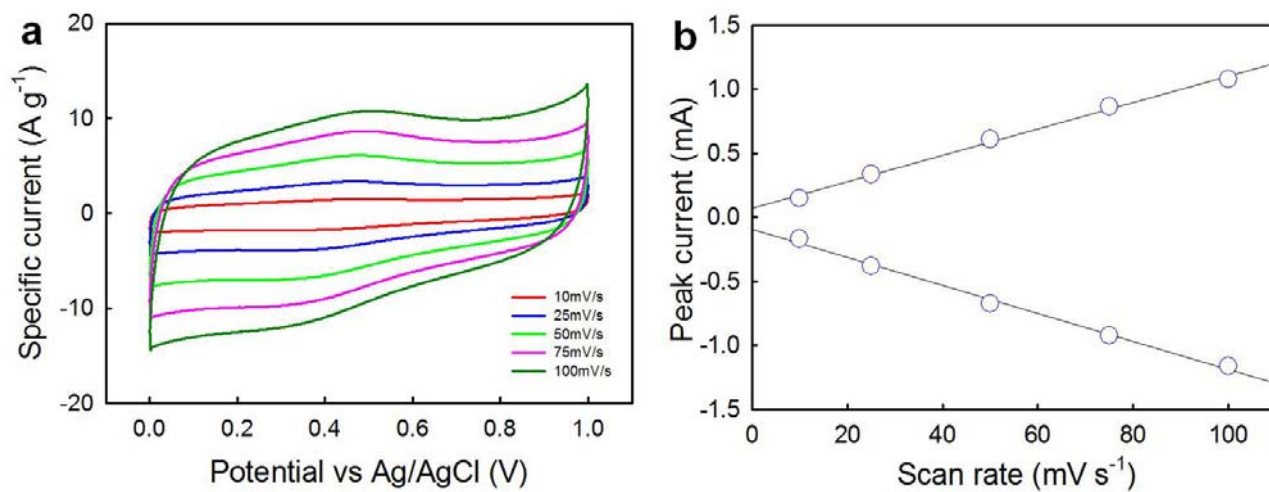


Fig. S5 (a) CV and (b) plot of peak current vs. scan rate of RGO/[bmpy][SCN] hybrid.

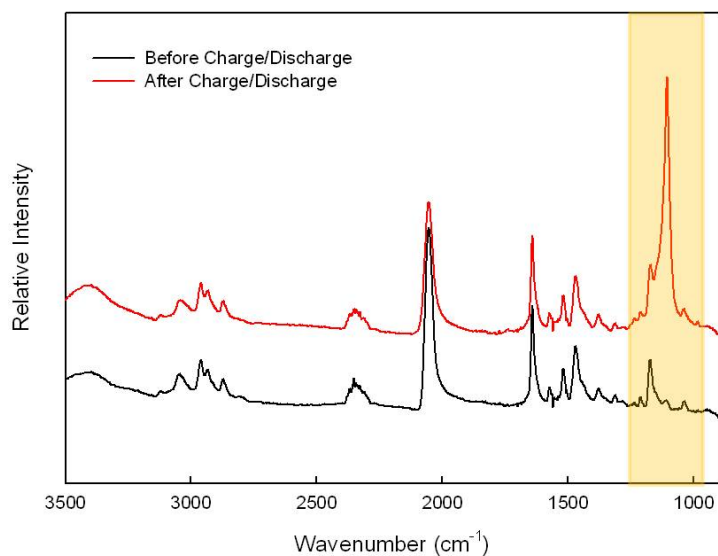


Fig. S6 FT-IR spectra of RGO/[bmpy][SCN] hybrid before and after the charge/discharge of 20 cycles.

FT-IR spectra show that all characteristic bands corresponding to RGO/[bmpy][SCN] hybrid remained intact even after the 20 cycles of charge/discharge except for the band at 1105 cm⁻¹. The emergence of strong band at 1105 cm⁻¹ was attributed to $\nu_{\text{SO}_2 \text{ stretch}}$ of sulfuric acid used as electrolyte. It means that the redox site of SCN anion was immobilized on the surface of RGOs.

