Supplementary Information for

Electrochemical Assembly of MnO₂ on Ionic Liquid/Graphene Films into Hierarchical Structure for High Rate Capability and Long Cycle Stability of Pseudocapacitors

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Electrodeposition of MnO₂ on IL-RGO composite films

 MnO_2/IL -RGO composite electrodes were fabricated by electrodeposition of MnO_2 on the surface of IL-RGO composite films with a simple three-electrode electrochemical cell. The electrodeposition was performed by potentiostatic deposition with IL-RGO composite films as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The electrolyte was a mixture of 1 M of MnSO_4, 1 M of Na₂SO₄, and 1 M of NaC₂H₃O₂. Fig. S1a shows linear sweep voltammetry of IL-RGO composites in electrolyte in voltage range from 0.2 V to 1.4 V. It was found that the onset potential is 0.8 V for deposition of MnO₂. Potentiostatic depositions were performed by ramping from the open circuit potential to 0.8 V and then holding for the requisite time period, where the current changes following the reaction time as shown in Fig. S1b. The manganese ions were absorbed on the surface of IL-RGO composite films and then formation of manganese oxide occurred through electrochemical reaction. In order to prepare control sample of MnO₂ film electrode, same experimetal procedure of MnO₂/IL-RGO composites was performed by changing the working electrode with Au electrode. Prior to electrodeposition, the Au electrode as working electrode was polished to a smooth surface finish using finer grades of SiC paper, and then washed with water and ethanol several times. The electrochemical reaction of MnO₂ deposited on Au electrode was described in Fig. S7.

Supramolecular assembly of IL-RGO: IL-functionalized RGOs were prepared by electrostatic and cation– π interactions. The starting material GOs were functionalized by ILs through strong electrostatic interactions between the carboxylic acid groups of GOs and imidazolium cations of ILs in aqueous solution. And then, during the reduction reaction of GOs functionalized by ILs, intermolecular interactions of RGOs and ILs were enhanced by the cation– π and/or π – π interactions between the imidazolium cations of ILs and the conjugated structures of RGOs. The effective exfoliation of RGOs with ILs was confirmed by TEM and AFM results (See supporting information of Fig. S2). From AFM image analysis, the IL-RGO sheets exhibited the thickness of 1.3 nm, respectively. Similar to other functionalized RGOs, the thickness of IL-RGOs was slightly higher than that of the ideal single graphene sheet of ~0.34 nm, due to the presence of IL functional groups on the surface of RGOs. In addition, we confirmed the chemical structures of IL-RGOs by FT-IR and XPS results (supporting information of Fig. S3). As shown in the C 1s XPS spectra in Fig. S3a, the reduction of oxygen containing groups of IL-RGOs, comparing to the GOs, indicates successful reduction of IL-RGOs. Functionalization of ILs and RGOs was also proved by FT-IR results. The newly appeared peaks related to the ILs on IL-RGOs, comparing to the RGOs, confirmed the surface composition changes with functionalization of ILs.



Fig. S1 (a) Linear sweep voltammetry scan of IL-RGO composite films in an electrolyte solution and (b) Current response of IL-RGO composite films during electrodeposition of MnO_2 .



Fig. S2 TEM images of (a) GO and (b) IL-RGO composites and AFM images of (c) GO and (d) IL-RGO composites.



Fig. S3 (a) XPS spectra of GO, IL-RGO composite, and MnO₂/IL-RGO composite and (b) FT-IR spectra of GO, RGO, and IL-RGO composites.

