Supporting Information

Graphene Oxide Based Conductive Glue as a Binder for Ultracapacitor Electrodes

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Experimental section

Sample preparation: GO was synthesized by a modified Hummer's method and purified extensively.[1] Unfunctionalized single walled carbon nanotubes (P2-SWCNTs, Carbon Solution, Inc) and PEDOT:PSS aqueous solution (1.5 wt. %, Clevios 4083, Heracus) were used as received. The gel was prepared by mixing dry GO (1 wt. %), SWCNTs (0.5 wt. %) and the PEDOT:PSS solution by sonication for 2 hours. MnO_2 nanoparticles were prepared by adding 20 ml of 0.2M $KMnO_4$ solution dropwise into 20 ml of 0.3M $Mn(CH_3COO)_2$ and 0.2g poly(ethylene glycol) aqueous solution. The precipitate was collected, washed and dried at room temperature. RuO_2 nanoparticles were prepared by dropwise adding 20 ml 0.2M NaOH solution dropwise into 20 ml of 0.1M $RuCl_3$ aqueous solution. The precipitate was collected, washed and dried at 80 ^oC overnight.

Sample characterization: SEM was conducted on FEI NOVA NanoSEM microscope. Shear viscosity measurements were performed over shear rates of 0.1-100 s^{-1} using a Paar Physica MCR 300 rheometer with a double-gap Couette fixture (DG26.7) for the gels and a 27 mm diameter bob (CC27) for GO, GO/CNT and PEDOT:PSS solutions. The conductivity of the films was measured using a four point probe electrode. The thickness of the films was ~35 nm measured by profilometer.

Electrochemical measurement: The electrochemical behavior of MnO_2 electrodes was characterized by cyclic voltammogram (CV) and impedance measurements in a three-electrode glass cell using an Autolab electrochemical interface instrument (PGSTAT 302N). Working electrode was prepared by mixing active material, the glue or PTFE/carbon black in water, and pressing the slurry into a thin sheet of uniform thickness loaded on a nickel foam support which served as current collector. The typical load of electrode material was 3 mg/cm^2. The conductive glue bound MnO_2 electrodes were prepared in a similar fashion. Na_2SO_4 solution (1 M) was used as the electrolyte. Platinum foil (Alfa Aeser) and Ag/AgCl electrode (0.199 V vs. NHE) were used as the counter and reference electrodes, respectively. The performance of RuO_2 was characterized using two electrode symmetrical supercapacitor in coin cells. H_2SO_4 solution (1 M) was used as the electrolyte and a filter paper (Waterman, Grade No 4) was used as the separator. The typical load of electrode material was 1.5 mg/cm^2 on stainless steel current collector. The conductive glue bound RuO_2 electrodes were prepared in a similar fashion.

References

[1] F. Kim, J. Y. Luo, R. Cruz-Silva, L. J. Cote, K. Sohn, J. X. Huang, *Adv. Funct. Mater.* **2010**, *20*, 2867.

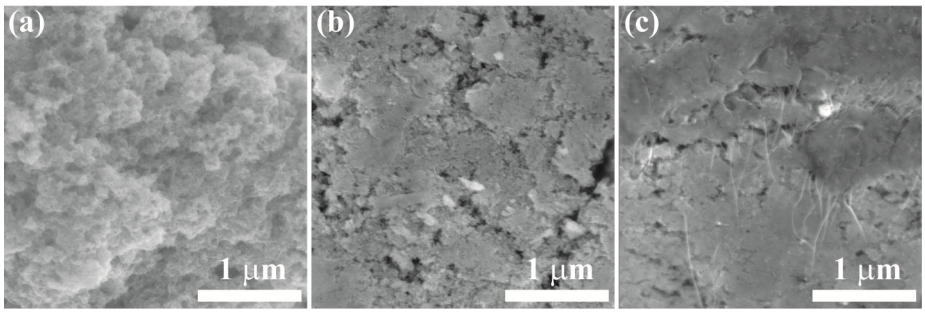
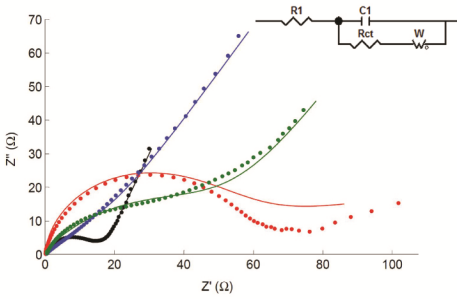


Figure S1. SEM images of (a) MnO_2 nanoparticles, (b) MnO_2 nanoparticles with carbon black + PTFE binder, showing granular structures, and (c) MnO_2 nanoparticles with the GO/SWCNTs/ PEDOT:PSS (G-T-P) glue forming continuous phase with interpenetrating SWCNTs.



