

Electronic Supplementary Information

Non-aqueous approach to the preparation of reduced graphene oxide/α-Ni(OH)₂ hybrid composites and their high capacitance behavior

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Experimental section

Preparation of reduced graphene oxide/ α -Ni(OH)₂ hybrid composites

Reduced graphene oxide/ α -Ni(OH)₂ composites were synthesized by controlling the mass ratio of Ni(OH)₂ and Graphite Oxide (GO). With the mass ratio of GO to Ni(OH)₂ varied at 1:10, 1:20, 1:30, and 1:40, the resulting composites were denoted as GN10, GN20, GN30, and GN40, respectively. For GN10, the typical synthesis procedure was as follows. Graphite oxide (GO) was obtained from natural graphite (Sigma-Aldrich) using the modified Hummers method as previously reported.^{1,2} The 25 mg of GO powder thus obtained was exfoliated in 50 mL of ethylene glycol under ultrasonication, with 640 mg of NiCl₂·6H₂O then completely dissolved. Subsequently, prepared solution containing precursors (A) was heated at 90 °C. To crystallize Ni(OH)₂, NaOH in an ethylene glycol solution (B) was prepared as follows. 1.50 g of NaOH was added to 50 mL of ethylene glycol, heated at 90 °C for 1 h, and kept at this temperature. The prepared NaOH in the ethylene glycol solution (B) was then rapidly poured into the above solution containing the precursors (A) and the temperature was then raised to 180 °C and held there for 6 h. After the reaction, the mixture (C) was cooled naturally to room temperature. A black precipitate was then isolated by centrifugation, washed with excess ethanol and water, and dried in a vacuum condition at room temperature. Pure α -Ni(OH)₂ and reduced graphene oxide (rGO) were also obtained by the aforementioned procedure for comparison.

Sample characterization

The crystal structures were analyzed by X-ray diffraction (XRD, Rigaku D/MAX-IIIC) equipped with Cu-K α radiation ($\lambda = 1.50405$ Å). Raman spectra were obtained using a Raman LabRAM HR UV-vis/NIR (Horiba Jobin Yvon, France) with an Ar ion CW laser (514.5 nm) as an excitation source. Fourier transform infrared spectroscopy (FT-IR) was carried out on an IFS66V/S & HYPERION 3000 (Bruker Optics, Germany) in a range of 600–4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) spectrum was recorded

with a Thermo VG Scientific Sigma Probe spectrometer. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were taken on a TECNAI F20 (Philips) at 200 kV.

Electrode preparation

To evaluate the electrochemical properties of the reduced graphene oxide/ α -Ni(OH)₂ composites, working electrodes were prepared as follows. The prepared reduced graphene oxide/ α -Ni(OH)₂ composites, vapor grown carbon fiber (VGCF, Showa Denko K.K., Japan, specific area: 13 m²g⁻¹, aspect ratio: 67) as a conducting material and poly(vinylidene fluoride) (PVdF) as a binder were mixed in a weight ratio of 80:15:5 to yield a paste. N-methyl-2-pyrrolidone (NMP) was used as a solvent. The obtained paste was incorporated into nickel foam (1cm × 1cm). The mass of the active materials ranged from 2.0 to 3.0 mg. The prepared working electrodes were dried at room temperature for 1 day, and then under a vacuum at room temperature overnight.

Electrochemical measurements

Electrochemical studies were carried out by measurement of cyclic voltammetry (CV) and impedance of half cells using AUTOLAB (ECO CHEMIE, PGSTAT 100). A beaker-type three-electrode cell equipped with reduced graphene oxide/ α -Ni(OH)₂ composites on nickel foam as a working electrode, an Ag/AgCl electrode (Metrohm AG 9101 Herisau, 3 M KCl, 0.222 V vs. SHE at 25 °C) as a reference electrode, and a platinum plate (2 cm × 2 cm) as a counter electrode was used. Electrochemical impedance measurements were conducted for the working electrode in a frequency range of 100 kHz–0.01 Hz with ac perturbation of 10 mV. For all electrochemical characterizations, a test solution of 6 M KOH was used as an electrolyte solution. All tests were performed at room temperature. The specific capacitance was calculated by integrating the area under the CV curve to obtain the charge (Q) and then dividing by the mass of active materials (m), the scan rate (v) and the potential window ($\Delta V = V_a - V_c$) according to the following equation:

$$C = \frac{Q}{\Delta V} = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V) dV$$