C 1s of GO showed the prominent three peaks at C-C (285.5 eV), C-O (287.4 eV), and C=O (288.4 eV), which werer in accordance with previous reports. IL-RGO composites obtained from chemical reduction represented increase of C-C (285.5 eV) peak and decrease of C-O (287.4 eV), and C=O (288.4 eV) peaks, indicating the reduction of oxygen containing groups of IL-RGO composites. After the deposition of MnO₂, C 1s of XPS spectra for MnO₂/IL-RGOs showed no change comparing to the IL-RGOs. The successful funcionalization and reduction of IL-RGO composites were also confirmed by FT-IR results. The characteristic bands of the FT-IR spectroscopy of GO were assigned as follows: 3431 cm^{-1} for v_{O-H stretch}, 1720 cm⁻¹ for v_{C=O}, 1627 cm⁻¹ for v_{adsorbed H2O}, 1396 cm⁻¹ for v_{O-H deform}, 1227 cm⁻¹ for v_{C-OH}, and 1089 cm⁻¹ for v_{C-O stretch}. Compared to the bands of GOs, IL-RGO composites revealed the emergences of the strong band at 1030cm⁻¹ for v_{BF4}, 1170 cm⁻¹ for v_{imidazolium ring}, and 1569 cm⁻¹ for v_{CH3-N}, indicating the presence of ILs.¹



Fig. S4 Stress and strain curve of IL-RGO composite films.



Fig. S5 XRD results of IL-RGO and MnO2/IL-RGO composites.

The peak at 24° in the XRD spectrum of IL-RGO composite films was observed, corresponding to an interlayer spacing of 0.36 nm in the RGO sheet.² MnO₂/IL-RGO composites showed main peak at 24° . The new weak and broad peaks at around 40° and 55° were attributed to the lack of crystalline nature of MnO₂ deposited on IL-RGO composite films, indicating the amorphous structure of MnO₂.³



Fig. S6 SEM images of surface of MnO2/IL-RGO composites observed at different reaction time intervals after electrodeposition of MnO2: (a) 0, (b) 0.5, (c) 1, (d) 5, (e) 10, and (f) 30 min.





Fig. S7 SEM image of (a) MnO_2/RGO composite and (b) pure MnO_2 film.



Fig. S8 (a) Nyquist plots for MnO₂/IL-RGO and physically mixed MnO₂/IL-RGO composites, measured at AC amplitude of 10 mV, in 1 M Na₂SO₄ aqueous electrolyte. (b) Galvanostatic charge-discharge behaviours of MnO₂/IL-RGO and physically mixed MnO₂/IL-RGO composites at constant current density of 200 mA g⁻¹ in 1 M Na₂SO₄ solution.

| Sample | Pore size [nm] ^[a,b] | Surface area $[m^2 g^{-1}]^{[a,c]}$ | Pore volume $[cm^3 g^{-1}]^{[a]}$ | |
|-----------------------------------|------------------------------------|-------------------------------------|-----------------------------------|------|
| IL-RGO | 3.28 | 3.73 | 0.003065 | 1020 |
| MnO ₂ /IL-RGO (5min) | 3.39 | 107.04 | 0.090 | 928 |
| MnO ₂ /IL-RGO (10 min) | 4.28 | 422.06 | 0.451508 | 890 |
| MnO ₂ /IL-RGO (15 min) | 2.45 | 138.92 | 0.085 | 758 |
| MnO ₂ /IL-RGO (30 min) | 5.14 | 134.06 | 0.0145 | 621 |

Table S1. Textural properties and electrical conductivities of IL-RGO and MnO₂/IL-RGO composites.

[a] Properties determined with a gas sorption analyzer. [b] Cacluated by using the Barret-Joyner-Hallender (BJH) Model.

[c] Calculated by using the Brunauer-Emmett-Teller (BET) equation.

[d] Electrical conductivities were measured by using the standard 4-point probe technique.

References

- [1] J. Wang, H. Chu and Y. Li, ACS Nano, 2008, 2, 2540.
- [2] K. Zhang, L. L. Zhang, X. S. Zhao and J. Wu, *Chem. Mater.*, 2010, 22, 1392.
- [3] P. Raupathy, D. H. Park, G. Campet, H. N. Vasan, S.-J. Hwang, J.-H. Choy, N. Munichandraiah, *J. Phys. Chem. C*, 2009, **113**, 6303.