	R_{ct} (Ω)	R_w (Ω)
MnO_2/G-T-P (90:10) (black line)	17.5434	1.2311
MnO_2/CB (90:10) (blue line)	21.4471	3.3035
MnO_2/CB/PTFE (90:5:5) (green line)	66.9571	7.7483
MnO_2/ PTFE (90:10) (red line)	86.8786	0.9867

Figure S2. Fitting curves and equivalent circuit of the Nyquist plots in Figure 3b. R_1 is ohmic resistance; C_1 is the double layer capacitance; R_{ct} is the charge transfer resistance; and W is the finite length Warburg contribution. The resultant values of R_{ct} and R_w from the fitting are shown in the right table.

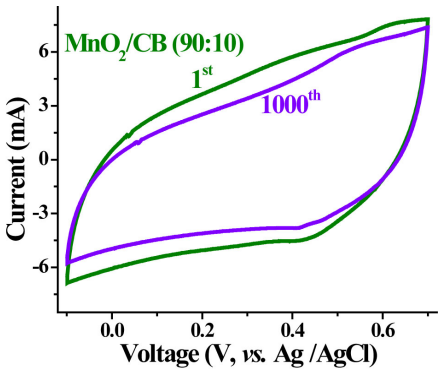


Figure S3. Cycling performance of MnO_2/CB (90:10) without PTFE binder showing only 75% of the initial capacitance was retained after 1000 cycles.

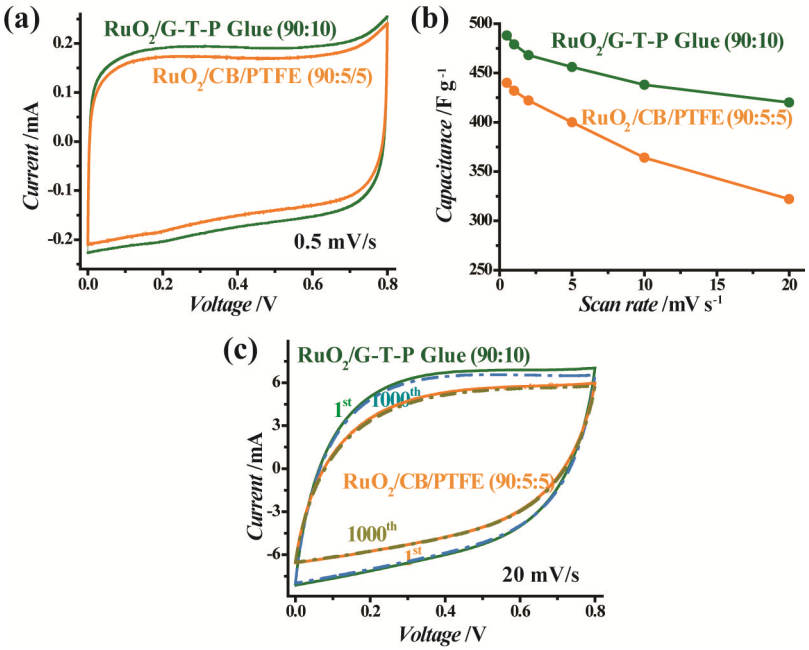


Figure S4. Electrochemical performance of RuO_2/G-T-P and RuO_2/CB/PTFE symmetrical ultracapacitors. (a) CV curves of RuO_2/G-T-P (green curve) and RuO_2/CB/PTFE (orange curve) symmetrical supercapacitors measured at a steady scan rate of 0.5 mV/s in 1M H_2SO_4 aqueous electrolyte. The ultracapacitor of RuO_2 nanoparticles glued by G-T-P show higher current than that using a combination of CB and PTFE. (b) Specific capacitance of RuO_2/G-T-P, and RuO_2/CB/PTFE electrodes calculated from CVs of their corresponding symmetrical supercapacitors at different scan rates showing significantly better capacitance retention of the G-T-P glued RuO_2 electrode at higher scan rates. (c) The symmetrical supercapacitors with G-T-P glued electrodes show comparable cycling stability (1000 cycles, 20 mV/s) to their counterpart bound by carbon black + PTFE.