**Supporting Information**

# Nitrogen-doped Carbon Nanotube/Graphite Felt as Advanced Electrode Materials for Vanadium Redox Flow Batteries

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## 1. Experiment details

*Growth of N-CNT/GF and CNT/GF.* N-CNT/GF was synthesized using a single-injection chemical vapor deposition (CVD) system, utilizing ferrocene (2.5 wt %) as a growth catalyst dissolved in ethylenediamine as an N-CNT source solution. Synthesis was carried out at 800 $^{o}$C under an inert gas flow and steady source solution injection in a horizontal quartz tube reactor chamber, in which the graphite felt was pre-placed in the center of the reactor as the growth substrate. After the reaction was allowed to proceed, the reactor chamber was cooled to 400 $^{o}$C, and air was admitted for 1 h in order to burn off any amorphous carbon species. In addition, CNT/GF was also grown in a similar way, but using toluene as the source solution instead of ethylenediamine.

*Physical characterization*. X-ray photoelectron spectroscopic (XPS) data were collected to determine the atomic compositions and provide insights into the atomic arrangement of N-CNT. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were collected with a Hitachi S5500 STEM microscope at 30 kV. The Raman spectra were collected with a Raishaw spectrometer.

*Battery testing.* The graphite felt-based materials were used as the electrode materials in the vanadium redox flow battery. A Nafion 117 membrane was sandwiched between two graphitic carbon felt electrodes and the assembly was clamped by two graphite polar plates with straight

flow channels. 1.0 M $V^{2+/}V^{3+}$ in 2.0 M $H_2SO_4$ solution and 1.0 M $(VO)^{2+}$/ $(VO_2)^{+}$ in 2.0 M $H_2SO_4$ solution, serving as negative and positive electrolytes, respectively, were circulated through the corresponding half-cell at a flow rate of 15 mL/min. The active area of the single cell was 5 $cm^2$ and the volume of the electrolyte solution was 20 mL for each half-cell. Charge–discharge cycling tests were conducted with an Arbin BT 2000 battery cycler (Arbin instruments). A maximum voltage of 1.7 V and a minimum voltage of 0.8 V for charge and discharge were employed to avoid corrosion of the carbon felts and graphite plates.

**2. Supplementary Results**

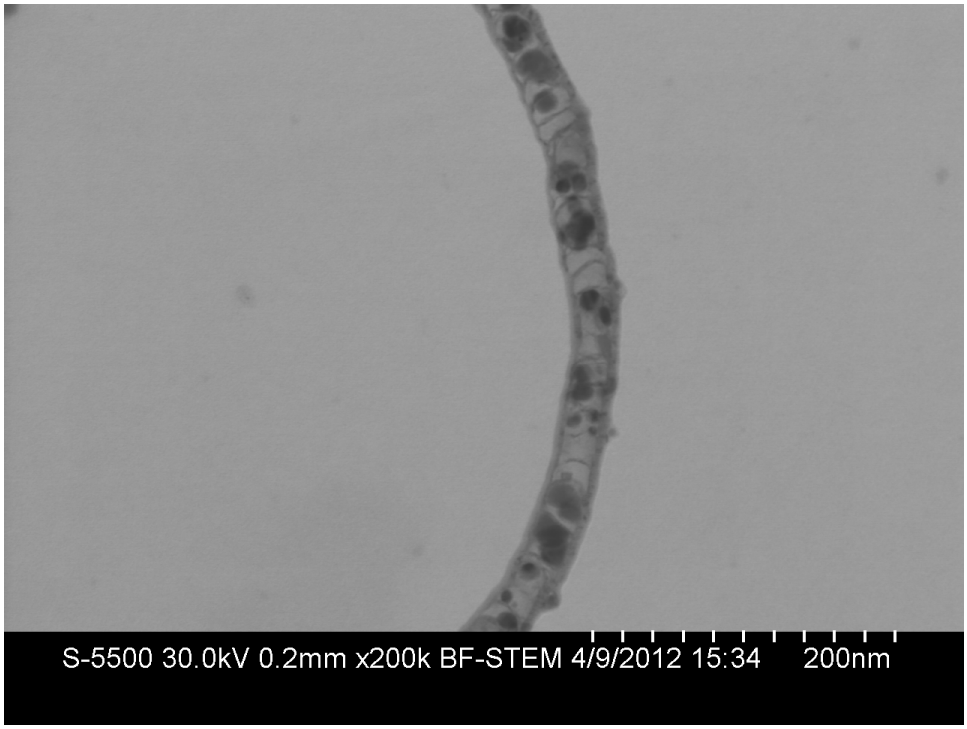


Figure S1. TEM image of N-CNT before acid treatment. Residual metal nanoparticles formed by the decomposition of ferrocene are observed.

