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Supporting Information

Stepwise Interfacial Assemblied Nickel-cobalt-hydroxide Hetero-oriented Nanocrystalline Walls on Reduced graphene oxide/nickel foams: An Adjustable Interface Design for Capacitive Charge storage

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I Experimental Section

Preparation of rGO/nickel foams: All the chemicals were directly used after purchase without further purification. GO was prepared using Hummer's method with a little modification.[S1,S2] The graphite powder (5 g, 500 mesh) was placed in concentrated H_2SO_4 (115 mL) at 0 °C. $KMnO_4$ (15 g) was added while keeping the temperature of the mixture below 20 °C. The mixture was stirred at 35 °C for 30 min. Then deionized water (230 mL) was added and the mixture was stirred at 90 °C for 15 min. Seventy milliliters of deionized water was then added to terminate the reaction. Subsequently, H_2O_2 (30%, w/w,10 mL) was added, and the color of the mixture changed to bright yellow. The mixture was centrifuged and washed with HCl (10%, w/w, 125 mL) to remove residual metal ions. The precipitate was then washed with deionized water until the solution became neutral and diluted to make a GO aqueous dispersion (5.0 mg/mL). A GO dispersion (50 mL) containing sodium isoascorbate (1g) was dispersed by stirring for 30 min. Nickel foams (40×40×0.25 mm, PPI: 110) were rolled to a thickness of 0.25 mm before use. The nickel foams were immersed in a 6 M HCl solution for 10 min and soaked in a 0.02 M $NiCl_2$ to get rid of the possible surface oxide layer before they were used. A piece of nickel foams was dipped into the dispersion and immediately removed. After drying in an electrical oven at 120 °C for 20 min, the dip-dry process was repeated one time to increase the loading on the nickel foam. The nickel foam was rinsed with deionized water and ethanol to remove residual ions.

Self-assembly of NCH nanoscale building blocks on the rGO /nickel foam: $NiCl_2$ and $CoCl_2$ were dispersed in 50 mL deionized water for a total of 0.2 M of metal cations (molar ratios: 0:1, 1:2, 1:1, 2:1), 1.9 g of NaOH in 50 ml ethanol was slowly added. The mixtures were digested for 0.5 h with stirring. The prepared rGO/nickel foams were dipped into the suspensions and immediately removed. After drying in an electrical oven at 120 °C for 10 min, the dip-dry process could be repeated to increase the loading on the nickel foam. The NCH/rGO/nickel foams were rinsed with deionized water and ethanol to remove residual ions.

Materials Characterization: The crystallographic structures of the materials were determined by a powder XRD system (Rigaku TTR-III) equipped with Cu K_α radiation (λ = 0.15406 nm); The microstructure of the samples was investigated by SEM-EDS (JEOL JSM-6480A microscope), and TEM (Philips CM 200 FEG, 200 kV); The absorption spectrum was tested by a Fourier transform infrared spectrometer (FTIR spectra; NiCOLET 5DX).

Electrochemical Measurements: NCH /rGO/nickel foams were used as working electrodes (1 cm X 1.5 cm, projected area of 1 cm X 1 cm). Electrochemical measurement was carried out on a CHI 760B electrochemistry workstation. Measurements were studied on a three-electrode system (consisting of a working electrode, a platinum foil (1 cm X 1 cm) counter electrode, a SCE reference electrode, and 2 M KOH aqueous solution as electrolyte).

Calculations: For cyclic volammograms (CV), capacitance and specific capacitance (F cm^{-2}) are calculated in the three-electrode configuration using the formula:

$$C=I/v \qquad (1)$$

$$C_s=\int IdV/(2vA\Delta V) \qquad (2)$$

where I (A) is the response current, v is the scan rate (V s^{-1}), ΔV is the applied potential region (V), A refers to the area (cm^2) of the electrode, and the integration is the area of the cyclic volammograms.

For galvanostatic charge-discharge (GCD) curves, capacitance, specific capacitance (F cm^{-2}), specific energy (Wh kg^{-1}) and specific power (KW kg^{-1}) are calculated in the three-electrode configuration using the formula:

$$C=\mathrm{It}/\Delta V \qquad (3)$$

$$C_s=\mathrm{C}/A \qquad (4)$$

$$E_m=\mathrm{C}_{\Delta}V^2/(7200m) \qquad (5)$$

$$P_m={}_{\Delta}V^2/(4000mR) \qquad (6)$$

where I (A) is the discharge current, t is the discharge time (s), ΔV is the applied potential region (V), A refers to the area (cm^2) of the electrode, m (g) is the mass of the NCH active materials or the electrodes, and R ($=V_{drop}/2I$, Ω) is the internal resistance of the device that is estimated from the voltage drop (V_{drop}, V) at the beginning of the discharge curve.