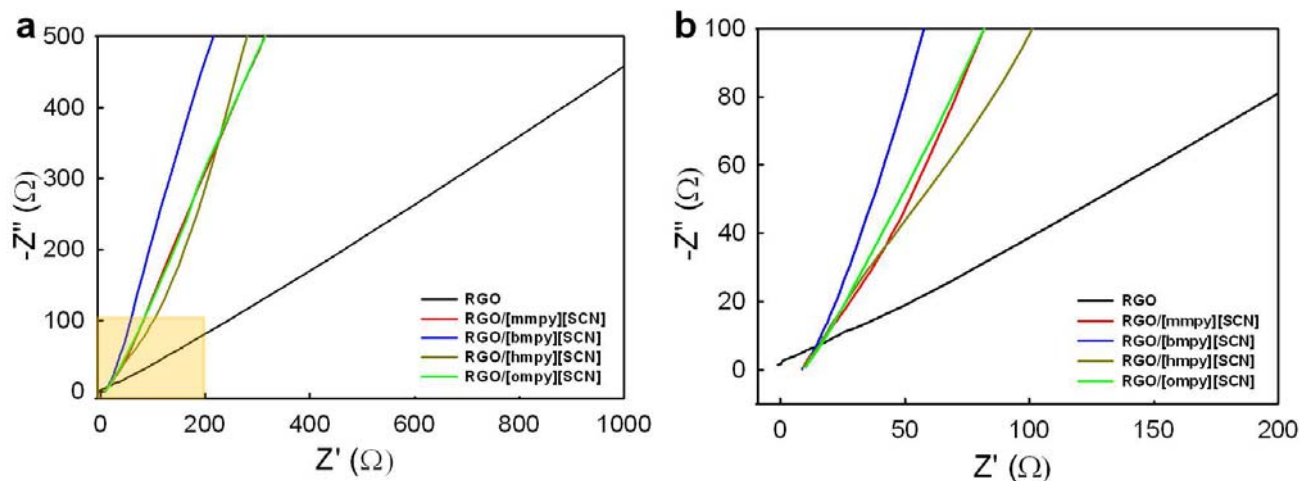


Fig. S7 Nyquist plots of RGO, RGO/[mmpy][SCN], RGO/[bmpy][SCN], RGO/[hmpy][SCN], and RGO/[ompy][SCN] hybrids (a) over a whole frequency range from 10^6 to 10^{-3} Hz and (b) in the high frequency region marked by orange color.

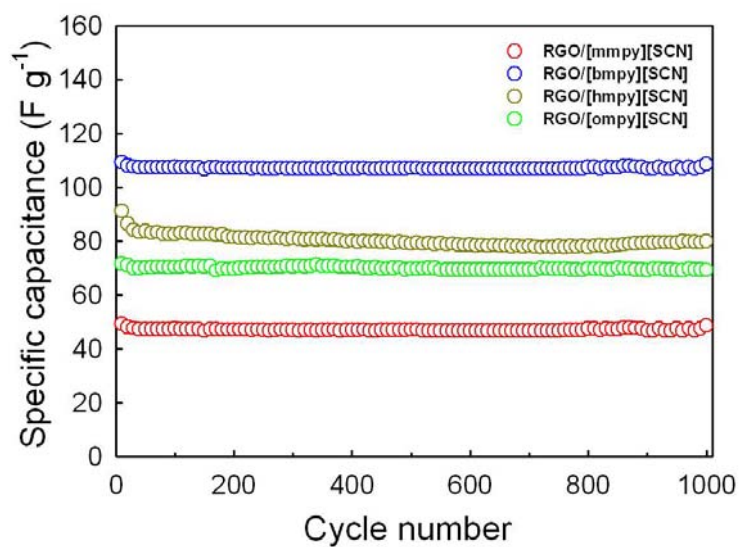


Fig. S8 Cyclic performances (constant current: 5 A g^{-1}) of RGO/[mmpy][SCN], RGO/[bmpy][SCN], RGO/[hmpy][SCN], and RGO/[ompy][SCN] hybrids.