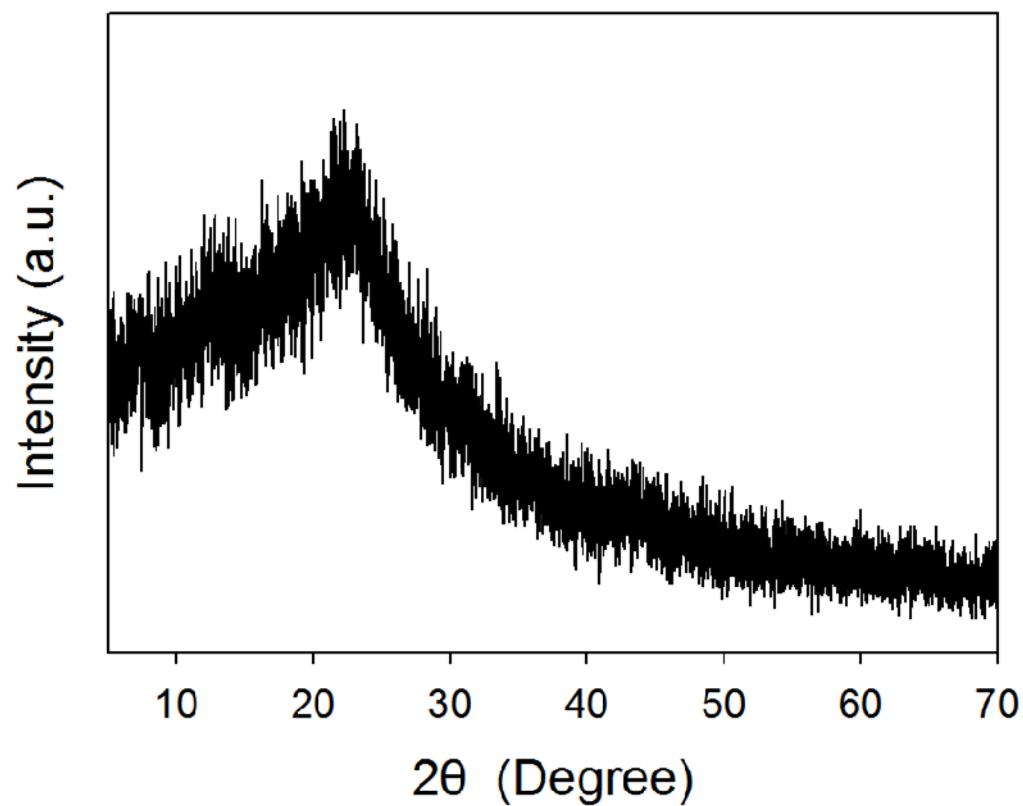


Fig. S1 XRD pattern of reduced graphene oxide (rGO).

