Realizing battery-like energy density with asymmetric supercapacitors achieved by highly conductive three-dimensional graphene current collectors

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Calculation of specific capacitance

(1) Gravimetric capacitance

The mass difference of the $Ni(OH)_2$/Ni-GN electrode before and after the deposition of $Ni(OH)_2$ carefully measured by a microbalance was 2.0 mg. When we calculated the capacitance value, we considered $Ni(OH)_2$ as the active material of the device (by ignoring the presence of Ni-GN and determined the mass of active materials to be 2.0 mg because the capacitance of the Ni-GN current collector is negligible compared to the specific capacitance value of the $Ni(OH)_2$/Ni-GN electrode (<6.6 vs. 3,179 F/g), as shown in Figure S10.

$$Weight\ of\ active\ material = Total\ weight - Weight\ of\ Ni - GN\ electrode$$

The capacitance was calculated by cyclic voltammograms (CV) curves and galvanostatic charge/discharge curves.

$Total\ of\ active\ material = 2\ mg$

- Galvanostatic charge/discharge curves

$$C_s = \frac{i}{m\ (\Delta V/\Delta t)}$$

$$C = \frac{(20 \times 10^{-3}\,A)}{(2 \times 10^{-3} g) \times (0.65 - 0.1 - 0.02597\ (IR\ loss))/(162.14\ s)}$$

- C → specific capacitance
- i → current density
- m → mass of active material
- △V → potential window range
- △t → discharge time

$$= \frac{10\ A/g}{(0.65 - 0.1 - 0.02597\ (IR\ loss))/(162.14\ s)}$$

= 3,179 *F/g*

(2) Volumetric capacitance

The volumetric capacitance was calculated by considering a volume of the electrode. The volume of the electrode was calculated after measuring area and height. We supposed that $Ni(OH)_2$ as an active material was fixed as 1 cm^2 (1 cm × 1 cm). The height of the electrode was measured by a micrometer (Mitutoyo Korea Corporation).

$$Total\ volume\ of\ electrode = active\ area\ \times\ height\ of\ electrode$$

In the case of the $Ni(OH)_2$/Ni-GN electrode with a total height of 266 um.

$$Total\ volume\ of\ electrode = 1\ cm^2\ \times\ 0.0266\ cm$$

= **0.0266 *cm³***

- Galvanostatic charge/discharge curves

$$C_s = \frac{i}{v\ (\Delta V/\Delta t)}$$

- C → specific capacitance
- i → current density
- v → volume of electrode
- △V → potential window range
- △t → discharge time

$$C = \frac{(20 \times 10^{-3}\,A)}{(0.0266\ cm^3) \times (0.65 - 0.1 - 0.02597\ (IR\ loss))/(162.14\ s)}$$

