High Performance Supercapacitors Based on Highly Conductive Nitrogen-doped Graphene Sheets

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Electronic Supplementary Information

Experimental Details

Preparation of graphene oxide (GO). GO sheets were prepared from natural graphite powder by oxidation with potassium permanganate according to a modified Hummers method. Concentrated H_2SO_4 (70 mL) was added to a mixture of graphite flakes (3.0 g) and $NaNO_3$ (1.5 g) in an ice water bath. And then $KMnO_4$ (9.0 g) was added slowly in portions to keep the reaction temperature below 20 °C. The mixture was stirred vigorously for 3 days, and poured onto ice (400 mL) water. 30% hydrogen peroxide was added slowly to remove excess potassium permanganate to give a greenish yellow suspension. The yellow suspension was then purified following the filtering, centrifugation and decanting with multiple washes. The resulting solid product was obtained by the conventional freeze-drying process.

Preparation of reduced graphene oxide (RGO). RGO sheets were prepared from the reduction of graphene oxide in the presence of hydrazine upon sonication treatment. The pH value of 100 mL graphene oxide suspension (~1 mg/mL) was tuned to 10 by 1 M sodium hydroxide solution. Subsequently, 0.05 mL hydrazine monohydrate was added and the

mixture was sonicated at 90°C for 2 hours. The resulting black powder was obtained by filtering and freeze-drying.

Preparation of nitrogen-doped graphene (NG). NG sheets were prepared from the thermal reduction of reduced graphene oxide sheets. The RGO powder was loaded into a silica tube reactor placed in a horizontal tube furnace and connected to a gas feed system. Initially, a flow of Ar gas (99.99 %) was maintained over the bed to get rid of air and H_2O. Then the flowing gas was switched to NH_3 with a flow rate of 30 cm^3 min^{-1}. The furnace was heated from room temperature to 700 °C at a rate of 30 °C min^{-1}, held at this temperature for 30 minutes. Finally, the furnace was allowed to cool down under a flowing Ar gas.

Fabrication of Supercapacitor Electrodes. Electrode sheets of commercially available activated carbon powder (or RGO powder) were prepared by mixing and kneading the AC powder (or RGO powder) with 10 wt% PTFE binder and 10 wt% carbon black conducting agent. While NGs electrode sheets were prepared by only mixing and kneading the powder with 10 wt% PTFE binder due to the high electrical conductivity in nature. The mixture was homogenized in water by being sonicated for 30 min, and then dried for overnight at vacuum oven at 100 °C to make water completely evaporate. The electrodes, which were pressed on a Ni foam current electrode (Φ = 10 mm), were separated by a porous proprietary cellulose-based separator and were sandwiched in a stainless steel (SS) cell. The electrolyte is 1M Et_4N BF_4/propylene carbonate. The mass of active material is ~6.5 mg.

General characterization. Typical tapping-mode atomic force microscopy (AFM) measurements were performed using a Veeco Innova system. Graphene oxide for AFM images were prepared by dip-coating the dispersion of graphene oxide in water onto a freshly

cleaved mica surface and allowing them to dry in air. Scanning electron microscopy (SEM) was performed on a JEOL 6700F at an accelerating voltage of 2 kV. Film thickness was determined by a Tencor Alpha-Step 200 surface profiler system and verified by repeating each test three times. BET surface area was characterized using a Coulter SA 3100 surface area analyzer. XPS spectra were measured on a Perkin-Elmer model PHI 5600 XPS system with a resolution of 0.3–0.5 eV from a monochromated aluminium anode X-ray source with Kα radiation (1486.6 eV).

Electrical conductivity measurements. The electrical conductivity of NG and RGO films was measured using the standard 4-point contact method. 3-5 samples were measured for each type of film. Surprisingly, the result revealed that the electrical conductivity of the NG samples is enhanced by 5-10 fold compared to the RGO samples. The surface resistance (R) of the RGO films ca. 60 μm (L) thick is in the range of 70-110 Ω/Square, while that of NG films falls in between 6-13 Ω/Square. Accordingly, the electrical conductivity, calculated from $1/(R \cdot L)$, is 150-240 S/m for the RGO films and 1000-3000 S/m for the NG films.

The possible mechanism for the enhancement is thought to originate from the better restoration of the graphene network after thermal annealing in NH_3. Generally, some of oxygenated functional groups contain in RGO, which largely thwarted the conjugation effect of the graphene network and thereby inflicted the low electrical conductivity. High temperature NH_3 treatment is a useful method to get rid of the oxygenated functional groups and better restoration of the graphene network by N-doping and the formation of C-N bonded groups. Therefore, banking on its high conductivity, the electrodes of NG-based supercapacitors **did not** require carbon additives.