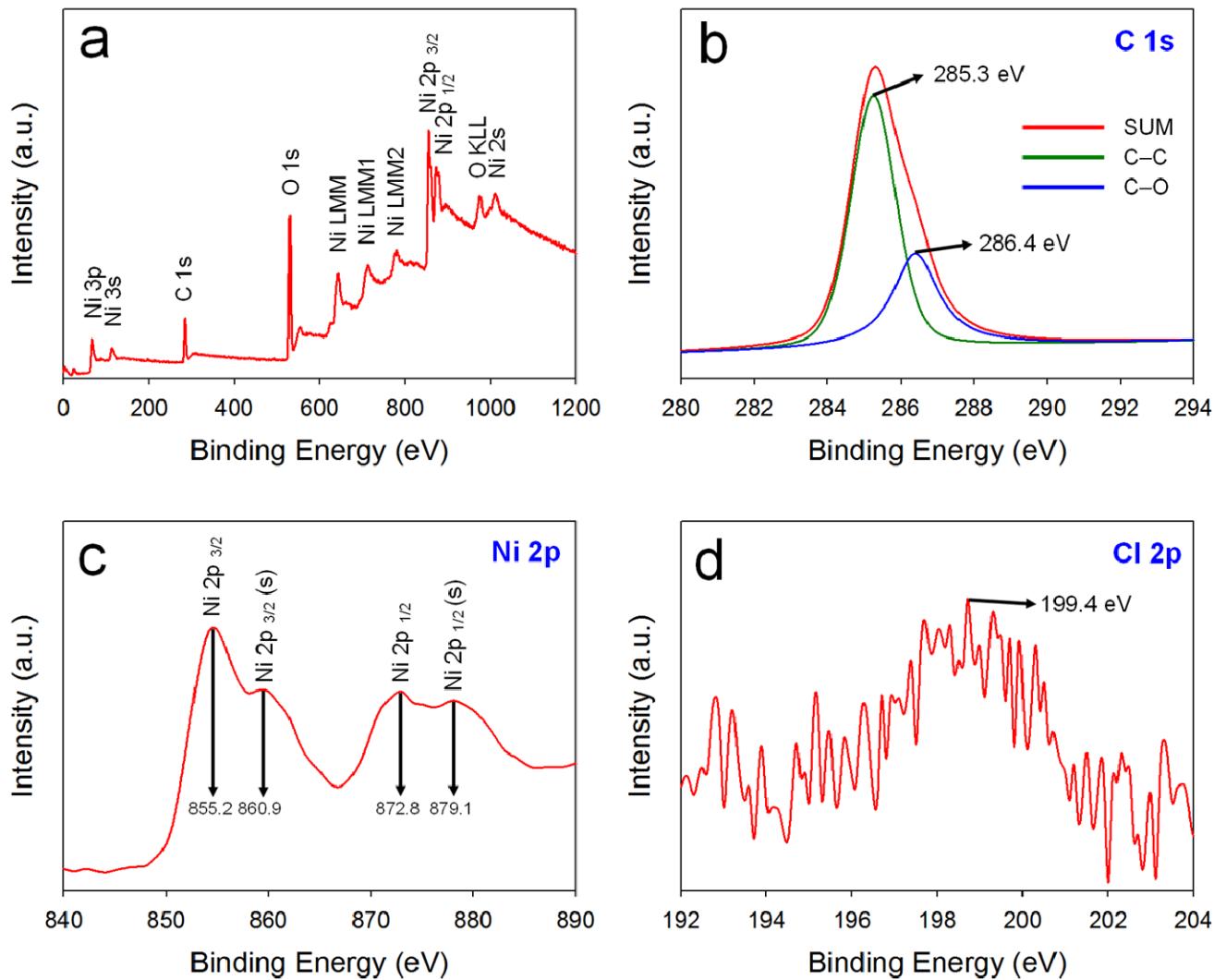


Fig. S2 XPS spectrum of GN20: (a) survey scan, (b) C 1s spectrum, (c) Ni 2p spectrum, and (d) Cl 2p spectrum.

Deconvolution of the C1s peak (Fig. S2b) of GN20 shows the presence of different oxygen containing functional groups of the non-oxygenated C at 285.3 eV and the carbon in C–O at 286.4 eV. A very weak Cl 2p peak (Fig. S2d) was observed at 199.4 eV, which can be explained by the fact that chloride ions of NiCl_2 were intercalated into the interlamellar space of $\alpha\text{-Ni(OH)}_2$, such as ethylene glycol and carbonate ions.

