

Electronic Supplementary Information

Ni(OH)₂/CoO/reduced graphene oxide composites with excellent electrochemical properties

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Experimental details

S1. Synthesis of GO

All the chemicals were commercially available and used without further purification. Graphite oxide (GO) was prepared using the well-known Hummers method.¹ In a typical procedure, 1.5 g of graphite, 1.5 g of NaNO₃ and 90 mL of H₂SO₄ (98 wt%) were prepared and mixed into a solution. Then 9 g of KMnO₄ was slowly added to the solution, while keeping the mixture in an ice bath until it reached ~ 15 °C upon stirring for 90 min. The solution was then transferred into a bigger container and 300 mL of deionized water was added. After that the solution was moved from ice-water bath into water bath and kept at ~ 95 °C upon further stirring for 45 min. When the suspension cooled to ~ 40 °C, 5 mL of H₂O₂ (30 wt%) was slowly added. Then, the suspension was thoroughly washed using hydrochloric acid (15 wt%), deionized water, ethanol in sequence. Finally, the products were collected by vacuum freeze-drying.

S2. Synthesis of rGO based composites

Here, composites of Ni(OH)₂/CoO/rGO, Ni(OH)₂/rGO and Ni(OH)₂/CoO were synthesized through a one-step solvothermal route using ethylene glycol as a solvent. In a typical synthetic procedure, taking Ni(OH)₂/CoO/rGO as an example, 12 mg of GO was dissolved in 24 mL of ethylene glycol under sonicating for 1 h, and 156 mg of nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O), 312 mg of cobalt acetate tetrahydrate (Co(CH₃COO)₂·4H₂O) and 90 mL of ethylene glycol were added in a Teflon-lined autoclave (120 mL) with a stainless-steel shell and a mixture of them was stirred for 15 min. Then GO suspension was added, the mixture solution

was further stirred for 2 h. The resulted solution in the Teflon-lined autoclave was heated at 160 °C and kept this temperature for 6 h. After the autoclave was cooled to ambient temperature naturally, black sediment was washed by deionized water and ethanol. Products were collected by centrifugation at 8000 rpm for 7 min, and then dried in an oven at 60 °C for 10 h and about 45 mg powders were obtained. Notably, the washing step was repeated for at least four times to remove completely all the ethylene glycol. The reduction of graphite oxide to graphene and the formation of Ni(OH)₂/CoO composites on rGO occurred simultaneously. In our experiment, to evaluate effect of the relative quantity of the reactants on the Ni(OH)₂/CoO/rGO composites, three mass ratios of the reactants, i.e., GO : Ni(CH₃COO)₂·4H₂O : Co(CH₃COO)₂·4H₂O = 1 : 13 : 13, 1 : 13 : 26 and 1 : 13 : 39 were applied, in which the second mass ratio was used in the above description. The Ni(OH)₂/CoO and Ni(OH)₂/rGO composites were synthesized by the same procedure as described above, except that Co(CH₃COO)₂·4H₂O or GO was involved or not for them, respectively.

S3. Sample characterization

Samples were characterized by using powder XRD (Rigaku D/Max 2550, Cu Kr radiation), TEM (JEOL, JEM-2010F) equipped with an X-ray energy-dispersive spectrometer (EDS) and SEM (Hitachi S-4800). Fourier transforms infrared spectroscopy (FT-IR) was carried out on a FTIR-Raman spectrometer (Thermo Fisher) in KBr pellet at room temperature. Raman spectra were taken by a Micro-Raman Spectroscopy System (Renishaw inVia-Reflex) with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) spectra were conducted on an Axis Ultra DLD X-ray photoelectron spectroscopy (Kratos Co.). The nitrogen adsorption-desorption isotherms were measured by using an Automated Surface and Pore Size Analyzer (Autosorb-1 MP), and the specific surface area and mesopore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods.