$= \mathbf{232.64}\ \boldsymbol{F/cm^3}$

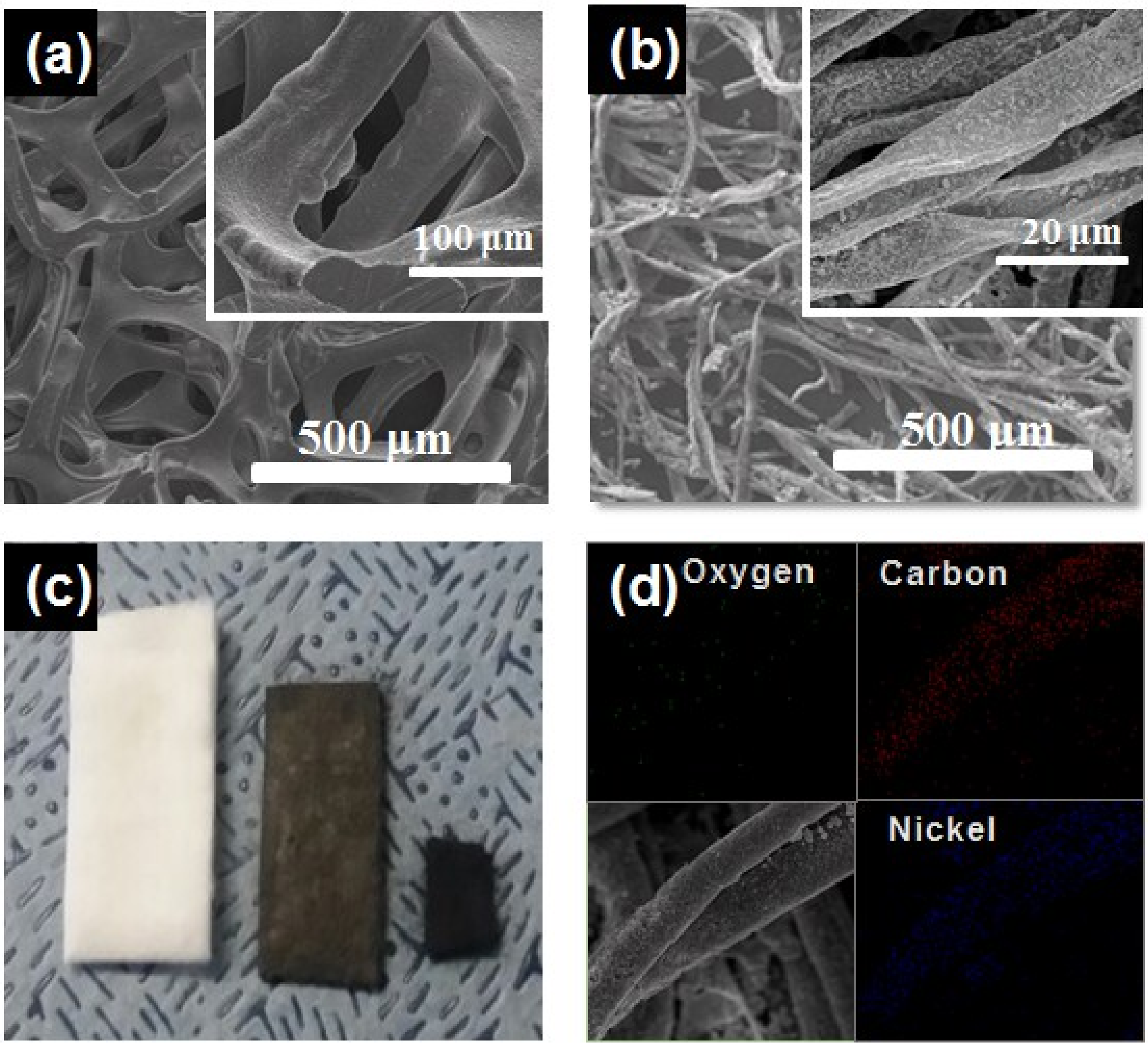


Figure S1. SEM images of commercial nickel foam (a) and Ni-GN (b). (c) Photograph of commercial medical cotton, Ni-GN, carbonized cotton without nickel from the left to right. (d) EDS (Energy dispersive spectrometer) image of each element in Ni-GN

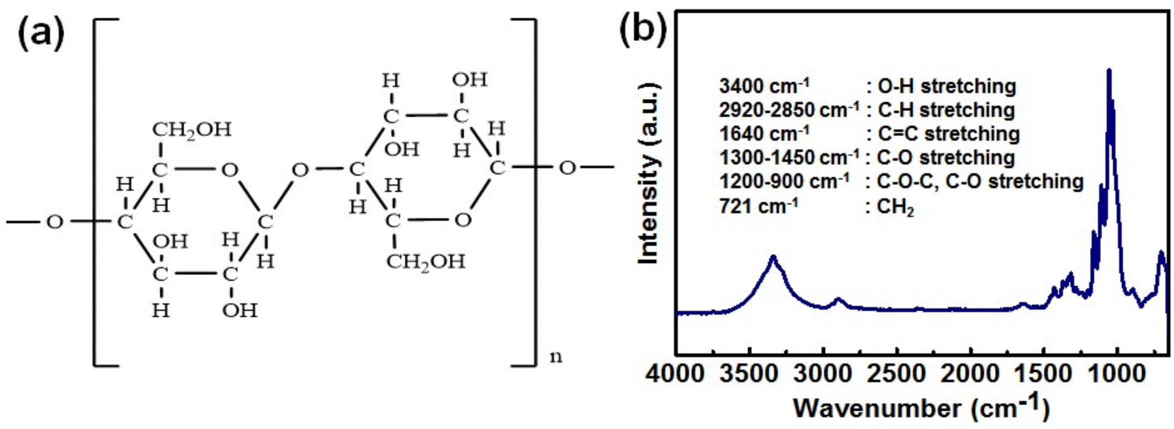


Figure S2. Chemical structure of cotton (a) and FT-IR spectra of a commercial medical cotton foam (b).

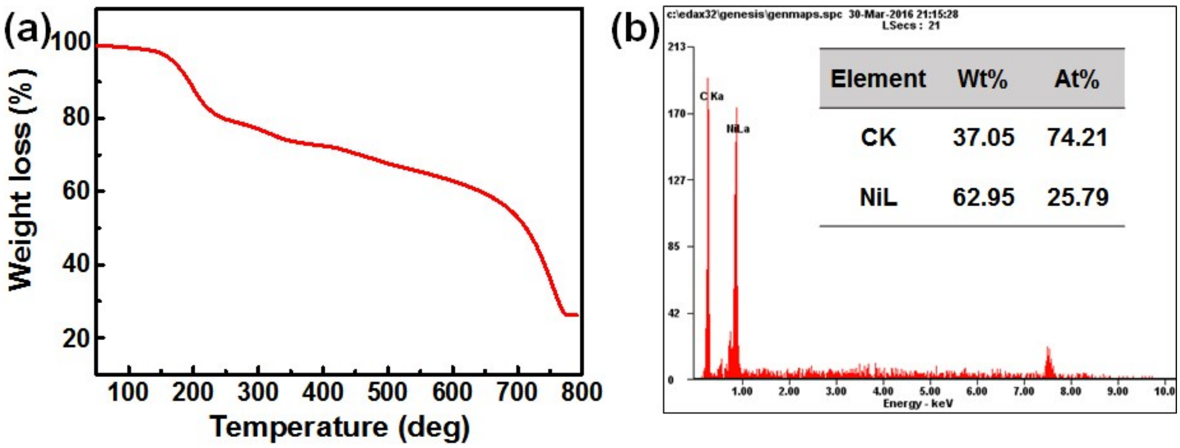


Figure S3. TGA curve of cotton with anhydrous nickel (a) and EDS data of Ni-GN (b).