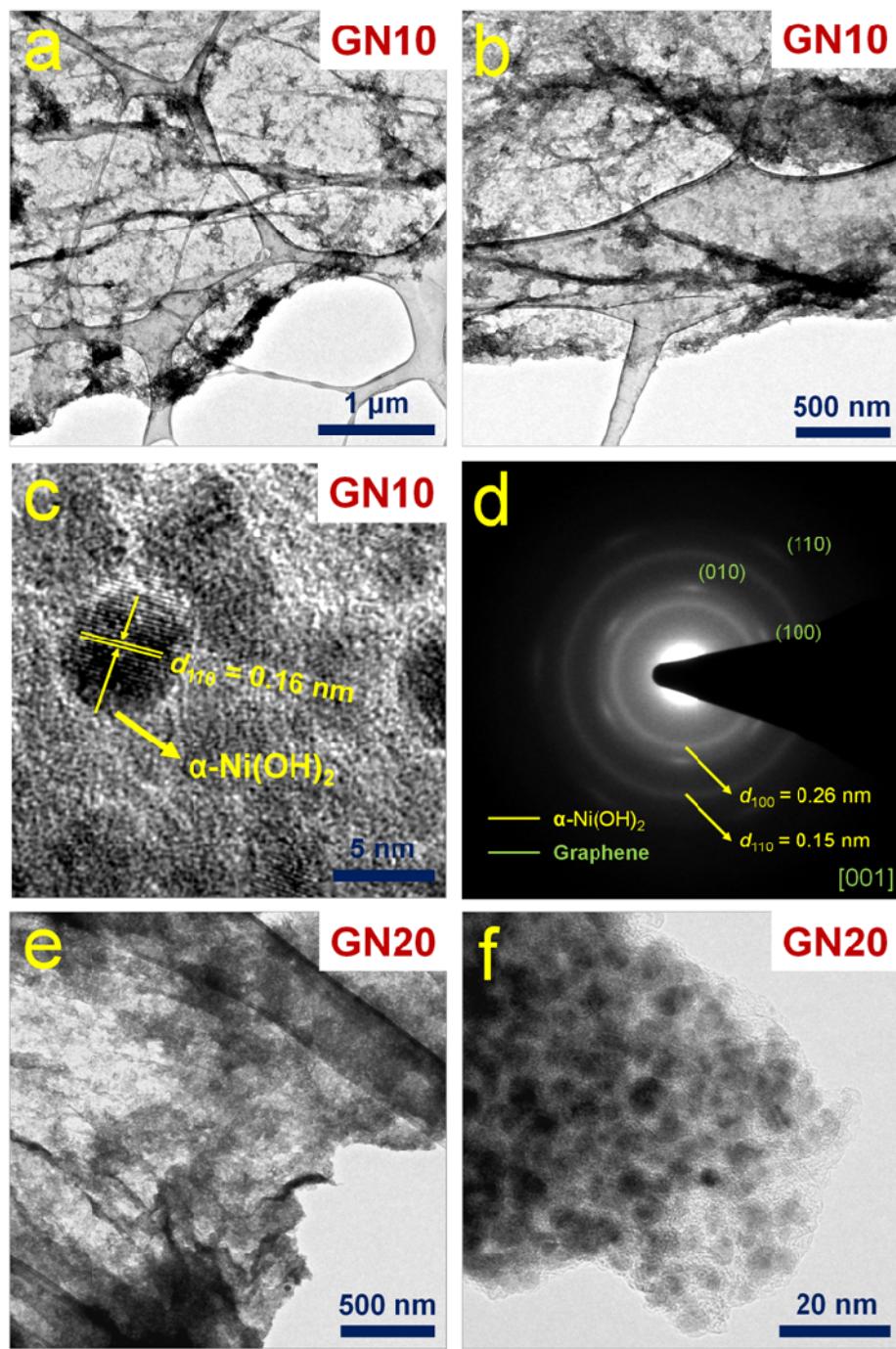


Fig. S3 (a–c) TEM images of GN10 at different magnifications, (d) SAED pattern of GN10 along the [001] direction, and (e–f) TEM images of GN20 at different magnifications.