Ⅱ Detailed analysis about the rGO/nickel foams

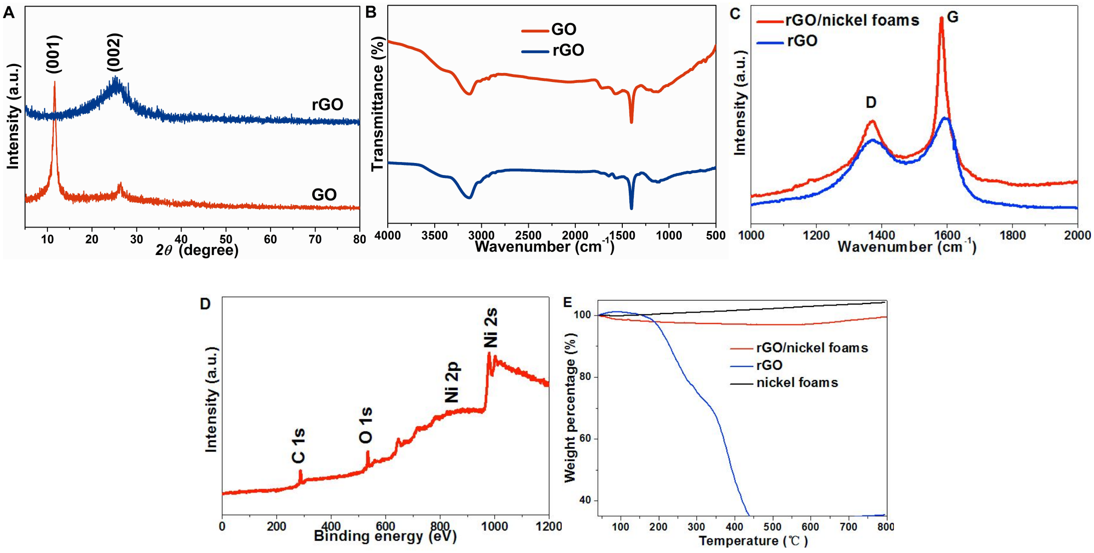

Figure S1. XRD (A) , FTIR analysis (B) of GO and rGO in the dip-dry process. (C) Roman spectra of rGO and rGO/nickel foams. (D) XPS of rGO/nickel foams. (E) TG of rGO, nickel foams and rGO/nickel foams

The differences in D band (structural defects or partially disordered structures of graphitic domains) and G band (related to graphitic carbon) [S3] imply that nickel foams are more likely to be wrapped homogenously by rGO than disordered rGO structures. XPS Surface atomic concentration chould be caculated from XPS. The results are O 1s 71.05%, O 2s 27.12%, Ni 2p 1.82%. It can be inferred that nickel foams should be wrapped homogenously by rGO. TG also shows that rGO coatings could prevent surface oxidation of nickel foams.

