

Supporting information

A Facile Self-assembly Strategy towards Naphthalene Diimide/Graphene Hybrids as High Performance Organic Cathode for Lithium-ion Battery

Experimental Section

N,N'-(2,2'-(1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(ethane-2,1-diyl))bis(N,N-dimethylhexan-1-aminium) bromide (NDI) was synthesized via the following procedure (Figure S1). Typically, naphthalic anhydride (25 mmol) and N,N'-dimethylethanediamine (**1**, 240 mmol) were first dissolved in N,N'-Dimethylformamide (DMF, 100ml). The solution was continuously stirred at 130 °C for 5h under N₂ atmosphere. After cooled to ambient temperature, tetrahydrofuran (THF, 500ml) was added to the mixture and the resulting suspension was vacuum filtrated and washed with THF. N,N'-bis[2-(dimethylamino)ethyl]-1,4,5,8-naphthalenetetracarboxylic-1,8:4,5-diimide (**2**, 5.0 g) was then obtained as yellow powder (Yield: 48.0%).

Subsequently, **2** (5 mmol) and 1-bromohexane (50 mmol) were dissolved in DMF (30 ml), which was continuous stirred at 130 °C for 24h under N₂ atmosphere. After cooled to ambient temperature, THF (500 ml) was added to the mixture and the resulting suspension was vacuum filtrated and washed with THF. NDI was then collected as yellow powder (2.9 g, Yield: 78.0%) after dried at 60 °C in vacuum oven. ¹H NMR (400 MHz, DMSO, ppm): δ 8.72 (s, 4H), 4.44 (t, *J* = 8.0 Hz, 4H), 3.55 (t, *J* = 8.0 Hz, 4H), 3.42 (t, *J* = 8.0 Hz, 4H), 3.18 (s, 12H), 1.32 (m, 16H), 0.87 (t, *J* = 8.0Hz, 6H).

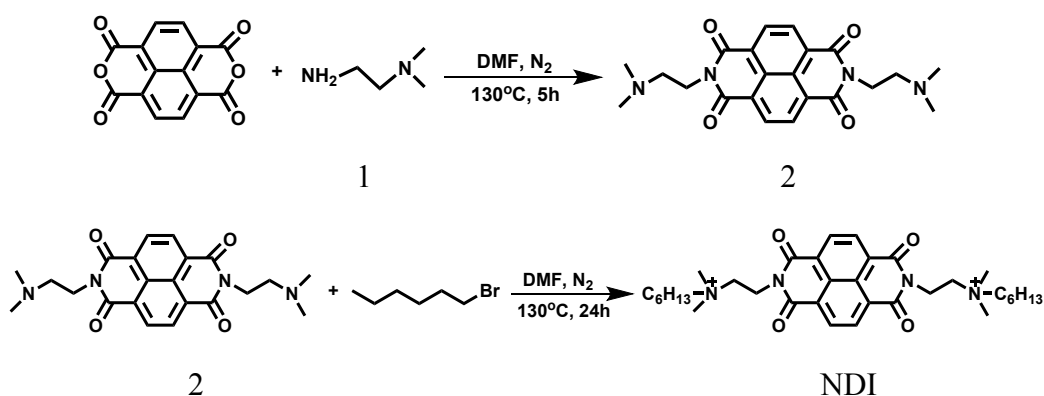


Figure. S1. The synthetic process of NDI

Graphene oxide (GO) was prepared from graphite flakes (Aldrich) by the modified Hummers method.

To produce NDI-RGO, NDI (64.5 mg) was first dispersed in DMF (80 ml). The aqueous dispersion of GO (1mg ml⁻¹, 40 ml) was then diluted with DMF (40 ml) and added dropwise to the solution of NDI. After stirred at 35 °C for 24 h, the mixture of NDI and GO was transferred to Telfon-lined autoclave and then thermally treated at 180 °C for 18h. After cooling to room temperature, the as-prepared sample was washed with DMF twice by centrifuging at 11000 rpm for 15 min to remove redundant NDI. Subsequently, the as-prepared sample was washed with distilled water by centrifuging at 11000 rpm for 15min to remove DMF and dried at 60 °C in vacuum oven.