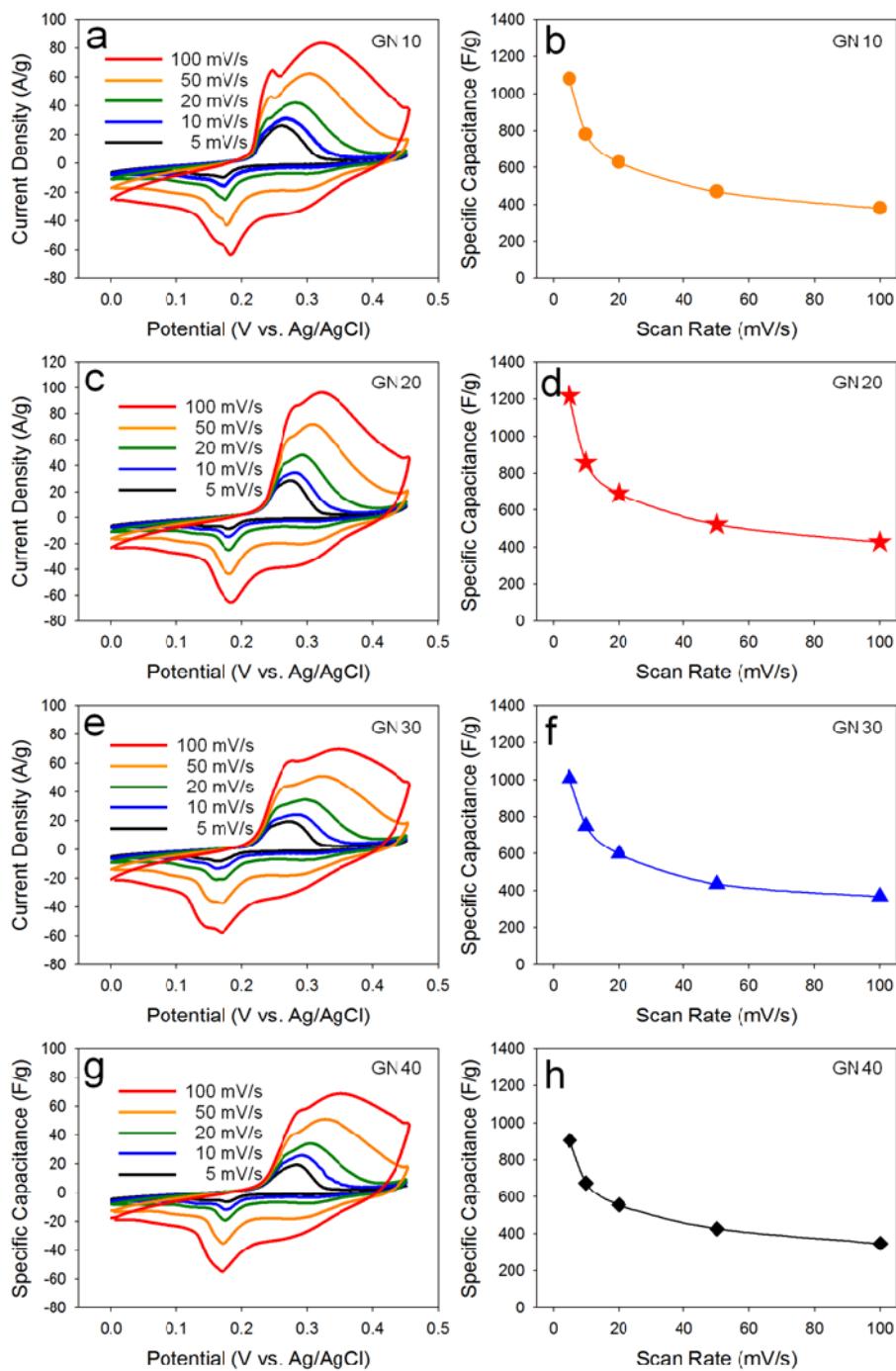


Fig. S4 (a,c,e,g) CV curves and (b,d,f,h) corresponding specific capacitance of the GN10, GN20, GN30, and GN40, respectively, at a function of scan rate.