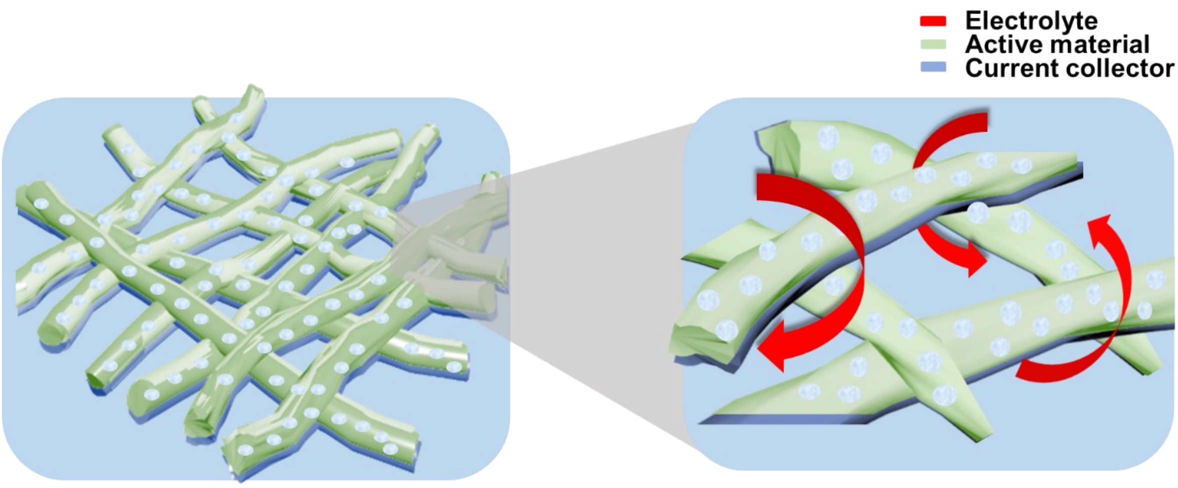


Figure S4. Schematic illustration of enhanced electrolyte transport in Ni-GN.

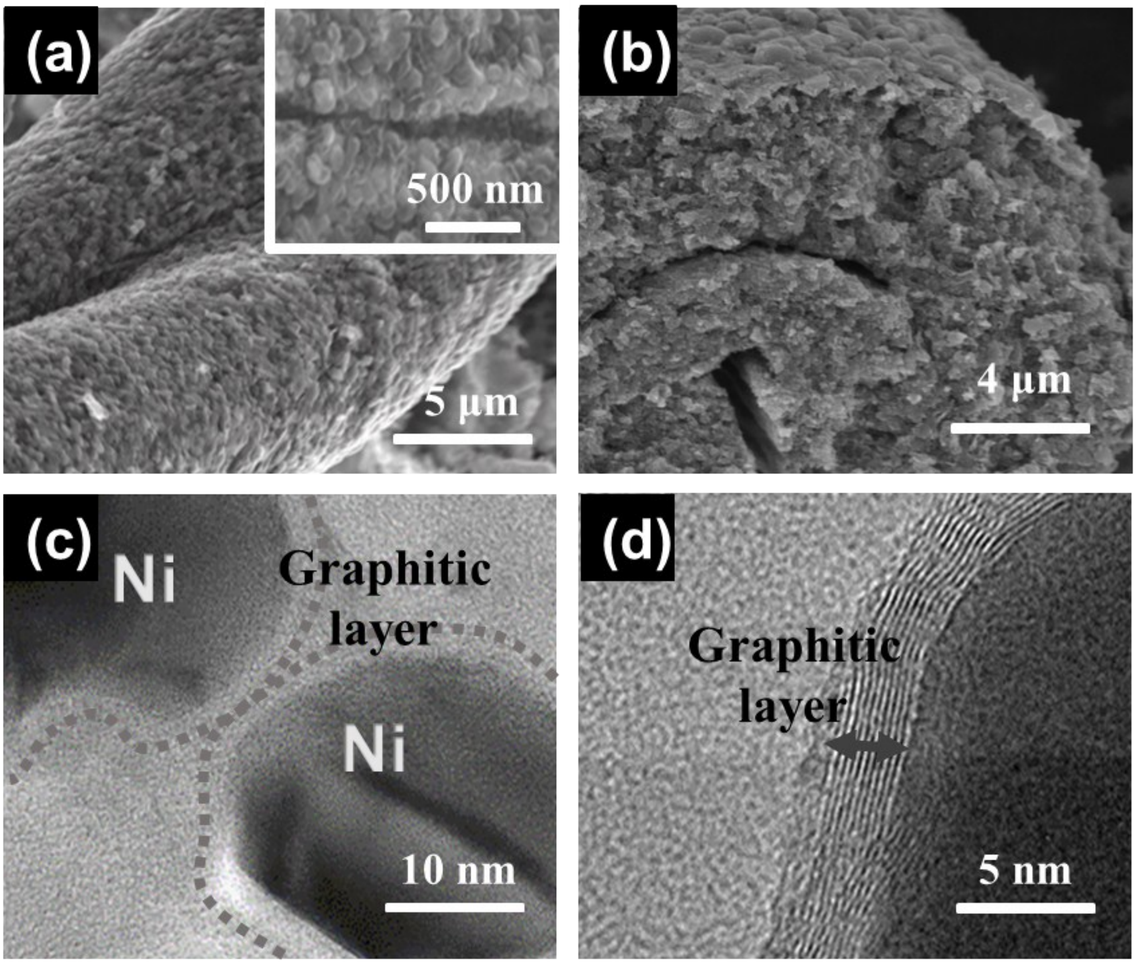


Figure S5. SEM images (a,b) of Ni-GN and TEM images (c,d) of the surface of Ni-GN.