To produce RGO, the aqueous dispersion of GO (40 ml, 1mg ml⁻¹) was diluted with DMF (120 ml). Then it was transferred to Telfon-lined autoclave and thermally treated at 180°C for 18h. After cooling to room temperature, the as-prepared sample was washed with distilled water by centrifuging at 11000 rpm for 15 min to remove DMF and dried at 60 °C in vacuum oven.

Structural Characterization

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Sirion 200, 25 kV). Elemental analysis was carried out on Vario-EL Cube (Elementar, Germany). Thermogravimetric analysis (TGA) curves were monitored on a Q5000IR apparatus (TA Instruments, USA). X-ray diffraction (XRD) measurements were carried out on a D/max-2200/PC (Rigaku Corporation, Japan) using Cu (40 kV, 30 mA) radiation. Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet 6700 Fourier transform infrared spectrophotometer from 4000 to 400 cm^{-1} using the KBr sample holder method. N_2 sorption analysis was conducted on a TriStar 3020 accelerated surface area and porosimetry instrument, equipped with automated surface area, at 77K using Barrett–Emmett–Teller (BET) calculations for the surface area.

Electrochemical measurements

The electrochemical characterizations were performed using 2032 coin-type cells assembled inside an argon-filled glove box with moisture and oxygen contents below 0.1 ppm. The working electrodes were made by coating the slurry of 80 wt% hybrids, 10 wt% of acetylene black and 10 wt% of polyvinylidene fluoride onto an aluminum foil current collector. Then, they were dried in a vacuum oven at 60 °C for 12 h to remove the solvent. Lithium metal foil was used as the counter electrode. The area of all the electrode is 0.94985 cm^2 . The active material loading in the electrode was about 0.6 mg cm^{-2} . The electrolyte was composed of 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate and dimethyl carbonate. The galvanostatic charge/discharge tests were performed using Land CA2001A testing system in the voltage range of 1.5 - 4.3

V (vs. Li/Li⁺). Cyclic voltammogram (CV) measurements were performed on CHI 760D electrochemical workstation using a voltage range of 1.5 - 4.5 V (vs. Li/Li⁺) at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was conducted on CHI 760D electrochemical workstation in the frequency range of 100 kHz - 0.01Hz.

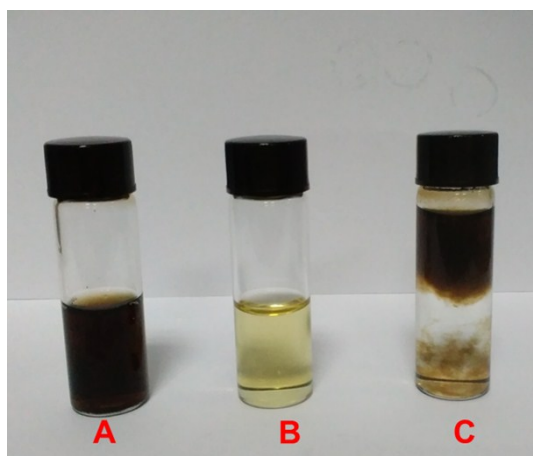


Figure S2. Photo image of the suspension of GO (A), NDI (B), and the flocculation of the mixed NDI and GO (C).

Table S1. Elemental analysis results for NDI-RGO.

Sample	Carbon /wt%	Nitrogen /wt%	Hydrogen /wt%
NDI-RGO	72.16	4.90	3.31

Based on the nitrogen content of NDI and NDI-RGO, the amount of NDI in NDI-RGO was approximately 64 wt%.