Supercapacitor characterization. The electrochemical properties and capacitance measurements of supercapacitor electrodes were studied in a two-electrode system by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using an Autolab work station (PGSTAT-30, Eco Echemie B.V. Company), and galvanostatic charge-discharge was carried out with a supercapacitor tester (Arbin Instrument, USA). Impedance spectroscopy measurements were carried out at a dc bias of 0.1 V with sinusoidal signal of 5 mV over the frequency range from 100 kHz to 1 mHz.
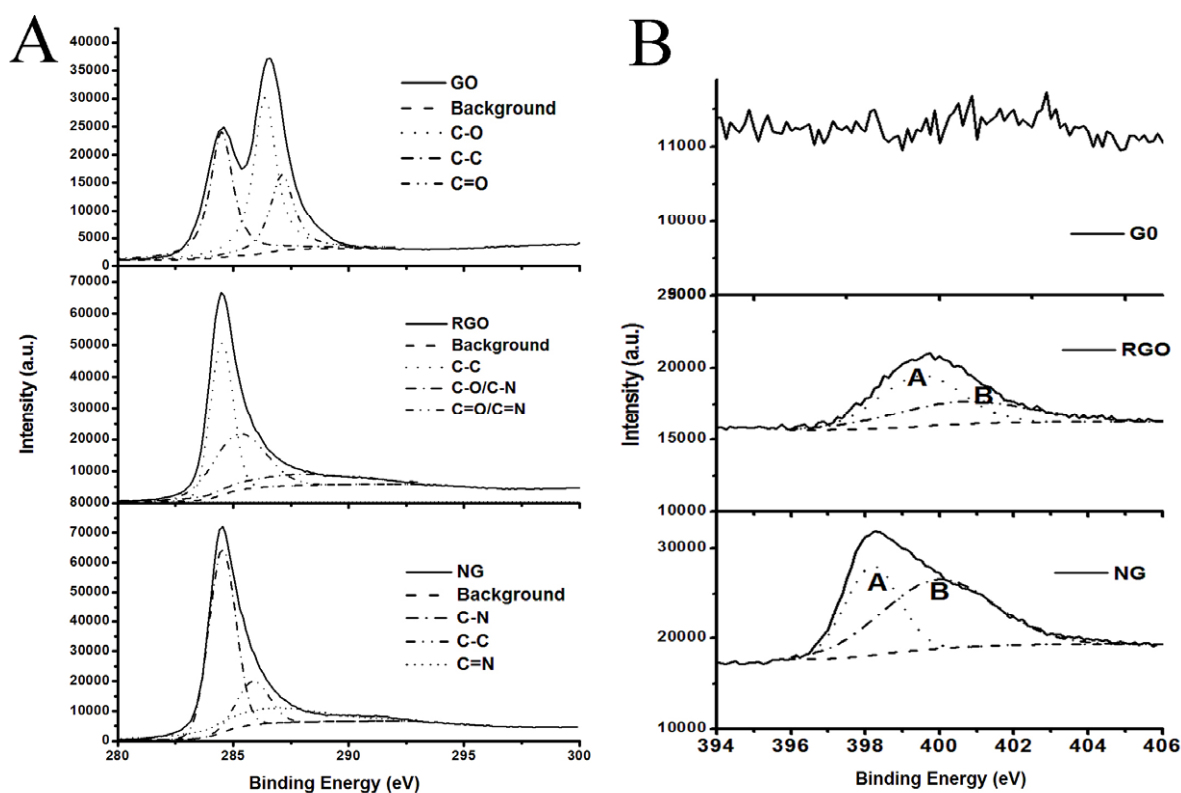
Figure S1. (a) C 1s and (b) N 1s XPS spectra of the as-prepared graphene oxide (GO), the graphene oxide reduced by hydrazine (RGO) and RGO after annealing in NH_3 (NG).
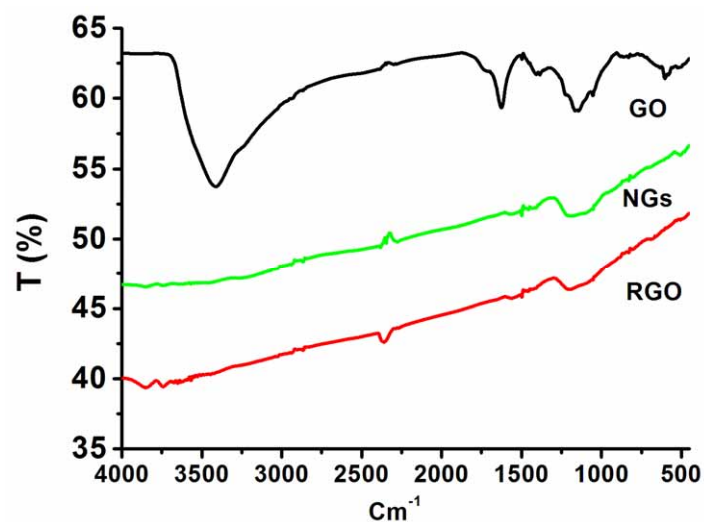
Figure S2. FT-IR spectra of the as-prepared graphene oxide (GO), the graphene oxide reduced by hydrazine (RGO) and RGO after annealing in NH_3.
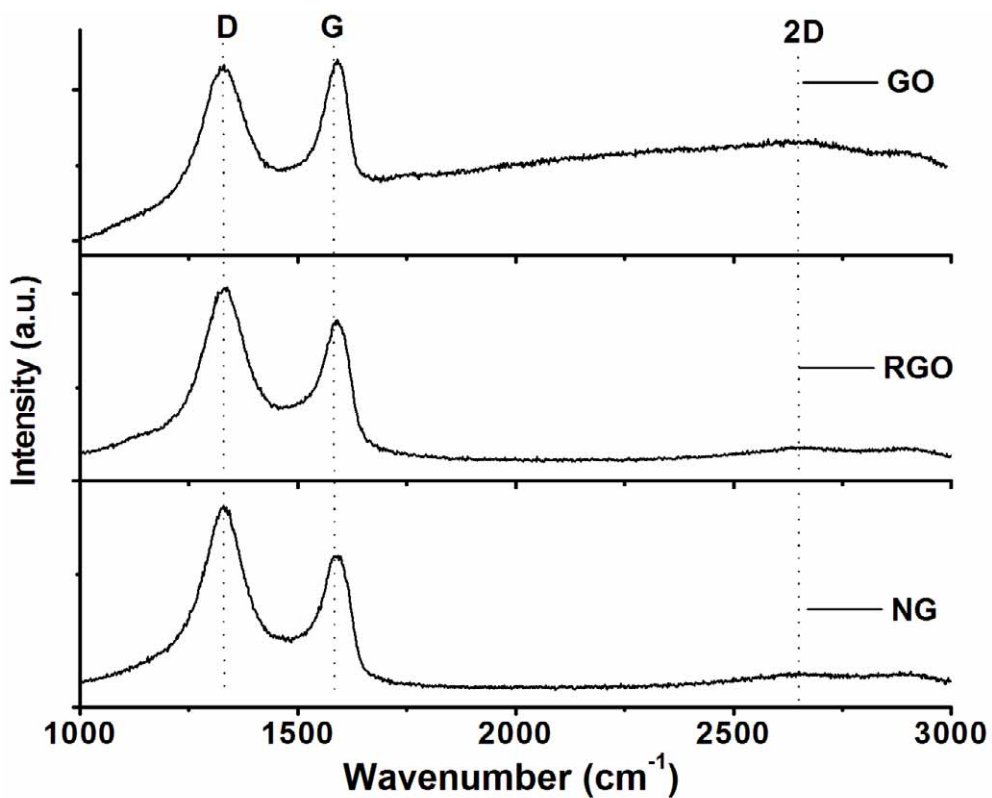

