

Supplementary Information

DNA hydrogel templated carbon nanotube and polyaniline assembly and its applications for electrochemical energy storage devices

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Experimental Details

Preparation of Dgel and PAH/Dgel. Dgel was synthesized following the methods previously reported.^[7-9] Briefly, DNA monomers were fabricated by annealing four single stranded oligonucleotides (40 bases each) which partially complement to each other. The annealed monomers have four branches and each branch is composed of 18 base pairs and 4 bases of palindromic sticky ends. The ligation of these four branched DNA monomers produces Dgel. To synthesize the Dgel used in this experiment, 10 nmole four branched DNA monomers were ligated using 6 units of T4 DNA ligase at room temperature for 12 hrs and then freeze dried (Operon) for at least 12 hrs for deposition of next layer. PAH layers were deposited on Dgel by dipping the dried Dgel in a positively-charged PAH (Aldrich, Mw 70,000 g/mol) solution for 30 min, followed by thorough and careful rinsing with a sterile deionized water (Bioneer). Wet PAH-coated Dgel (PAH/Dgel) was subjected to the same freeze drying process.

Preparation of negatively charged aqueous CNT solutions. The negatively-charged aqueous single wall carbon nanotube (SWCNT) solutions were prepared by three different methods. First, 15 mg of prepurified SWCNTs (Iljin) was dispersed in 100 ml of H₂SO₄:HNO₃ (3:1, v/v)

mixture using the ultrasonic homogenizer (HD 2200, Bandelin sonoplus, 200 W) for 12 hrs. The dispersed suspensions were diluted with excessive DI water. This CNT suspension was filtered with 1µm PTFE filter under vacuum and thoroughly washed with a 0.1M aqueous NaOH solution to remove the fragmented carbon debris, and then rinsed with 0.1M HCl for pH neutralization. Second, a mixture of 15 mg of CNT and 30mg of 4-dodecylbenzenesulfonic acid (SDBS) was dispersed in 30 ml of DI water using the same sonicator for 2 hrs. Third, 15 mg of CNT was dispersed in the 200 mg/ml of aqueous poly(acrylic acid) (Aldrich, Mw 1,800 g/mol) solution for 2 hrs with the same sonication protocols. The excessive dispersion agent in CNT suspension was removed by the dialysis (SnakeSkin Dialysis Tubing, molecular weight cutoff of 12k) for at least 24 hrs.

Raman spectra. Raman spectra with resolution of about 1 cm^{-1} were collected in a backscattering configuration at room temperature using Renishaw inVia Raman microscope. The samples were illuminated by a 514 nm He-Ne laser (power 4 mW) on a Leica microscope with a 20× objective.

Measurement of sheet resistance and conductivity. The sheet resistance of p-CNT/PAH/Dgel were measured using a four point probe (Hall measurement system, Nanometrics) with HL5500WIN Hall System ver 2.23. The voltage - current behavior of dried PANI film with

different level of doping was obtained using the Keithley 4200 semiconductor characterization system.

Comparison of morphology for CNT/PAH/Dgel with different dispersion methods.

The uniformity of electrostatically assembled CNTs on PAH/Dgel was compared by the SEM images for CNTs with different dispersion agents. From the insets of Fig S2, uniformity of CNT coating is better for s-CNT and p-CNT than a-CNT.