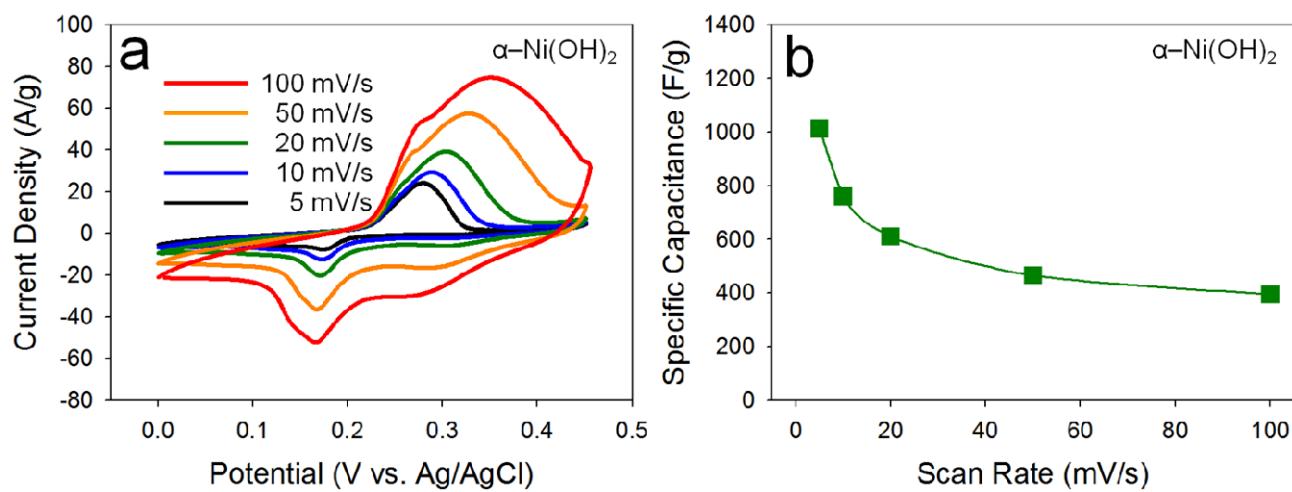


Fig. S5 (a) CV curves and (b) corresponding specific capacitance of $\alpha\text{-Ni(OH)}_2$ at a function of scan rate.

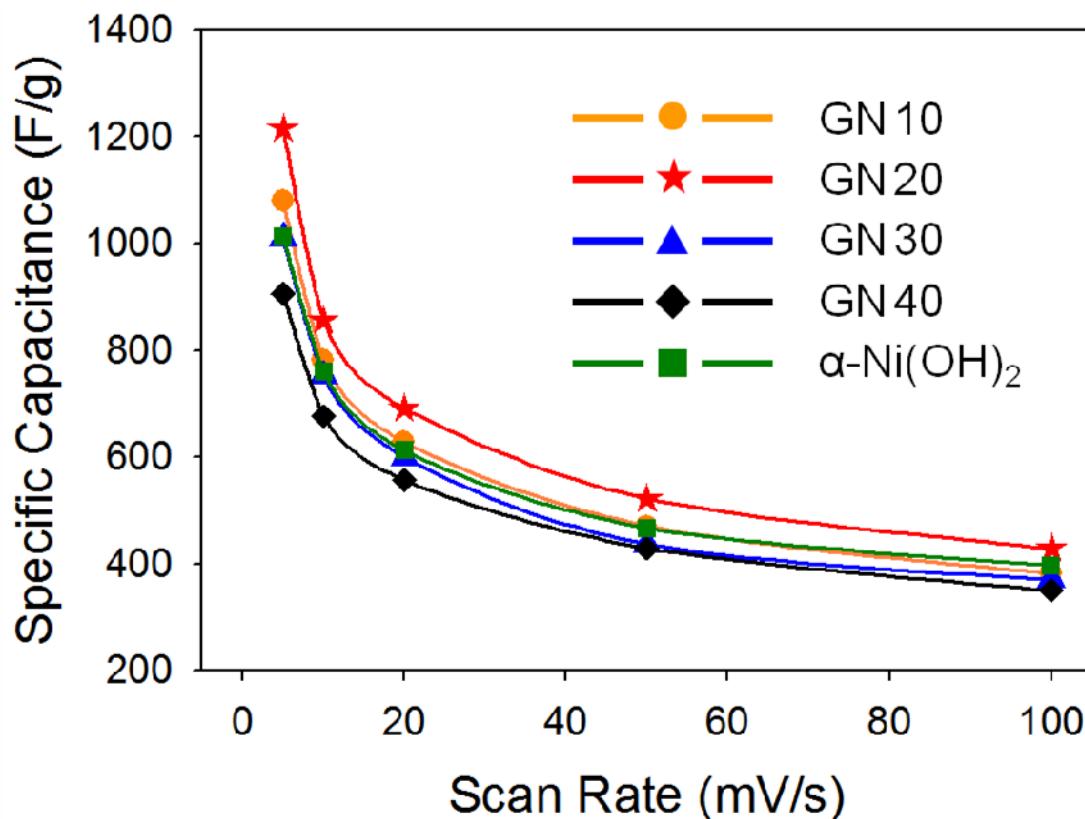


Fig. S6 Specific capacitance of GN10, GN20, GN30, GN40, and α -Ni(OH)₂ at a function of scan rate.