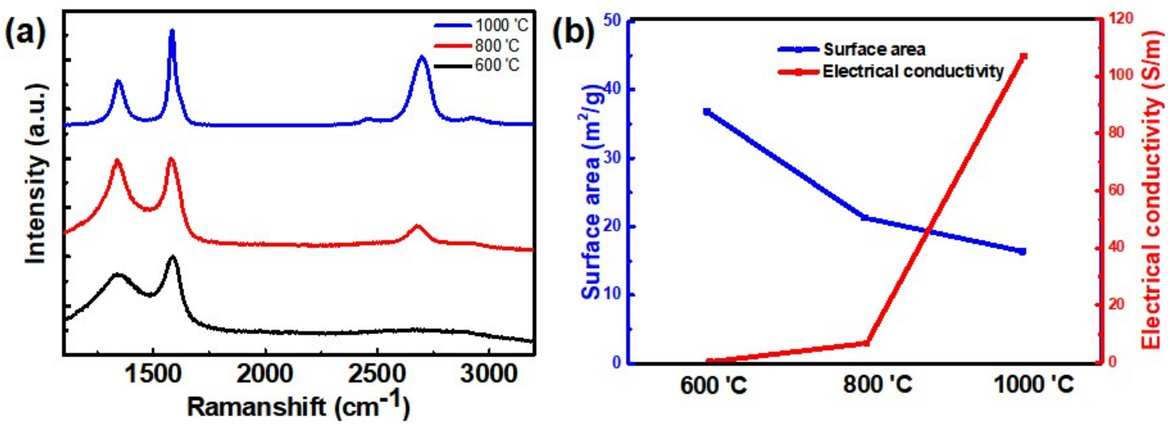
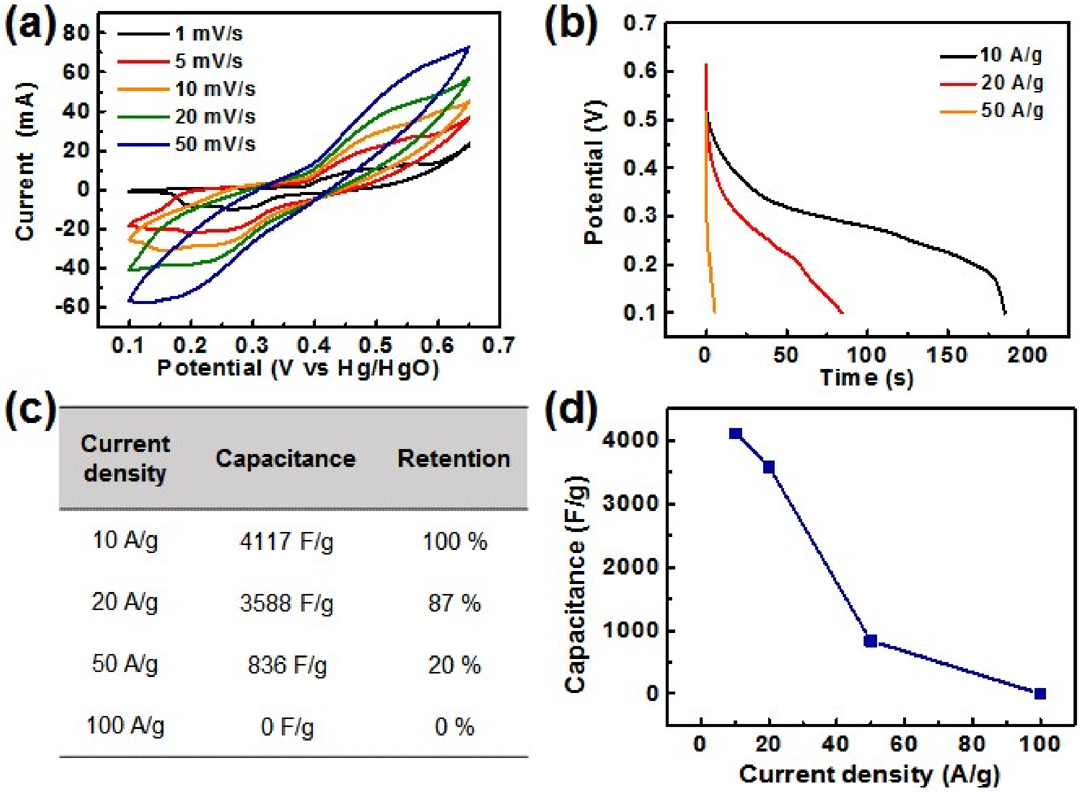
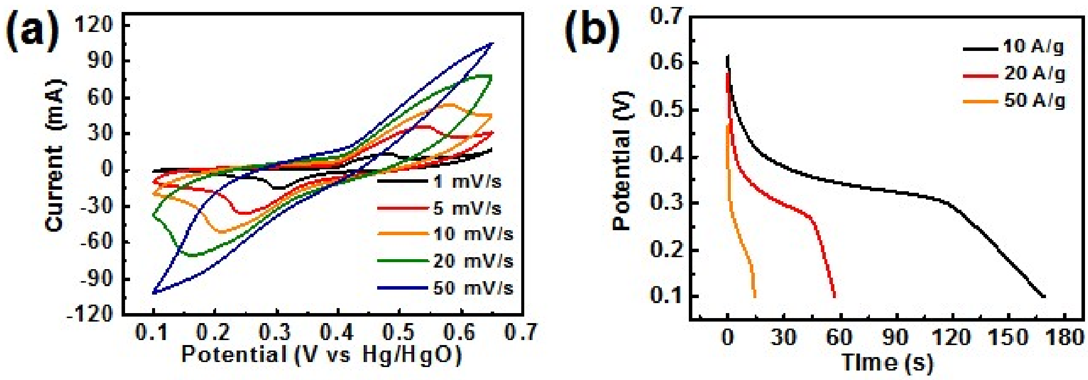


