Electronic Supplementary Information:

Enhanced Electrochemical Performance of MWNT@MnO₂ Composites in Polymerized Ionic Liquids

Ning Wang¹, Tao Jiang¹, Yanqiu Yang¹, Chuxin Wu² and Lunhui Guan²

¹Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, P.R. China

²State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou, Fujian 350002, P.R. China

Experimental section

Synthesis of samples

The multi-walled carbon nanotubes (MWNT) with diameter of 20-60 nm purchased from Shenzhen nanoport company, and it was treated with concentrated HNO₃ (16 mol/L) in 140 for 14 h. The pure MnO₂ was synthesized using potassium permanganate (KMnO₄) and manganous sulfate (MnSO₄) as the starting materials. The MWNT was dispersed into KMnO₄ solution by untrosonicating to synthesize MWNT@MnO₂ composites. The dispersed mixture was stirring for 24 h at 70 ℃, following with filtering and washing. MWNT@MnO₂, 1-vinyl-3-ethyl imidazole salt bromine ([VEIm]Br), azodiisobutyronitrile (AIBN) and with mole ratio of 5:1:2 were mixed and grinded for 10 min. The mixture reacted for 6 h at 60 ℃ in N₂ airflow. The non-reactive monomers and initiators were removed by washing and filtering. The sample was signed for MWNT@MnO₂@PIL.

Characterization

The thermogravimetric analysis (TGA) was carried out on NETZSCH STA-449C in a range from 30-1000 ℃ with a heating rate of 10 ℃/min in air flow. Infrared spectroscopy was performed in a Tensor 27 FT-IR spectrometer. X-ray diffraction pattern(XRD) were recorded on a Miniflex II
Diffractometer equipped with Cu/Kα radiation (λ = 0.15405 nm) (30 kV, 15 mA). The size was calculated according to the Debye–Scherrer equation of \( D = \frac{K \lambda}{\beta \cos \theta} \). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images, selected-area electron diffraction (SAED), as well as energy-dispersive X-ray spectroscopy (EDS) were performed on a JEOL JEM-2010 with an acceleration voltage of 200 kV.

The Cyclic voltammetry and galvanostatic charge/discharge studies were performed using an electrochemical workstation (CHI 660d) with a conventional three-electrode electrochemical cell. The electrodes were prepared by casting the slurry mixtures of 90 wt.% samples and 10 wt.% polyvinylidene difluoride (PVDF) onto a nickel foam current collector. The electrolyte was 1 M Na₂SO₄ aqueous solution. The as-prepared samples were used as working electrodes, a platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammetry was measured in the potential range between 0 and 1 V versus SCE at room temperature at various scan rates from 5 to 200 mV/s. Galvanostatic charge-discharge measurements were carried out between 0 to 1 V at different current density from 1 to 20 A/g.

**Supplementary Figures**

Figure S1. IR spectra of MWNT, MWNT@MnO₂ and MWNT@MnO₂@PIL.
Figure S2. TEM images of MWNT@MnO$_2$@PIL.