S4. Electrochemical measurement

The electrochemical measurements were carried out using electrochemical workstation (Autolab PGSTAT302N potentiostat, Switzerland) with a three-electrode mode in a 1 M NaOH solution. Approximately 2.64 mg of Ni(OH)₂/CoO/rGO composites was deposited and compressed into a Ni foam support for electrochemical measurements in a three-electrode beaker cell with a Hg/HgO (in 1 M NaOH) reference electrode and 1 M NaOH aqueous electrolyte. For the electrochemical measurements, the as-prepared sample was mixed with carbon black and poly (vinylidifluoride) at a weight ratio of 80 : 15 : 5 and stirred for 24 h. The mixture was then pasted onto the Ni foam and dried at 120 °C for 4 h to remove the solvent. The obtained piece of Ni foam covered with sample was then used as a working electrode with 1 M NaOH as electrolyte. Platinum foil and Hg/HgO electrode were used as counter- and reference electrodes. Standard CV

curves were measured between -0.05 and 0.55 V.

The specific capacitance of the electrode were calculated from the CV curves according to the following equation, $C = Q/(\Delta V \cdot m)$, where C ($F \cdot g^{-1}$) is the specific capacitance, m (g) is the mass of $Ni(OH)_2/CoO/rGO$ on the electrode, Q (C) is an average charge during the charging and discharging process, and ΔV (V) is the potential window. The discharge specific capacitance was calculated from the discharge curves using the following formula, $C = I \cdot \Delta t/(\Delta V \cdot m)$, where I (A), m (g), Δt (s), and ΔV (V) are the discharge current, mass of the active materials (or mass of the total electrode materials), discharge time consumed in the potential range of ΔV and the potential windows, respectively.²

S5. Results

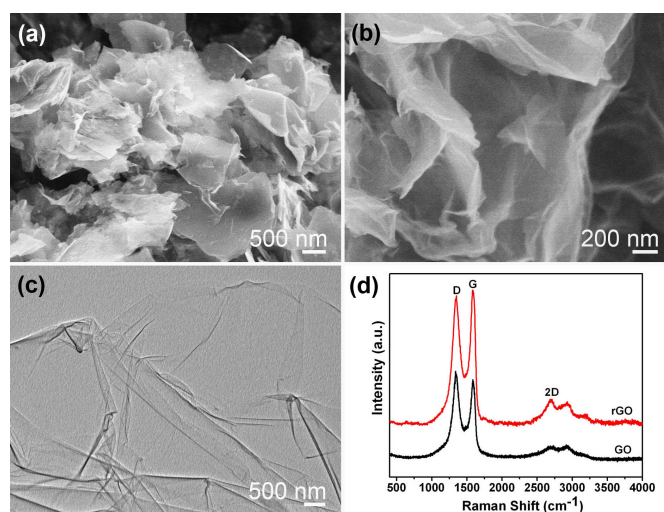


Fig. S1 SEM images of as-prepared GO (a) and rGO (b), TEM image of rGO (c), and Raman spectra of as-prepared GO and rGO (d). As prepared GO and rGO nanosheets appear like a flexible thin film with many wrinkles, and have a side length in a range of a few to dozens of microns. The Raman spectra display the G band at 1584 cm^{-1} and the D band at 1352 cm^{-1} . The 2D band of the graphene (oxide) sheets is centered at 2693 cm^{-1} with a shoulder at a high wave number, indicating the GO and rGO were prepared.³

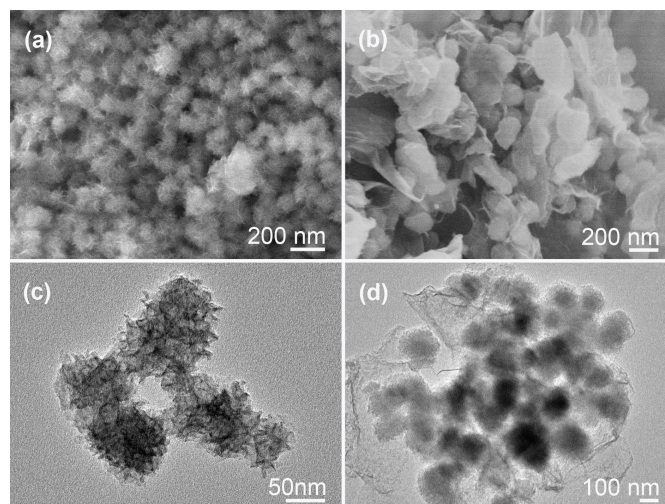


Fig. S2 (a-d) SEM and TEM images of as-prepared $\text{Ni}(\text{OH})_2/\text{CoO}$ and $\text{Ni}(\text{OH})_2/\text{rGO}$ composites, respectively.