Figure S3. Raman spectra of the as-prepared graphene oxide (GO), the graphene oxide reduced by hydrazine (RGO) and RGO after annealing in NH_3.
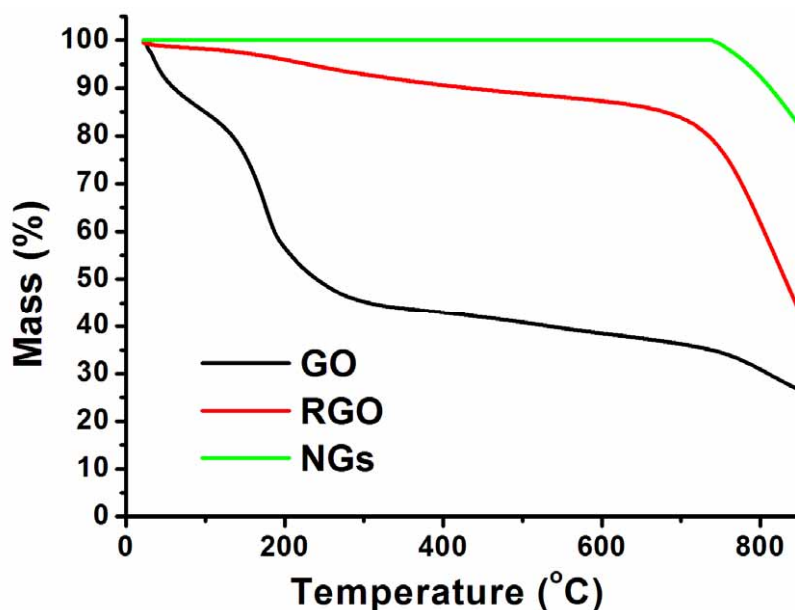
Figure S4. TGA traces of the as-prepared graphene oxide (GO), the graphene oxide reduced by hydrazine (RGO) and RGO after annealing in NH_3 measured in N_2 gas.