Table S1 Specific capacitance of GN10, GN20, GN30, GN40, and α -Ni(OH)₂.

	5 (mV/s)	10 (mV/s)	20 (mV/s)	50 (mV/s)	100 (mV/s)
GN10	1079 (F/g)	780 (F/g)	627 (F/g)	470 (F/g)	381 (F/g)
GN20	1215 (F/g)	855 (F/g)	690 (F/g)	521 (F/g)	428 (F/g)
GN30	1009 (F/g)	750 (F/g)	599 (F/g)	436 (F/g)	370 (F/g)
GN40	905 (F/g)	676 (F/g)	556 (F/g)	428 (F/g)	349 (F/g)
α -Ni(OH) ₂	1013 (F/g)	759 (F/g)	611 (F/g)	466 (F/g)	396 (F/g)

Specific capacitances (F/g) are calculated from CV curves.

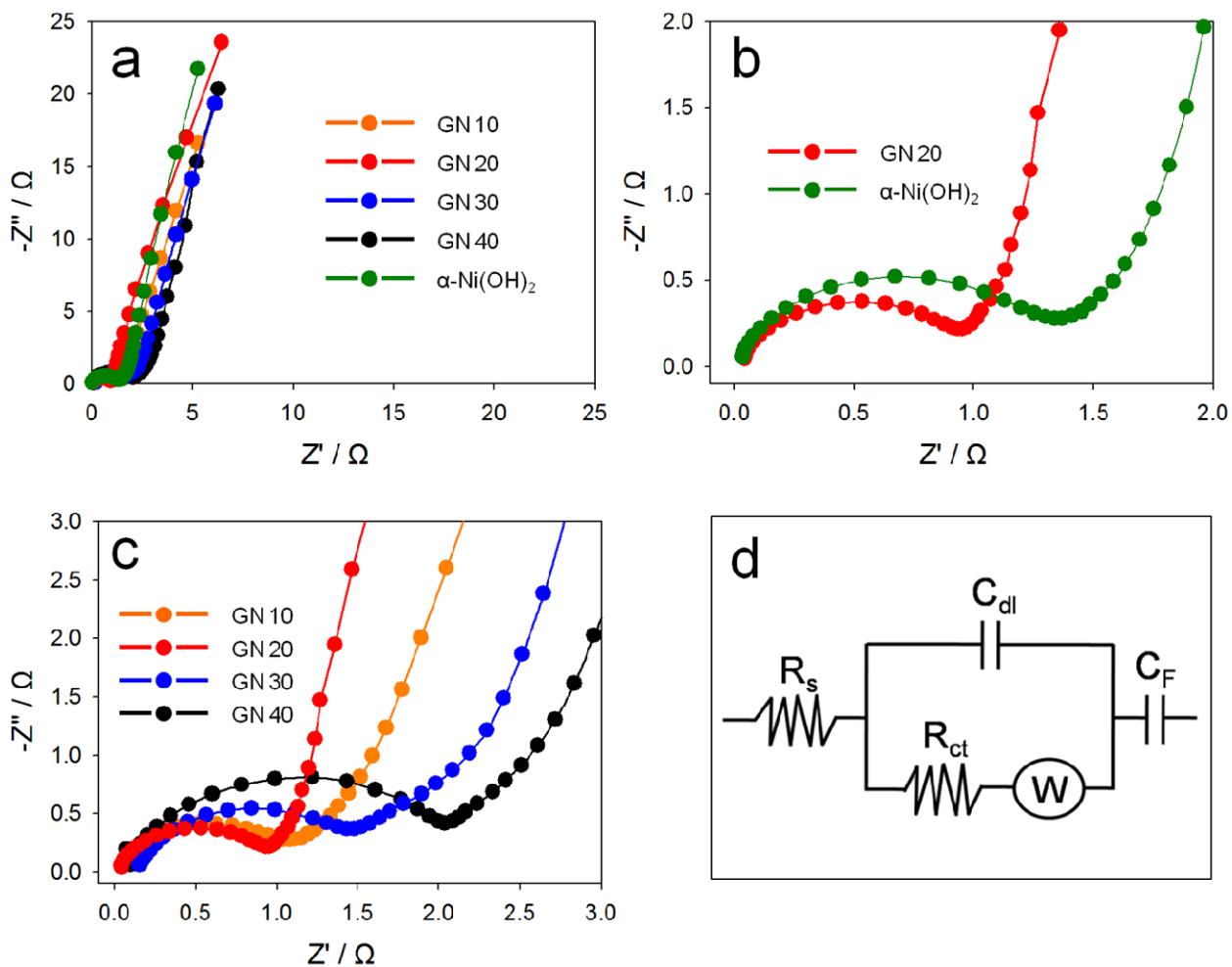


Fig. S7 (a) Nyquist plots of the rGO/α-Ni(OH)₂ composites and α-Ni(OH)₂, (b) an enlarged plot of the high-frequency region of GN20 and α-Ni(OH)₂, (c) an enlarged plot of the high-frequency region of the rGO/α-Ni(OH)₂ composites, and (d) the proposed equivalent circuit for the EIS spectra.