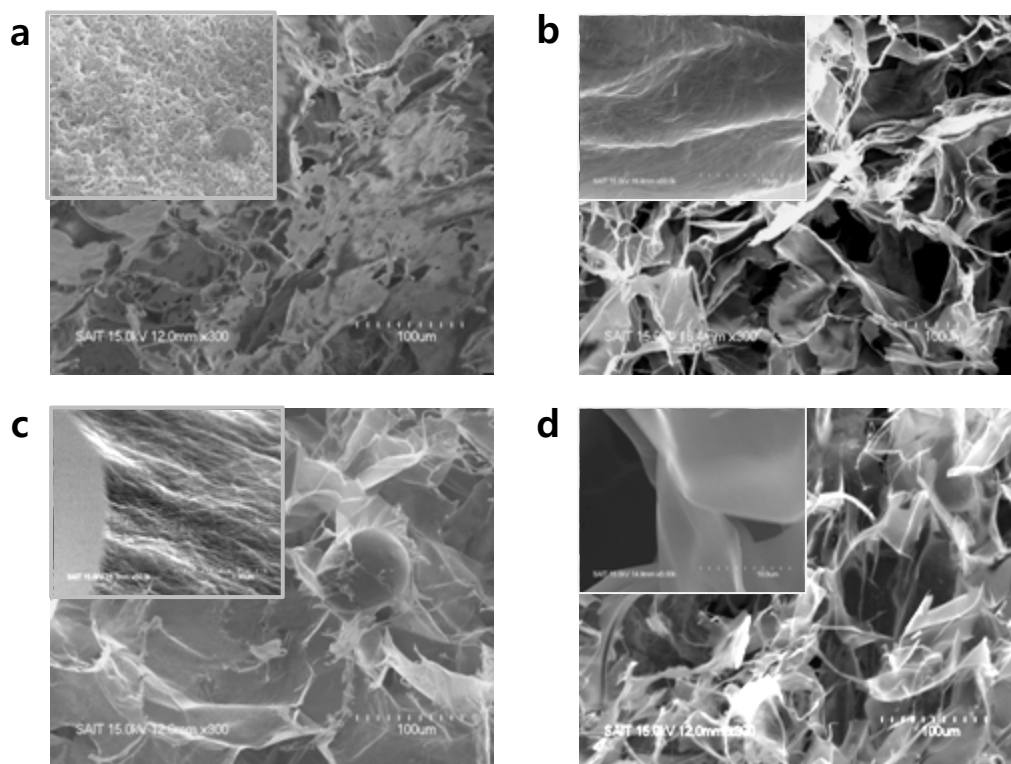


Figure S1. Morphology of CNT/PAH/Dgel. SEM images of **a**, a-CNT, **b**, s-CNT and **c**, p-CNT on PAH/Dgel, and **d**, Original PAH/Dgel for reference.

Comparison of morphology for PANI/p-CNT/PAH/Dgel for different PANI concentrations.

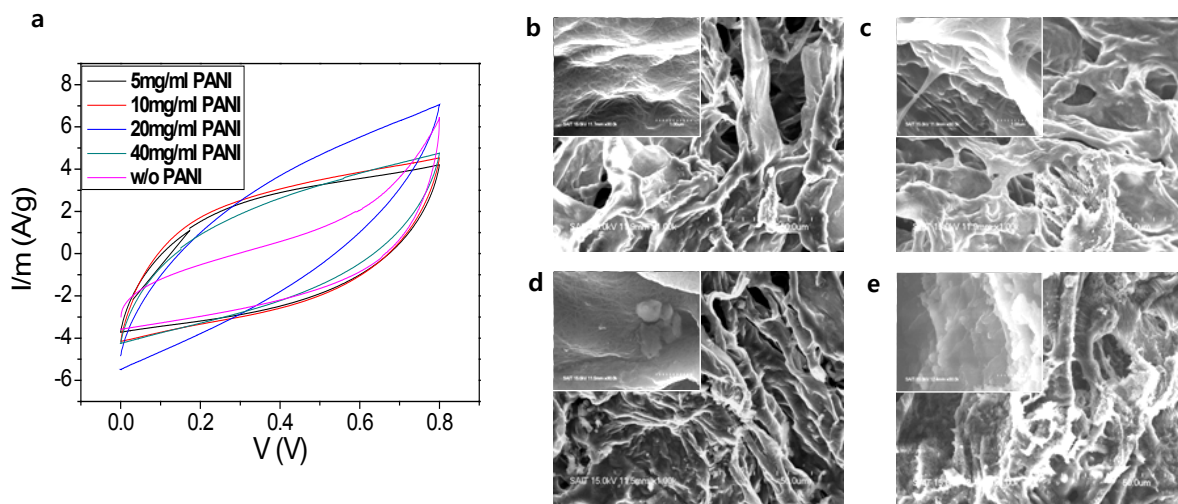


Figure S2. Cyclic voltammograms and morphological change of PANI/p-CNT/PAH/Dgel under the effect of PANI concentration. a) Comparison of cyclic voltammograms at different PANI concentration and microstructural images of PANI/p-CNT/PAH/Dgel at PANI concentration of b) 5 mg/ml, d) 10 mg/ml, d) 20 mg/ml, and e) 40 mg/ml..