The high-resolution C 1s XPS spectrum of the GO sheets (Figure S1) shows a second peak at higher binding energy of ~286-290 eV, corresponding to large amounts of sp^3 carbon with C-O bonds, carbonyl (C=O), and carboxylates (O-C=O), as also confirmed by FT-IR spectra (Figure S2). The shoulder peak at ~286-290 eV, is associated with little amounts of sp^3 carbon with carboxylates (O-C=O) and C-N bonds. Carboxylic acid groups are unlikely to be reduced by hydrazine under the given reaction conditions. The formation of C-N bonds is due to N incorporation into the sp^2 network of RGO and NG, as also evidenced by the high-resolution N 1s XPS spectra of RGO and NG. In contrast the RGO sample is ~0.2% N content, the large amounts of N content of NG (~2%) is due to N-doping and C-N species by annealing of RGO in NH_3.

The Raman spectrum of the as-prepared graphene oxide (GO) sheets displays a D-band at 1338 cm^{-1} and a broad G-band at 1599 cm^{-1}. The former is derived from the structural imperfections created by the attachment of hydroxyl and epoxide groups on the carbon basal plane (i.e,, defect-induced mode), while the latter corresponds to the first-order scattering of the E_{2g} mode. The intensity of the 2D-band with respect to the D and G peaks is very small. After reduction, by virtue of the Raman spectra of the RGO and NG samples, there are no obvious shifts for the D- and G-bands. The extent of reduction of graphene oxide films can be estimated from the XPS results (Figure S1).