Fig. S7 shows the EIS spectra of the capacitive electrode used here at an open circuit voltage of 0.19 V (vs. Ag/AgCl). The equivalent circuit for the impedance analysis is shown in Fig. S7d, where R_s is the solution resistance of the electrochemical system, C_{dl} is a double-layer capacitor, C_F is a Faradaic pseudocapacitor, W is the Warburg impedance, and R_{ct} is the Faradaic interfacial charge transfer resistance.

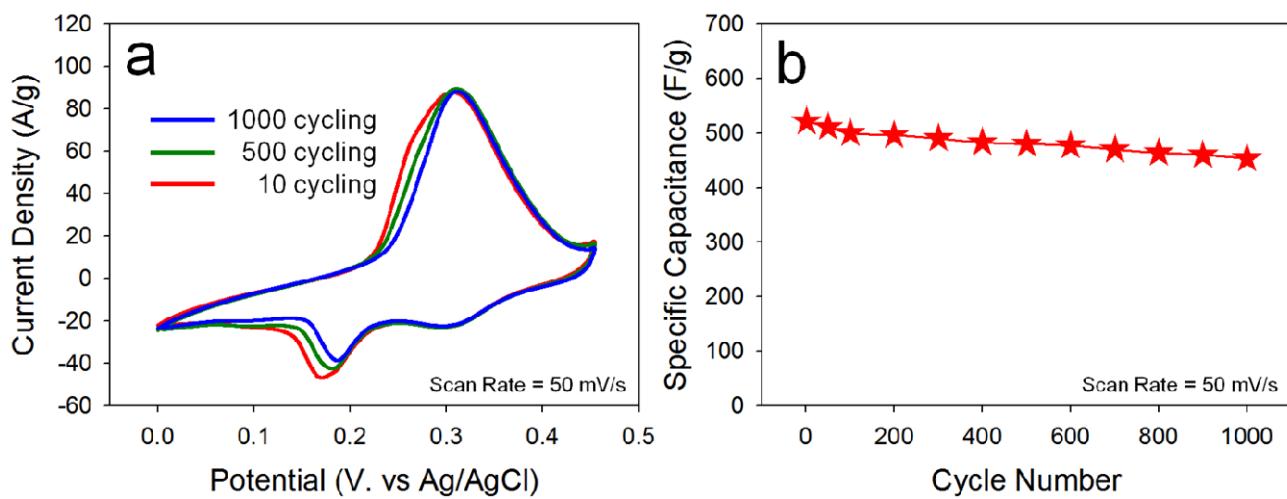


Fig. S8 Cycle test of GN20: (a) CV curves of 10 cycles to 1000 cycles at a 50 mV/s scan rate and (b) variation in the specific capacitance as a function of the cycle number at a 50 mV/s scan rate.

References

- 1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 2 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.