Electrical and optical characterization of water-soluble PANI film prepared at different pHs

Electrical properties of dried PANI was characterized using I-V measurement between two electrode terminals. PANI films prepared at lower pHs exhibited more conductive behavior due to the higher level of proton doping, resulting in greater number of electron carriers.

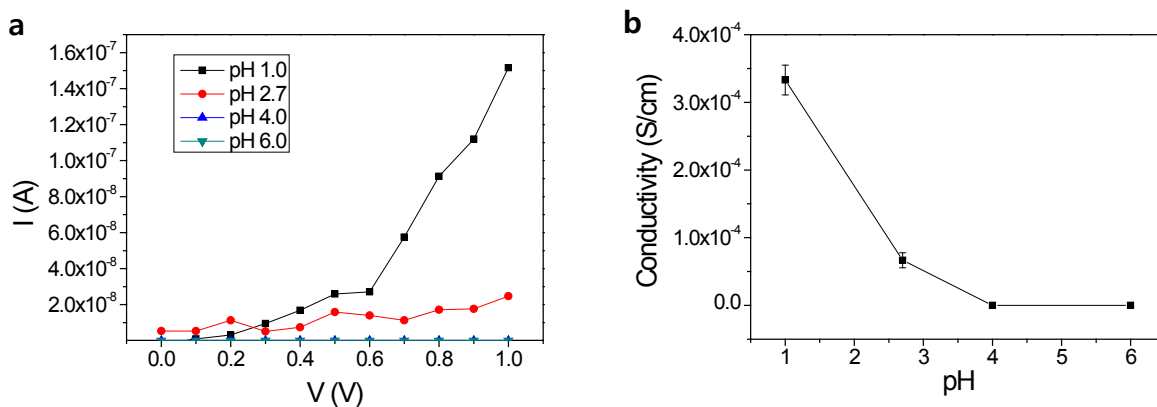


Figure S3. a) I-V and b) Conductivity measurement of PANI film at different pHs (pH of 1.0, 2.7, 4.0, and 6.0).

Measurement of internal resistance for PANI/p-CNT/PAH/Dgel electrodes

The internal resistance of PANI/p-CNT/PAH/Dgel was estimated by the IR drop of GCD measurements at different pHs. The resistance was measured to increase as the pH of electrolyte solution increased. It is because the electrical property of hybrid electrode is highly affected by the solution pHs due to the most outer PANI layer.

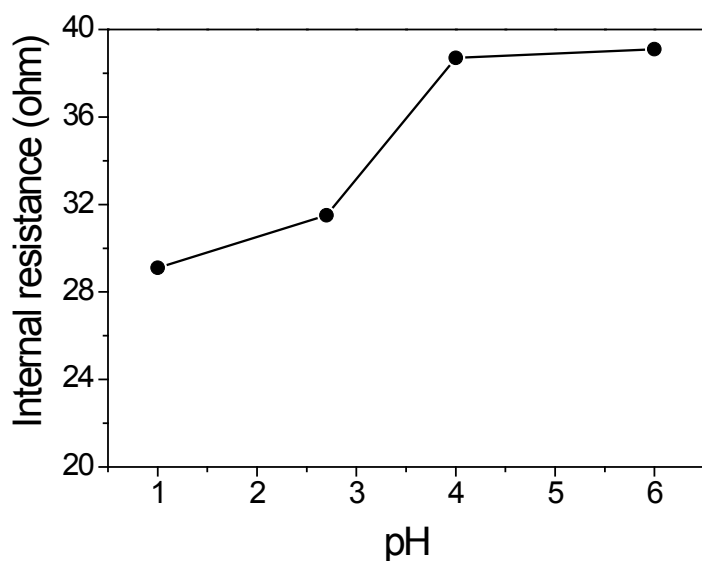


Figure S4. Internal resistance of PANI/p-CNT/PAH/Dgel electrode in different electrolyte solution with different pHs (pH of 1.0, 2.7, 4.0, and 6.0) at discharge current density of 2.0 A/g.

The values are calculated from IR drop in GCD measurements.