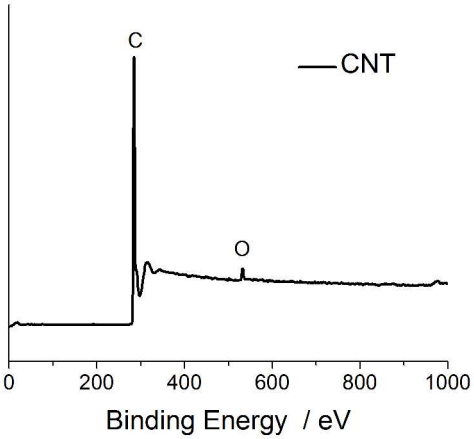


Figure S2. XPS survey spectrum of undoped CNT.

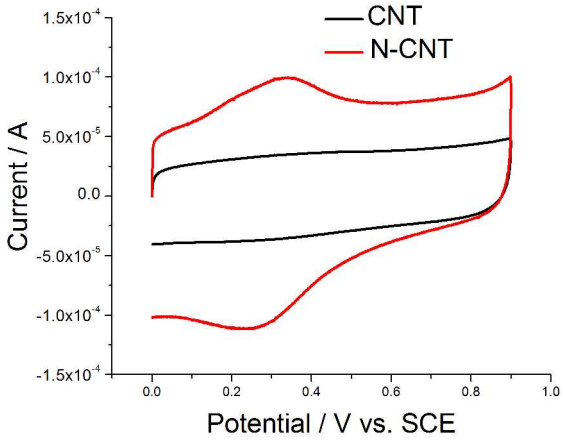


Figure S3. CV curves of CNT and N-CNT in 1 M $H_2SO_4$ at a scan rate of 50 mV/s.

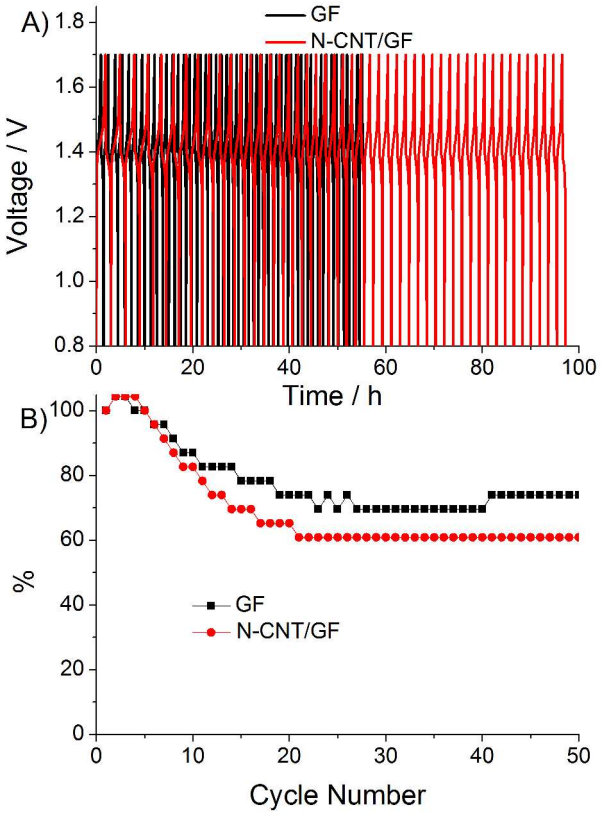


Figure S4. (A) Continuous Charge-Discharge cycles of VRFBs with GF (black) and N-CNT/GF (red) as electrode materials at a constant current density of 20 mA $cm^{-2}$; (B) The plot of the capacity decay (retention) against the cycle number.

Table S1. Efficiencies of the different electrode materials charged and discharged at a current density of 10 mA $cm^{-2}$

| Sample | CE (%) | VE (%) | EE (%) |
|---|---|---|---|
| GF | 72.6 | 93.9 | 68.2 |
| CNT/GF | 77.5 | 94.1 | 72.9 |
| N-CNT/GF | 81.3 | 94.7 | 77.0 |