Figure S6. Raman spectra (a), electrical conductivity and surface area (b) of Ni-GN carbonized at various temperature.



Current density	Capacitance	Retention
10 A/g	4117 F/g	100 %
20 A/g	3588 F/g	87 %
50 A/g	836 F/g	20 %
100 A/g	0 F/g	0 %

Figure S7. CV curves at various scan rates of (a), GCD curves (b), kinetic property (c) and specific capacitance vs current density (d) of $Ni(OH)_2$/Ni-GN carbonized at 600 °C.



(c)

Current density	Capacitance	Retention
10 A/g	3381 F/g	100 %
20 A/g	2532 F/g	75 %
50 A/g	2237 F/g	66 %
100 A/g	0 F/g	0 %

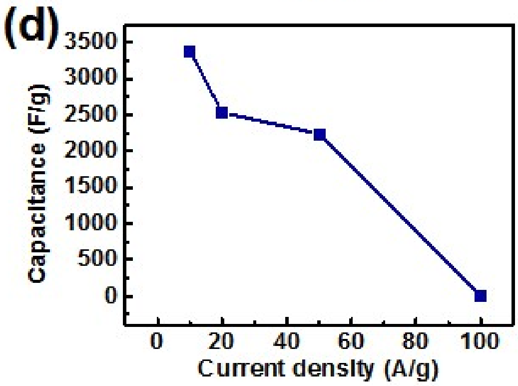


Figure S8. CV curves at various scan rates of (a), GCD curves (b), kinetic property (c) and specific capacitance vs current density (d) of $Ni(OH)_2$/Ni-GN carbonized at 800 °C.

Ni-GN pyrolyzed at the relatively low temperature range (600-800 °C) showed low quality of carbon materials due to insufficient energy to activate the graphitization. This resulted in a bad performance of the supercapacitor due to the low charge transport and low electrical conductivity of the current collector.

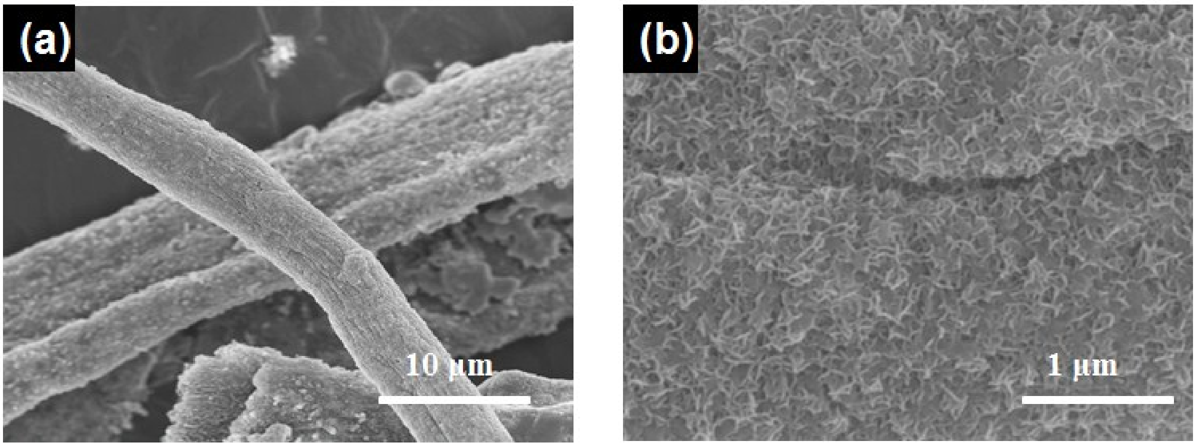
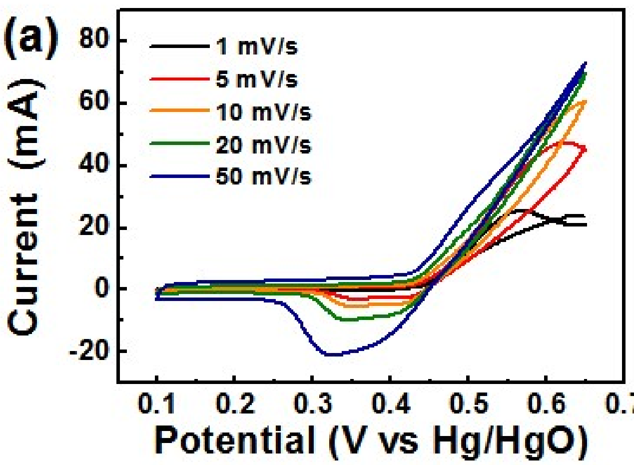


