CVD-Graphene for Low Equivalent Series Resistance in rGO/CVD-graphene/Ni based Supercapacitors

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1. **CVD-graphene growth on Ni-foil**

For direct growth of graphene, the Ni-foil was immersed in a diluted hydrochloric acid aqueous solution for 1 minute to remove native oxide present on the nickel. The foil was washed with deionized water and immersed in acetone and methanol for 5 minutes, respectively, followed by sonication for 5 minutes. Finally, the surface of the nickel foil was washed with an isopropanol solution and blown off with a nitrogen gas. The nickel foil was placed on a sample stage made of quartz, and then put into the CVD chamber. In the first step, the temperature inside the CVD chamber is raised to 1000 °C in the hydrogen gas atmosphere at flow rate of 100 sccm. At 1000 °C, the annealing was performed for 1 hour under the same flow rate of the hydrogen gas. At the end of the annealing process, 200 sccm of methane gas was passed inside the chamber for 20 minutes while the other conditions were maintained the same. After 20 minutes, the flow of the methane gas cylinder is stopped and the quenching process is performed keeping hydrogen gas at the same flow rate. The cooling rates were maintained at 20, 40 and 100 °C/min., respectively. During CVD growth process pressure inside the chamber was maintained at ~ 16 torr by controlling the gate valve. The complete process has been summarized in schematic diagram as shown in Figure S-1.

![Figure S1 Schematic of graphene synthesis on Ni-foil using chemical vapor deposition method.](image-url)
2. Graphene oxide reduction and rGO dispersion

To synthesize rGO, chemically exfoliated graphene oxide (GO) was dispersed at concentration of 0.19 mg/ml in de-ionized water for 3 hours using an ultrasonic processor (sonication, CLEANER 410, 230 W). The bath water was replaced repeatedly, to maintain the bath temperature less than 40 °C for the dispersion of the graphene suspension. Ammonia water (ammonium hydroxide solution 28% in H₂O₂) was added using a syringe to adjust pH to 10, and stirred at 500 rpm for 10 minutes. Hydrazine monohydrate (N₂H₄, reagent grade, 98%) was added as a reducing agent to GO (weight ratio, 70:10). The beaker was then enclosed with Teflon tape and then subjected to a reduction process in a laboratory oven maintained at 80 °C for 12 hours.

Figure S-2 (a, b) is a photograph which shows the apparent change before and after reduction, where the color of GO is brown, whereas the color of rGO is pure black. The chemical reduction has changed the microstructure and properties of the graphene oxide (GO). In other words, optical observation is a method of directly confirming the change of GO before and after reduction. The ammonia was removed after reduction due to its volatile nature.

The rGO was filtered using a filter membrane with polyvinylidene fluoride (PVDF) filter paper with a pore size of 0.45 μm. After washing with 1 L of de-ionized water, the reduced graphene powder was dispersed in a mixed solution of distilled water and isopropyl alcohol (molar ratio 0.228:0.771). For uniform dispersion, the graphene suspension concentration 0.01 mg/ml, dispersion was dispersed for 3 hours using an ultrasonic processor. During the ultrasonic treatment, the internal temperature of the bath was maintained at less than 40 °C to keep the dispersibility of the graphene suspension.

3. Raman spectra of GO and rGO

Figure S-2 (c, d) shows the Raman spectra of GO and rGO samples. The peak of the GO (1588.3 cm⁻¹) in the G-band was red-shifted compared to the peak of graphite (1580 cm⁻¹). This is ascribed to the presence of an isolated double bond that resonates at a higher frequency than the G-band of graphite¹⁻². The G-band of the rGO appears at 1581.3 cm⁻¹, corresponding to the recovery of the hexagonal network of defective carbon atoms. The ratio of D and G-band band peak intensity (I_D/ I_G) in rGO was significantly increased, which is a typical behavior in the reduction process indicating the structural change of the oxidized graphene.²
Figure S2 (a) Graphene oxide solution (left), reduced graphene solution (right). (b) Stable dispersion of rGO without precipitation of graphene. (c-d) Raman spectra of GO and rGO. (e) SEM image of rGO coated on an electrode. (f) Nitrogen adsorption and desorption isotherm for reduced graphene rGO.
4. Specific surface (Brunauer-Emmett-Teller) area of rGO

The GO, obtained from Angstron Materials, Inc., has specific surface area ~400 m² g⁻¹. The BET analysis was performed at the liquid nitrogen temperature. The rGO powder was inserted into a sample cell with a minimum of 50 mg for reliable measurement, and then pretreated in a vacuum atmosphere at 150 °C for 3 hours to remove moisture, and the sample cell was placed in liquid nitrogen for the measurement. The adsorption isotherm curve as shown in Figure S-2(f) was obtained from the relationship between relative pressures (P/P₀) and amount of nitrogen adsorbed on the rGO surface. The specific surface area of rGO after the reduction was estimated as 366.88 m² g⁻¹. The surface area is found to be decreased by 8.28% from that of the GO as-purchased, suggesting that the reduction process effectively suppressed the aggregation of graphene.

Finally, rGO was spray-coated onto a current collector to fabricate electrodes of the supercapacitor. The SEM image of the rGO coated electrode indicating high roughness with many pores is shown in Figure S-2(e).
5. Electrochemical calculations

The capacitance of the various electrodes were calculated from CV at different scan rates: 0.05, 1, 2 and 10 Vs\(^{-1}\) scan rates are shown in Table S-1. The specific capacitances per unit mass (F/g) were converted into those per unit area (µF/cm\(^2\)) by using the BET result of the specific area 366.88 m\(^2\)g\(^{-1}\).

Table S-1. Capacitance calculations from CV curves for all electrodes at various scan rates

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Electrode/Scan rate (Vs(^{-1}))</th>
<th>Specific Capacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.05 (µF/cm(^2))</td>
</tr>
<tr>
<td></td>
<td>Unit</td>
<td>F/g</td>
</tr>
<tr>
<td>1.</td>
<td>CVD-G20</td>
<td>42.06</td>
</tr>
<tr>
<td>2.</td>
<td>CVD-G40</td>
<td>58.27</td>
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<tr>
<td>3.</td>
<td>CVD-G100</td>
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</tr>
<tr>
<td>4.</td>
<td>rGO</td>
<td>39.46</td>
</tr>
</tbody>
</table>
6. Supercapacitor cell structure

The schematic of the symmetric cell assembly is shown in Figure S3.

![Fig. S3 Schematic of rGO/CVD-G/Ni electrodes based assembled cell](image)
References