Ⅲ Selectively anchored NCH at the rGO coatings

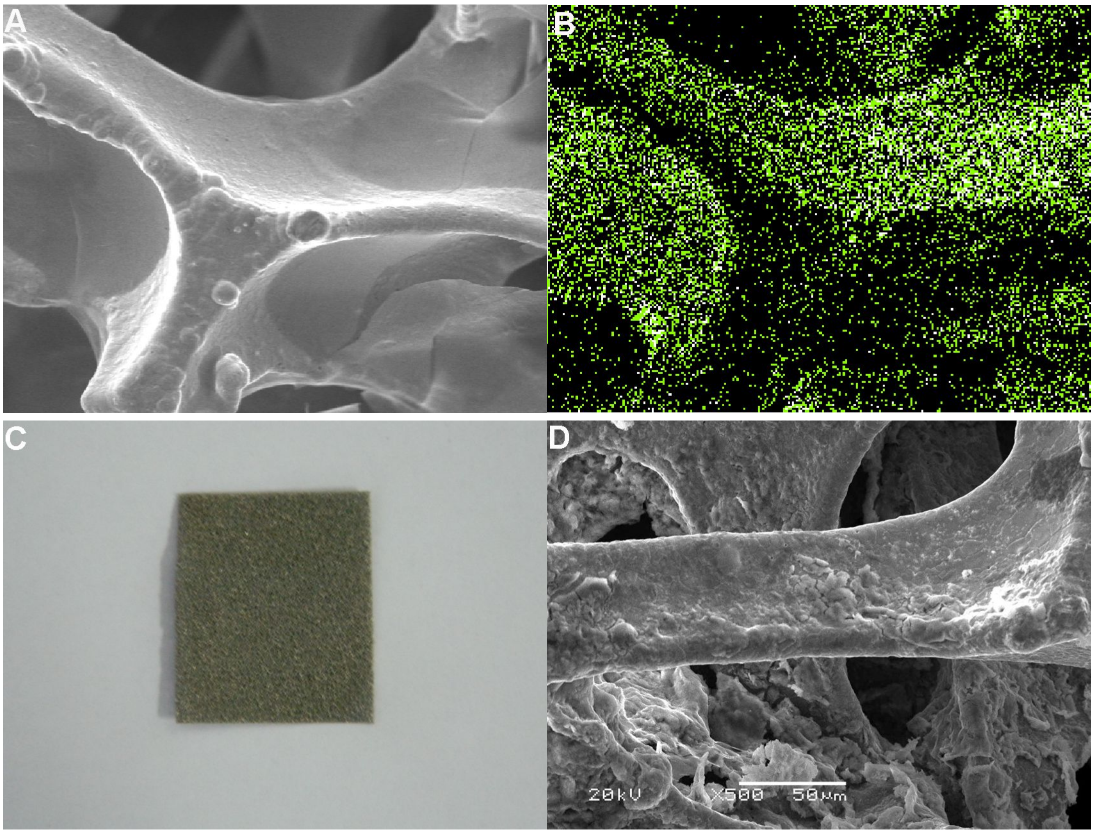

Figure S2. (A) SEM images of rGO/nickel foams and (B) corresponding element mapping image of C. (C) Photograph of the NCH/nickel foams with Ni-content in a molar fraction. Of 0.67 (dipping number:4). (D) SEM image of the NCH//nickel foams.

EDS implies that nickel foams could be uniformly wrapped by rGO. It seems that the self-assemblied hetero-accumulated nanocrystalline walls are more disordered on the NF than rGO-wrapped. NCH tends to wrap the rGO/nickel foams, but it adhere to the nickel foams loosely and unevenly. NCH is more likely to ahchored on rGO than nickel foams.