Furthermore, from the TGA traces in Figure S4, in contrast NG sample shows rather high thermal stability (up to 750°C), the weight loss for GO and RGO samples above 180 °C is ascribed to the decomposition of oxygenated functional groups.
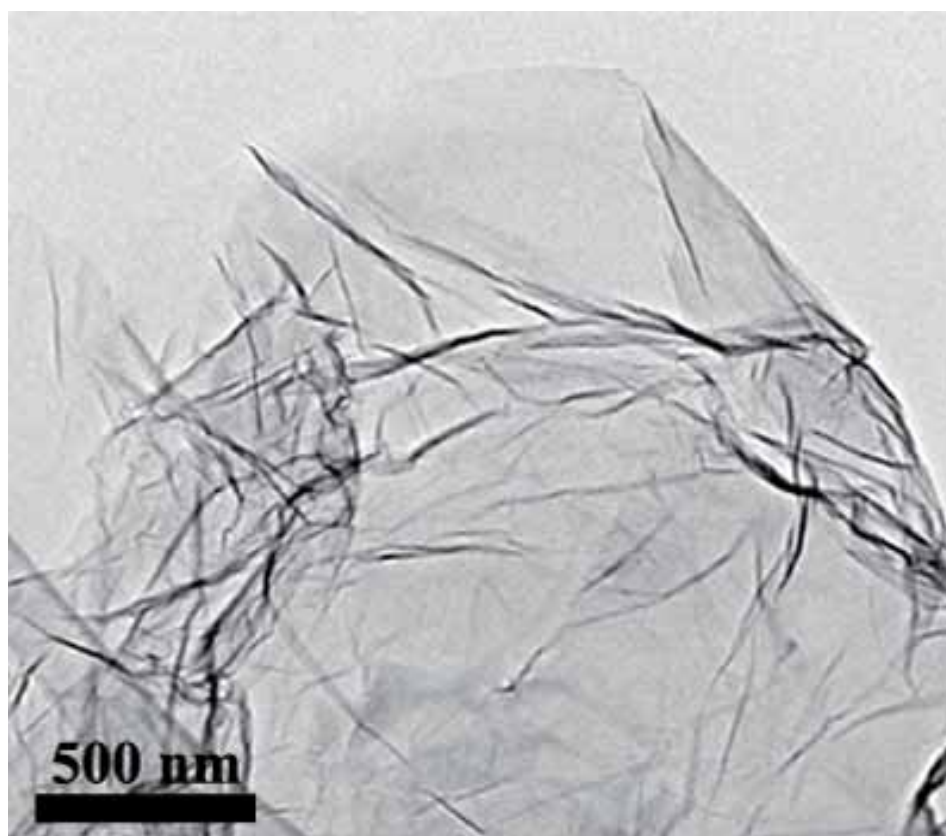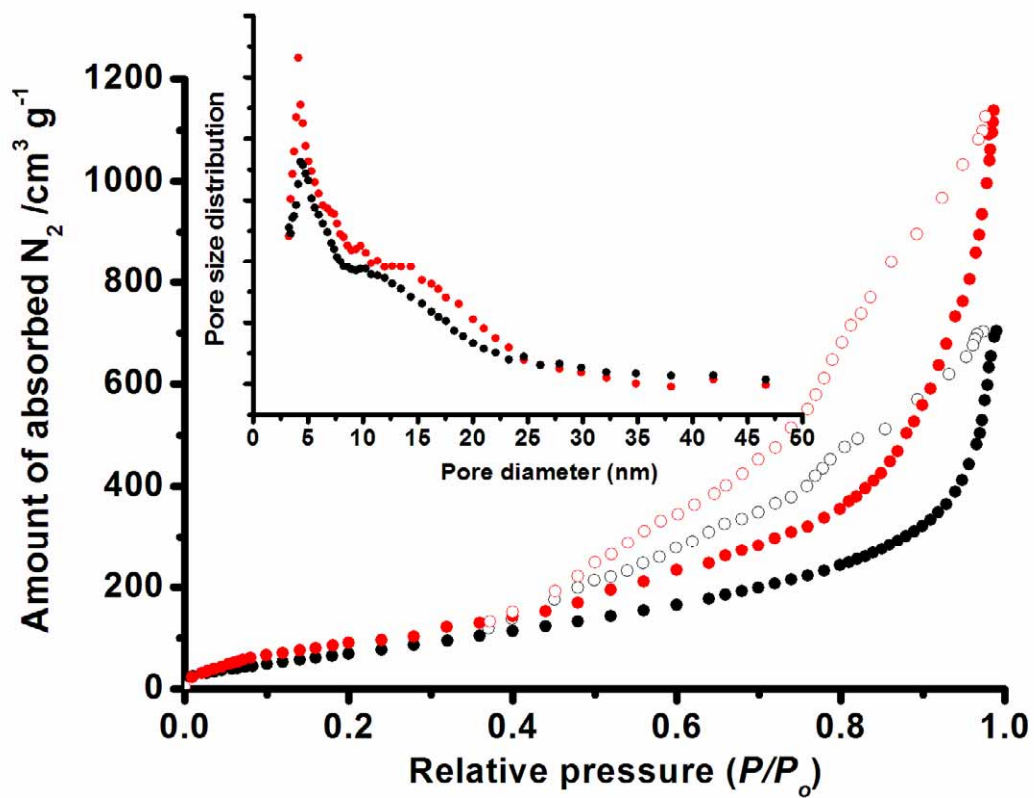
Figure S5. A typical TEM image of NG.

Figure S6. N_2 sorption isotherms of the RGO (black) and NG (red) samples. Inset: pore size distributions of the RGO and NG samples.