Figure S9. Large area (a) and magnified SEM image (b) of $Ni(OH)_2$/Ni-GN.

The prepared Ni-GN electrode, Pt mesh and Ag/AgCl (sat.) electrode was used as a working electrode, counter electrode and reference electrode, respectively. Electrodeposition was performed at -5 mA of current on the working electrode for 5 mins at 25 °C in a 100 mM nickel nitrate hexahydrate solution. And then $Ni(OH)_2$/Ni-GN electrode was washed using DI water and ethanol and dried at 120 °C for 12 hours in a vacuum oven.



(b)

Scan rate (mV/s)	Capacitance (F/g)
1	6.5954
5	5.5135
10	2.8666
20	1.6910
50	1.2917

Figure S10. CV curves (a) and the capacitance value (b) of Ni-GN only (without active materials) at various scan rates.

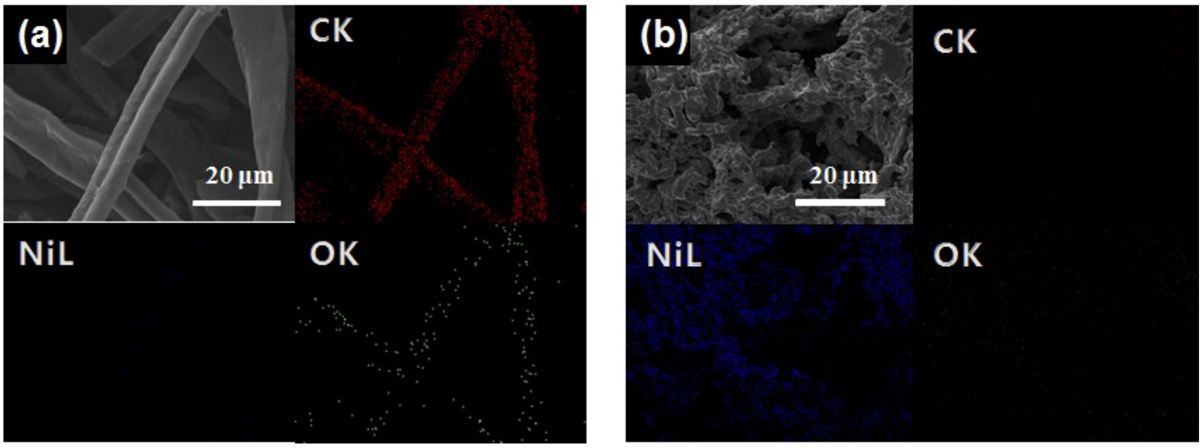


Figure S11. SEM and EDS images of Ni_1-GN_9 (a) and Ni_9-GN_1 (b).

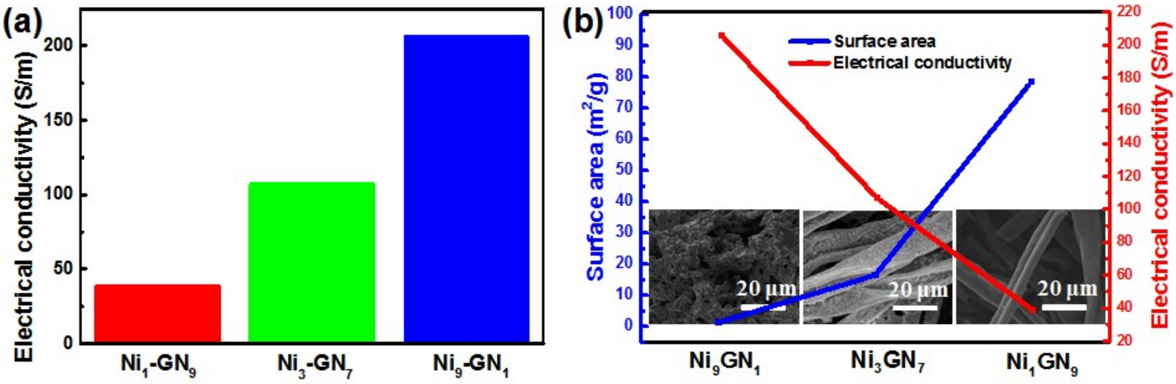
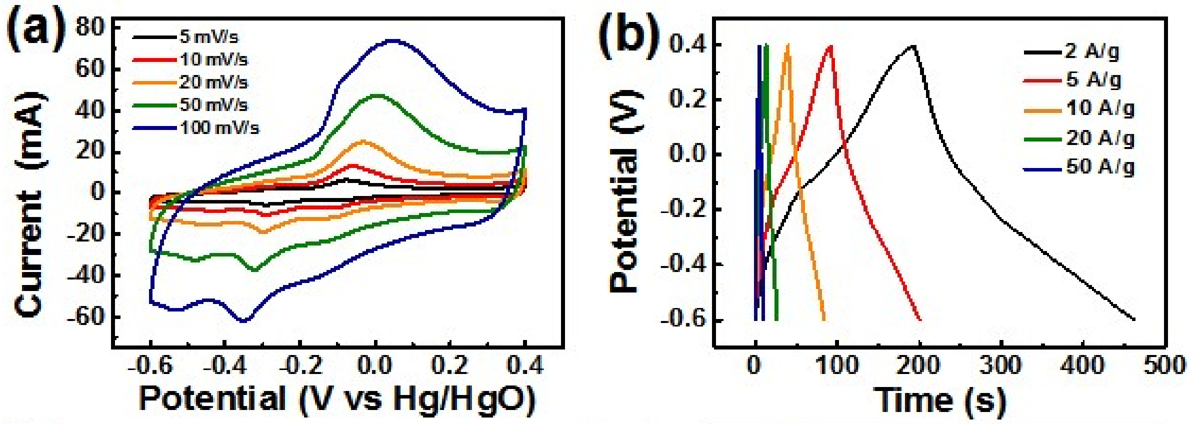