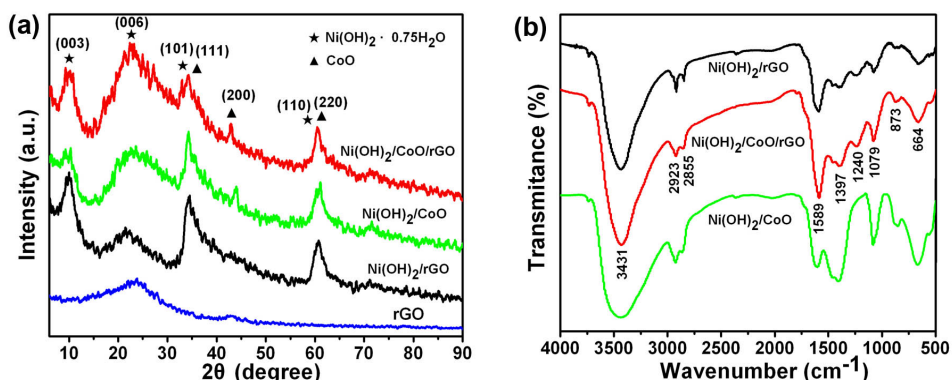


Fig. S3 (a) XRD patterns of rGO and as-prepared $\text{Ni}(\text{OH})_2/\text{CoO}/\text{rGO}$, $\text{Ni}(\text{OH})_2/\text{rGO}$ and $\text{Ni}(\text{OH})_2/\text{CoO}$ composites, (b) FT-IR spectra of as-prepared $\text{Ni}(\text{OH})_2/\text{CoO}/\text{rGO}$, $\text{Ni}(\text{OH})_2/\text{rGO}$ and $\text{Ni}(\text{OH})_2/\text{CoO}$ composites. The main peaks of $\text{Ni}(\text{OH})_2/\text{CoO}$ composites are in good agreement with the standard powder diffraction patterns of $\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$ (JCPDS card no.: 38-0715) and CoO (JCPDS card no.: 65-2902). In the patterns from the rGO based composites of $\text{Ni}(\text{OH})_2/\text{CoO}/\text{rGO}$ and $\text{Ni}(\text{OH})_2/\text{rGO}$, a relatively wide peak at $\sim 24.5^\circ$ is due to the (002) plane of rGO,⁴ a few broad diffraction peaks at $\sim 10.6^\circ$, $\sim 22.7^\circ$ and $\sim 34.1^\circ$ correspond to the (003), (006) and (101) lattice planes of $\alpha\text{-Ni}(\text{OH})_2$,⁵ respectively, while two peaks at $\sim 42.8^\circ$ and $\sim 60.9^\circ$ are related to the (200) and (220) lattice planes of CoO ,⁶ respectively. These results indicate that rGO based composites of $\text{Ni}(\text{OH})_2/\text{CoO}/\text{rGO}$ and $\text{Ni}(\text{OH})_2/\text{rGO}$ were successfully synthesized. FT-IR spectra were used to demonstrate the functional groups within the as-prepared composites' surface. In the cases of rGO based composites ($\text{Ni}(\text{OH})_2/\text{CoO}/\text{rGO}$ and $\text{Ni}(\text{OH})_2/\text{rGO}$), a broad band at 3431 cm^{-1} corresponds to vibration of hydroxyl groups from Ni-OH and intercalated water, while peaks around at 2923 and 2855 cm^{-1} are attributed to the -C-H vibration mode of -CH₂;⁷ a strong peak at 1589 cm^{-1} is due to the skeletal vibration of rGO, and the absorption at 1397 cm^{-1} may be attributed to tertiary C-OH groups;⁸ peaks at 1240 and 1079 cm^{-1} are assigned to the epoxy C-O stretch,⁹ and bands at 664 and 873 cm^{-1} correspond to the presence of $\delta_{\text{O-H}}$ and carbonate ions in $\text{Ni}(\text{OH})_2$ layers, respectively.¹⁰ Comparatively, in the case of $\text{Ni}(\text{OH})_2/\text{CoO}$ composites, the peaks at ~ 1240 , 1397 and 1589 cm^{-1} , which are originated from rGO (i.e., epoxy C-O, tertiary C-OH and skeletal vibration from rGO, respectively), are absent, and only other peaks (at 3431 , 2923 , 2855 , 664 and 873 cm^{-1}) are present, which are attributed to Ni-OH, intercalated water, -CH₂, $\delta_{\text{O-H}}$ and carbonate ions in $\text{Ni}(\text{OH})_2$ layers, respectively.