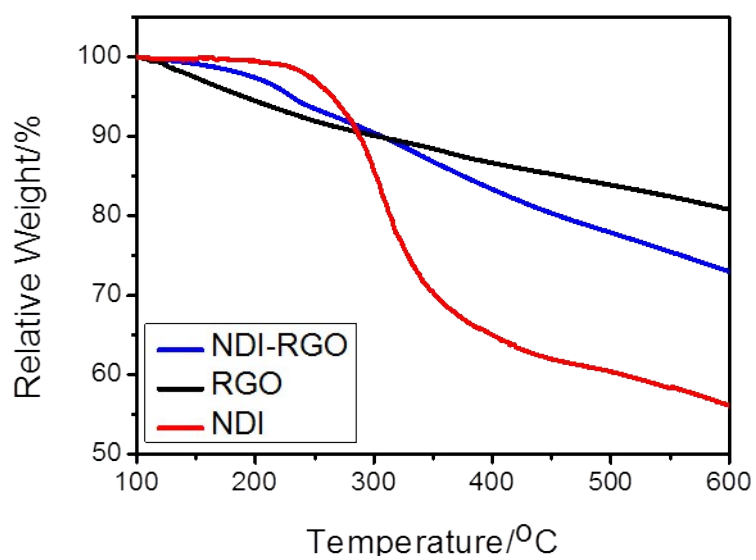


Figure S3. TGA curves of RGO, NDI and NDI-RGO

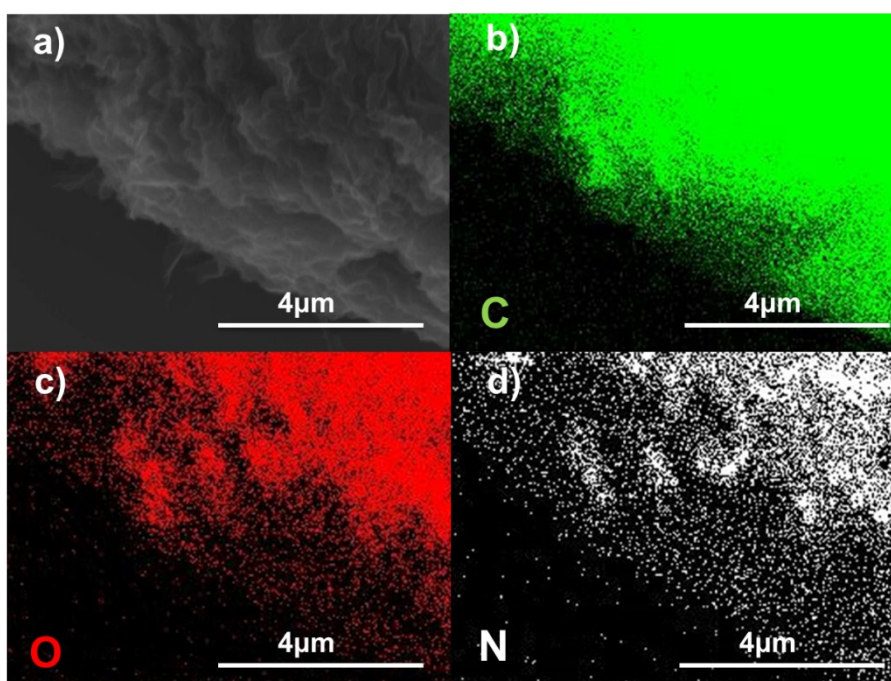


Figure S4. SEM image of NDI-RGO and the corresponding elemental mapping

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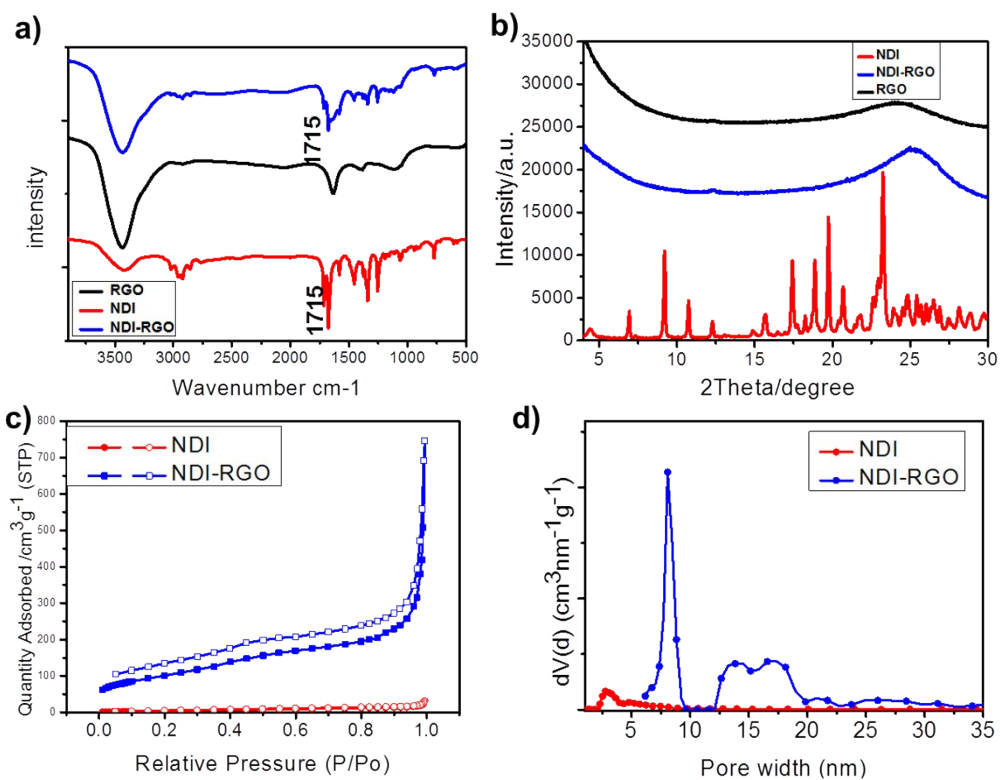


Figure S5. a) FTIR spectra of RGO, NDI and NDI-RGO. b) XRD patterns of RGO, NDI and NDI-RGO. c) N₂ adsorption/desorption isotherms of NDI-RGO and NDI. d) pore size distribution for NDI-RGO and NDI.

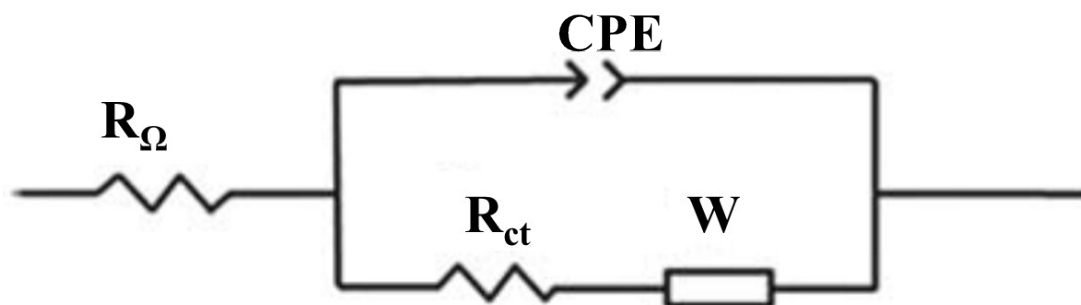


Figure S6. Equivalent circuit for NDI-RGO and NDI. R_{Ω} is the solution resistance and R_{ct} is the charge-transfer resistances.

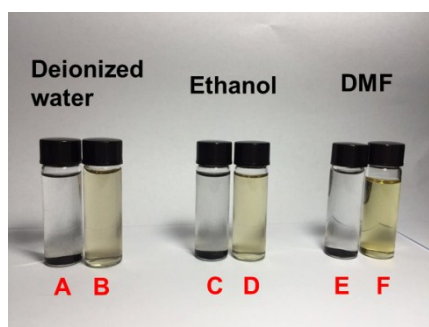


Figure S7. The comparison of the solubility of NDI-RGO (A, C and E) and NDI (B, D and F) in deionized water, ethanol and DMF.

As shown in Figure S7, NDI has decent solubility in deionized water, ethanol and DMF and the color of the solvents turned to yellow right after the addition of NDI. In contrast, the three solvents have negligible solubility for NDI-RGO, which remain colorless after mixing with NDI-RGO.