Figure S12. Electrical conductivity of Ni-GN by the increment of Ni-NPs (a) and surface area and electrical conductivity vs the nickel contents (b).

The highest capacitance value was obtained from the Ni_3-GN_7 electrode where two important factors, the conductivity and the surface area, are optimized (Figure 5 and Table 1). Ni_3-GN_7 optimally exhibits large surface area (16.4 vs 1.21 m^2/g of Ni_3-GN_7, and Ni_9-GN_1) and high electrical conductivity (107 S/m vs 39 S/m of Ni_3-GN_7, and Ni_1-GN_9).



(c)

Current density (A/g)	Capacitance (F/g)	Retention (%)
2 A/g	547 F/g	99 %
5 A/g	552 F/g	100 %
10 A/g	447 F/g	81 %
20 A/g	288 F/g	52 %
50 A/g	296 F/g	54 %

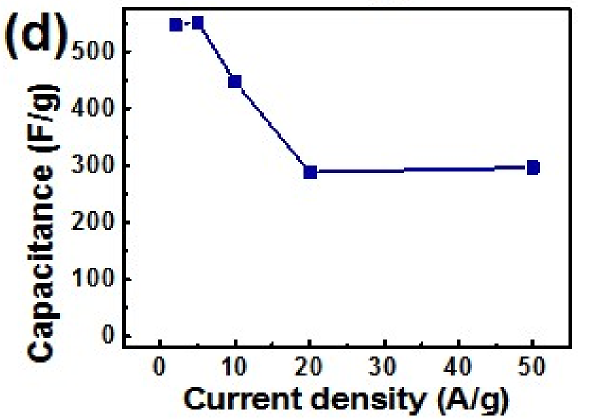
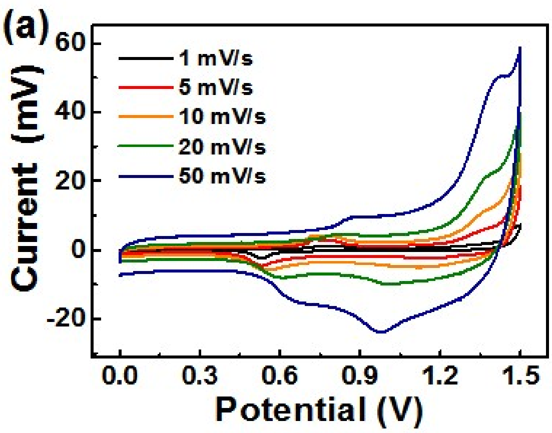


Figure S13. CV curves (a) at various scan rates and GCD curves (b) of MnO_2@Ni-GN of Ni-GN. Kinetic property (c) and specific capacitance vs current density (d) of MnO_2@Ni-GN of Ni-GN.



(b)

Scan rate (mV/s)	Capacitance (F/g)	Retention (%)
1	995.2364	100 %
5	750.0260	75 %
10	678.9929	68 %
20	576.2888	58 %
50	492.3935	49 %

Figure S14. (a) CV curves of $Ni(OH)_2$@Ni-GN and MnO_2@Ni-GN devices at different scan rates. (b) Energy efficiency of $Ni(OH)_2$@Ni-GN and MnO_2@Ni-GN devices at different scan rates.