Ⅳ More detailed electrochemical analysis

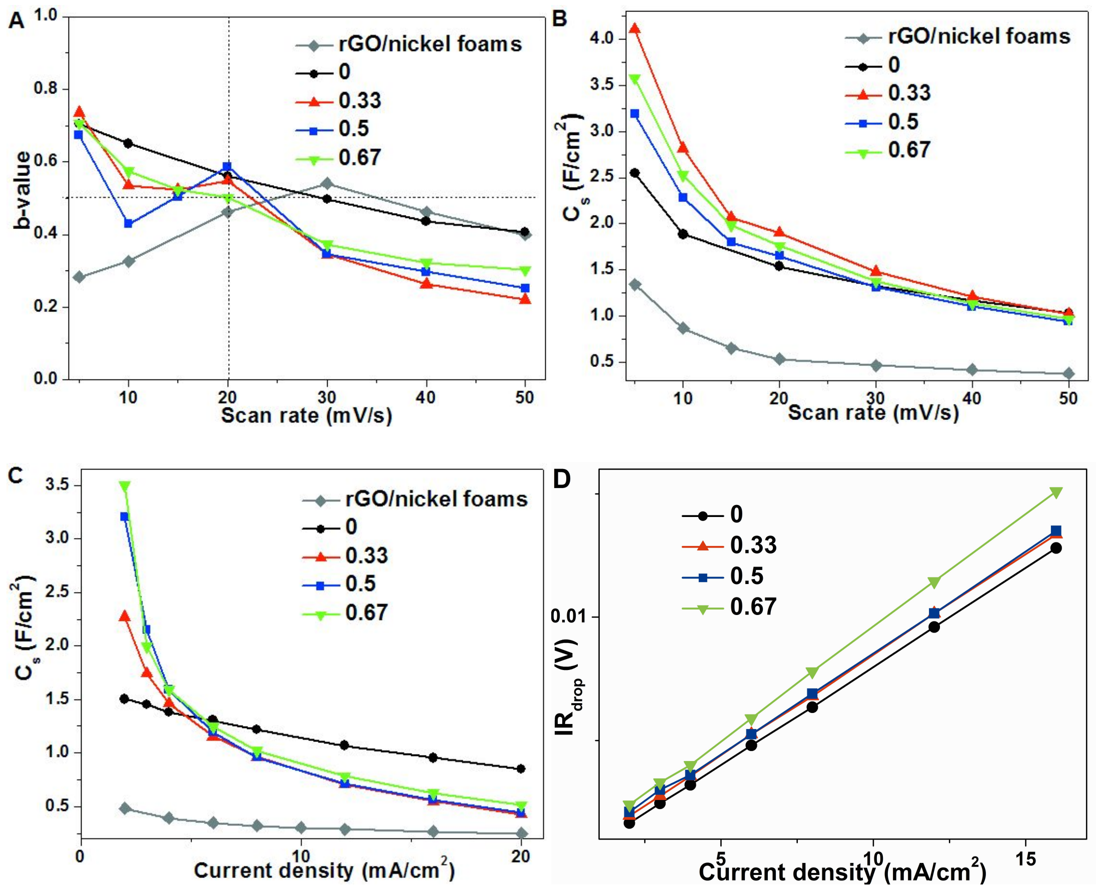

Figure S3. (A) *b*-value from 5 to 50 mV/s. (B) Specific capacitance (F cm^{-2}) versus scan rate. (C) Specific capacitance (F cm^{-2}) at different current densities (mA cm^{-2}). (D) Voltage drop associated with the electrode internal resistance (IR loss) versus discharge current density.

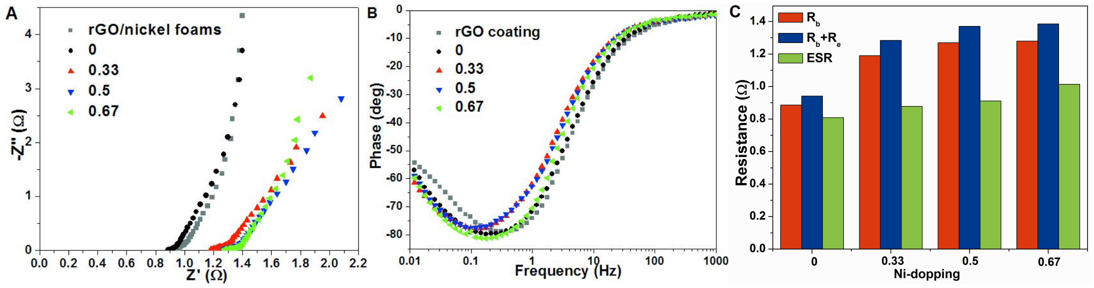

Figure S4 (A,B) Electrochemical impedance spectra (EIS) for different Ni-content in a molar fraction. (C) Re (interface resistance between electrolyte and electrode, calculated by EIS), Rb+Re (interface and charge-transfer resistance, calculated by EIS), ESR (equivalent series resistance, calculated by discharge curves) with Ni-dopping.