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┌RESULTS SUMMARY───────────────────────────────────────────────────────────┐
│ Rs:         137 ohm/sq    RHs:  -7.78e-05 m²/C        Ns:  -8.02e+18 /cm²  │
│ R :       0.548 ohm-cm    Mob:    0.00568 cm²/V-s     N :  -2.00e+21 /cm³  │
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  CONTACT CHECK
  Pair    ohms
   12     402
   23     597
   34     702
   41     472
   13     477
   24     669

  RGO
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┌RESULTS SUMMARY───────────────────────────────────────────────────────────┐
│ Rs:        5.87 ohm/sq    RHs:  -0.000459 m²/C        Ns:  -1.36e+18 /cm²  │
│ R :      0.0235 ohm-cm    Mob:      0.782 cm²/V-s     N :  -3.40e+20 /cm³  │
└───────────────────────────────────────────────────────────────────────────┘

  CONTACT CHECK
  Pair    ohms
   12     133
   23     62
   34     31
   41     100
   13     113
   24     53

  NG
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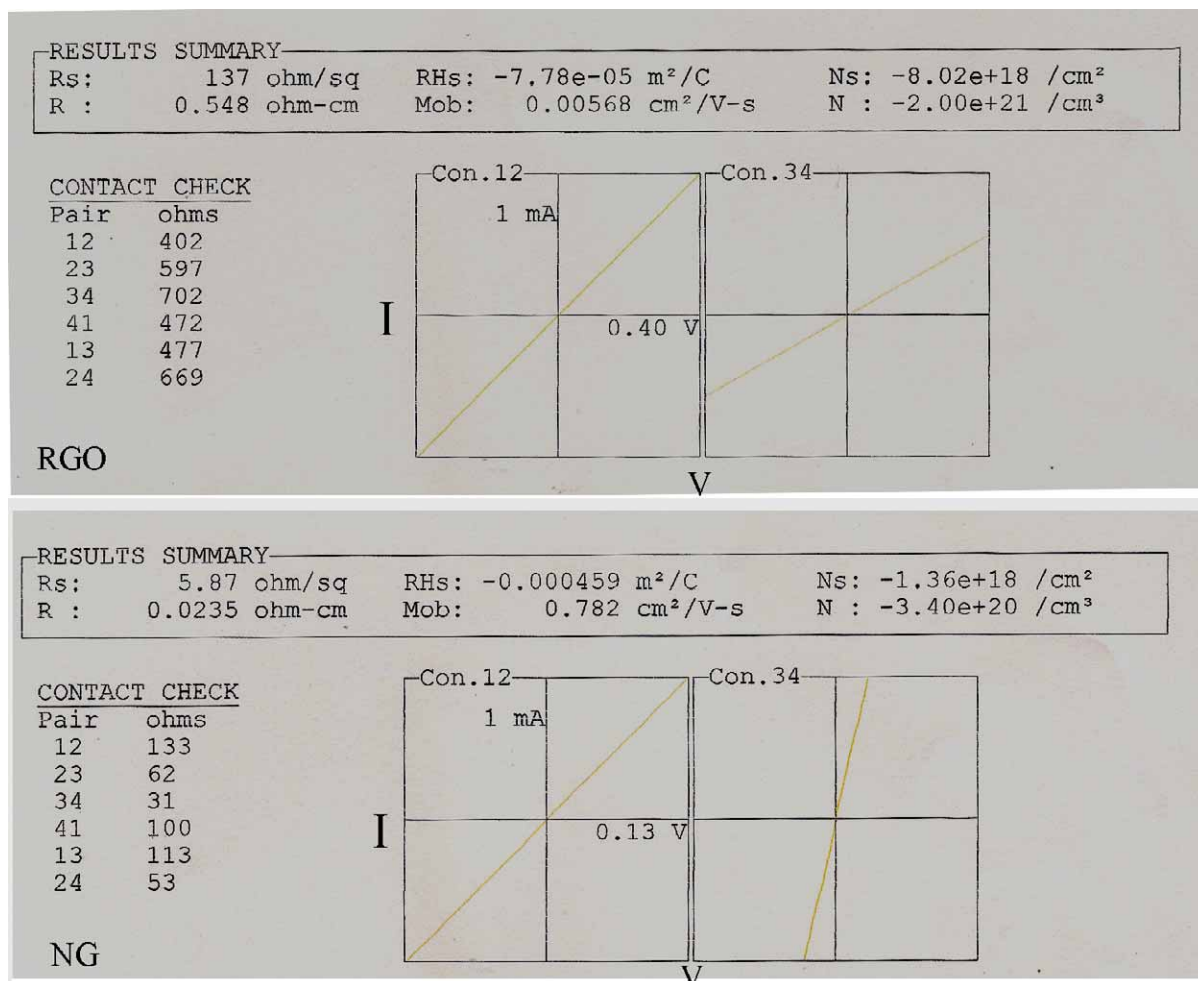
Figure S7. The measured conductivity profiles of RGO and NG samples.