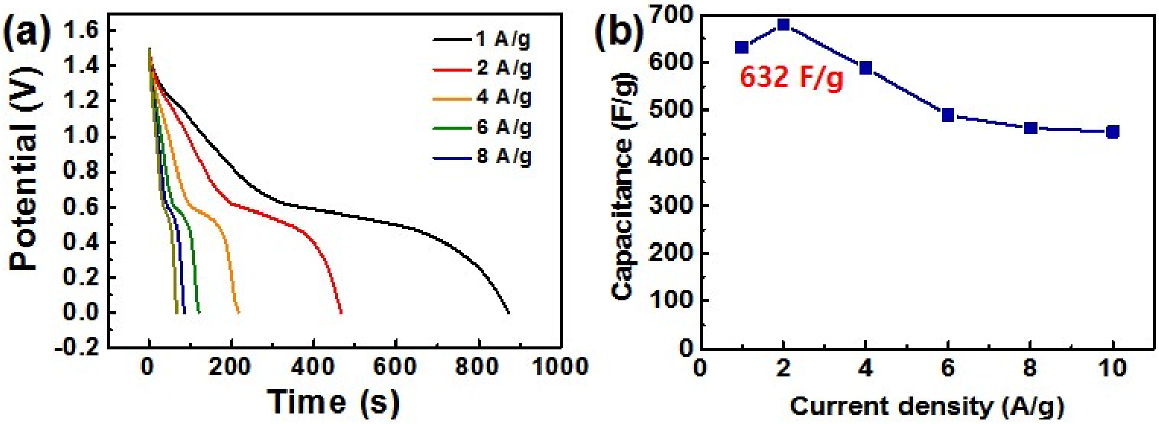


Figure S15. GCD curves (a) and specific capacitance (b) of our $Ni(OH)_2$@Ni-GN and MnO_2@Ni-GN electrode.

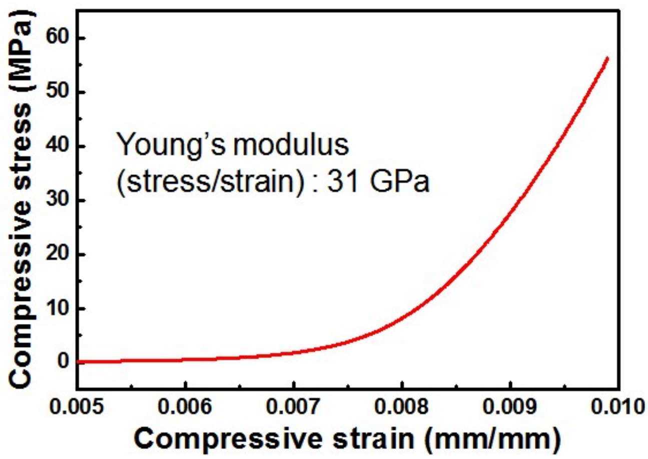


Figure S 16. Compressive stress and compressive strain curve of Ni-GN.

The mechanical strength of the Ni-GN current collector was measured by Dual Column Floor Frames (Instron Co. 5982). A compression force of 9,000 N was applied on the Ni-GN current collector at a rate of 0.5 mm/min. The Young's modulus of Ni-GN is 31 GPa, which is much higher than that of a similar electrode (~ 0.81 GPa)[1] due to the formation of the welded 3D-network in Ni-GN.

Table S1. Capacitance of previously reported $Ni(OH)_2$-based supercapacitors tested in the aqueous electrolyte.

Materials/current collector	Specific capacitance	Retention	Electrolyte	Reference
$Ni(OH)_2$//rGO	1,717 F/g at 0.5 A/g	89 % after 10,000 cycles	2 M KOH	[13]
$Ni(OH)_2$//Ni foam	2,384 F/g at 1 A/g	75 % after 3,000 cycles	2 M KOH	[18]
$Ni(OH)_2$//NPG	3,168 F/g at 5 A/g	90 % after 30,000 cycles	1 M KOH	[19]
$Ni(OH)_2$//hexagonal platelets-Ni foam	2,534 F/g at 1mV/s	97 % after 2,000 cycles	2 M KOH	[21]
Porous $Ni(OH)_2$ nanoflakes/graphene sheet//Ni foam	2,194 F/g at 2mV/s	95 % after 2,000 cycles	6 M KOH	[32]
Our work	3,179 F/g at 10 A/g	90 % after 10, 000 cycles	1 M KOH	

Table S2. Energy density and power density of previously reported $Ni(OH)_2$-based supercapacitors tested in the aqueous electrolyte.

Materials	Energy density (Wh/kg)	Power density (W/kg)	Electrolyte	Reference
$Ni(OH)_2$/graphite//AC	35.7	490	1 M KOH	[35]
$Ni(OH)_2$/CNT& PEDOT:PSS//rGO/CNT	58.5	780	1 M KOH	[14]
$Ni(OH)_2$/graphene// porous graphene	77.8	174.7	6 M KOH	[12]
$Ni(OH)_2$/CNT/NF//AC	50.6	95	6 M KOH	[36]
Our work	189	1460	1 M KOH	

Table S3. Energy density and power density of various supercapacitors tested in the organic electrolyte.

Materials	Energy density (Wh/kg)	Power density (W/kg)	Electrolyte	Reference
VN/graphene	162	200	1 M $LiPF_6$	[37]
B doped Si/SiO_2/Carbon	128	1229	1 M $LiPF_6$	[38]
Fe_3O_4/graphene	147	150	1 M $LiPF_6$	[39]
N doped AC	230	1747	1.2 M $LiPF_6$	[40]
$TiNb_2O_7$/Carbon	110	99.58	1 M $LiPF_6$	[41]