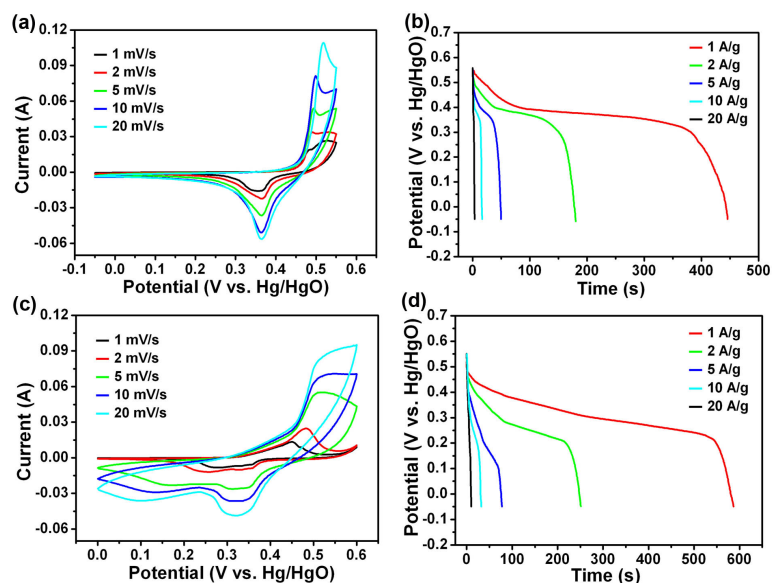


Fig. S4 (a) CV curves and (b) galvanostatic discharge curves of as-prepared $\text{Ni(OH)}_2/\text{rGO}$, (c) CV curves and (d) galvanostatic discharge curves of as-prepared $\text{Ni(OH)}_2/\text{CoO}$.

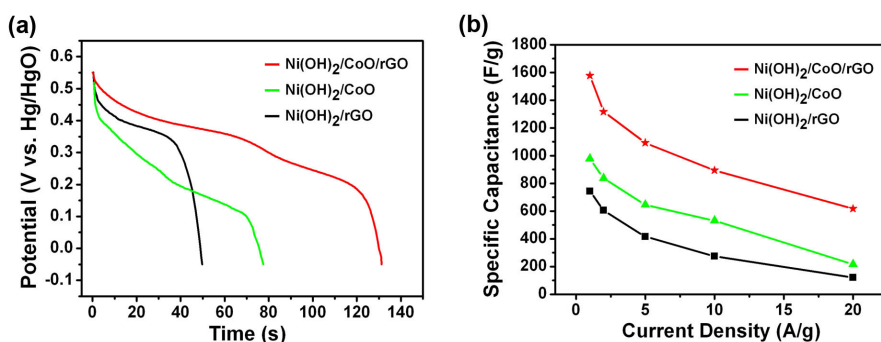


Fig. S5 Electrochemical characterizations of as-prepared $\text{Ni(OH)}_2/\text{rGO}$, $\text{Ni(OH)}_2/\text{CoO}$ and $\text{Ni(OH)}_2/\text{CoO}/\text{rGO}$ composites: (a) galvanostatic discharge curves at a current density of $5 \text{ A} \cdot \text{g}^{-1}$, (b) specific capacitance as a function of the current density. It is obviously observed that the specific capacitance of the as-prepared composites decreases in the order of $\text{Ni(OH)}_2/\text{CoO}/\text{rGO} > \text{Ni(OH)}_2/\text{CoO} > \text{Ni(OH)}_2/\text{rGO}$, which can be comparable to that calculated from the CV curves. A specific capacitance decreases with the current density increasing, as suggested by the CV studies.

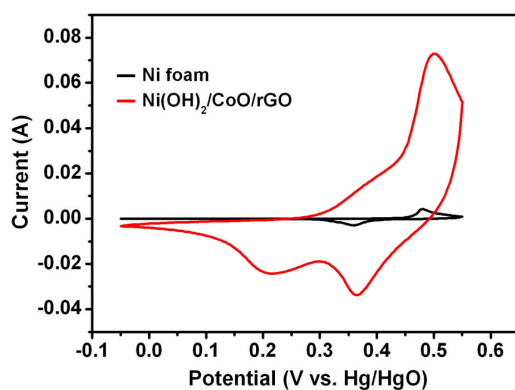


Fig. S6 CV curves of the Ni foam without active material and Ni(OH)₂/CoO/rGO electrode at the scan rate of 5 mV·s⁻¹. The mass of the active material of the Ni(OH)₂/CoO, Ni(OH)₂/rGO or Ni(OH)₂/CoO/rGO is 2.5 ~ 4.5 mg, which covers an area of 1 cm² on the Ni foam. Considering this fact, we had a blank CV scan on the Ni foam with an equal area of 1 cm², i.e., ~ 43.6 mg. The Ni foam without active material shows a redox process, which is attributed to the reversible reaction of Ni(II)/Ni(III) occurred on the Ni surface. So long as the contribution of the Ni foam is excluded, a calibrated specific capacitance value of the active materials can be obtained.¹¹ The specific capacitance of the Ni foam was calculated from the CV curves according to the following equation, $C = Q/(\Delta V \cdot m)$, where C (F·g⁻¹) is the specific capacitance, m (g) is the mass of Ni foam without active material, Q (C) is an average charge during the charging and discharging process, and ΔV (V) is the potential window.² The specific capacitance of this Ni foam calculated from CV curves is 4.3, 4.2, 4.0, 3.4 and 2.7 F·g⁻¹ at 1, 2, 5, 10 and 20 mV·s⁻¹, respectively. So, the specific capacitance of as-prepared Ni(OH)₂/CoO/rGO electrode materials have been correspondingly calibrated to be 1510, 1316, 1056, 831 and 649 F·g⁻¹ at 1, 2, 5, 10 and 20 mV·s⁻¹, respectively. With the same method, the specific capacitance of Ni(OH)₂/rGO and Ni(OH)₂/CoO electrode materials also have been correspondingly calibrated.

Table S1. Specific capacitance of as-prepared composites

As-prepared composites	Specific capacitances (F·g ⁻¹) calculated from CV curves.				
	1 mV/s	2 mV/s	5 mV/s	10 mV/s	20 mV/s
Ni(OH) ₂ /CoO/rGO (1 : 13 : 13)	1292	1045	767	617	299
Ni(OH) ₂ /CoO/rGO (1 : 13 : 26)	1510	1316	1056	831	649
Ni(OH) ₂ /CoO/rGO (1 : 13 : 39)	972	863	750	563	342
Ni(OH) ₂ /rGO	828	581	386	263	144
Ni(OH) ₂ /CoO	1055	848	706	510	323

Note: 1 : 13 : 13, 1 : 13 : 26 and 1 : 13 : 39 represent for three mass ratios of the reactants (GO : Ni(CH₃COO)₂·4H₂O : Co(CH₃COO)₂·4H₂O) as described in the experimental details.

Table S2: Surface area and average pore size distribution calculated by BET and BJH methods

Samples	Surface area (m ² /g)	Average pore size distribution (Å)
Ni(OH) ₂ /CoO/rGO	172.17	18.94
Ni(OH) ₂ /rGO	183.69	72.45
Ni(OH) ₂ /CoO	55.97	19.67

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