Ⅴ Role of rGO in the composite electrodes

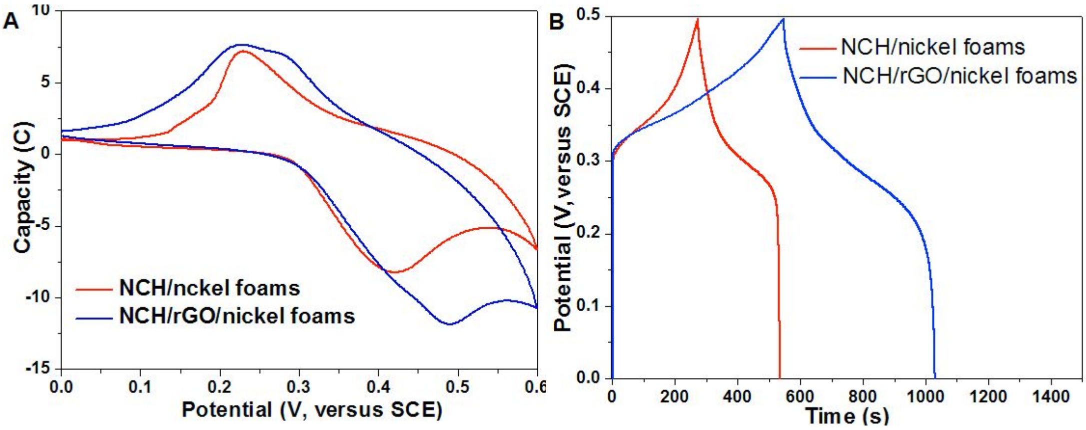

Figure S5. (A) Cyclic volammograms for 0.67 (Ni-content in molar fraction, dipping number:4) at a scan rate of 5 mV s^{-1}. (B) Charge and discharge curves for NCH/nickel foams and NCH/rGO nickel foams at a current density of 6 mA cm^{-2}.

From the SEM images, we could konw that NCH adhere to nickel foams and rGO differently. Although it seems that rGO doesn’t contribute to the specific capacitance directly and obviously, CV and GCD show the difference whether nickel foams are wrapped by rGO or not. Perhaps, it’s better to say that rGO acts as a bind-like additive to improve the transport.

Ⅵ Different C_s calculated with different equations

By definition, capacitance could be calculated using the formula:

$$C=U/Q \qquad (7)$$

For CV, v ($\mathrm{d}E/\mathrm{d}t$) is constant, so Equation (1) (transient) and (2) (average) could be used. But for GCD, I is constant, so Equation (4) (average) could be used. It is claerly that Equation (2) and (4) are calculated at different operational states. Perhaps, it is better to say that GCD is more close to an actual device. However, CV tested before GCD often gives more information for the process. C_s based on Equation (2) could help us learn about the process better. It's not an efficacious evaluation, but a meaningful parameter to supplement.

Ⅶ SEM images after the cycling

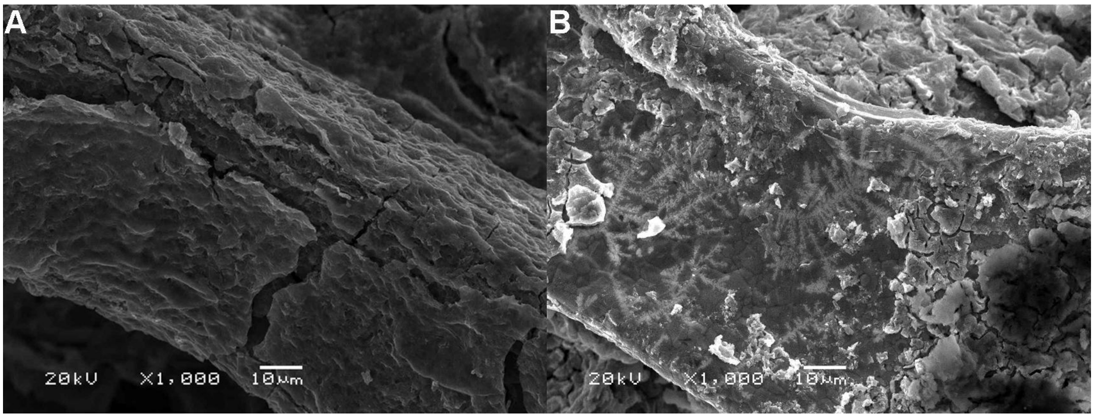

Figure S6 SEM images of the electrodes with Ni-content in a molar fraction (A:0; B:0.67) after the cucling.

Ⅷ Hope for the optimal performance

The cycling performance of the NCH sample with a Ni molar fraction of 0 and 0.67 has been tested. But for a Ni molar fraction of 0.5, both the electrochemical performance and the “dip-drp” process indicate it’s the worst one. So the cycling performance is not very meaningful.

How about the sample with a Ni molar fraction of 0.33? In fact, we arranged it not to be tested. The challenges for our “dip-dry” process have centered on the following two points: (1) Better cycling performance (higher capacitance retention after cycling) (2) Increased resistance with a large mass loading of active materials. $Co_{0.67}Ni_{0.33}(OH)_2$ could be a precursor for spinel $NiCo_2O_4$, which possesses much better electrical conductivity and higher electrochemical activity than nickel oxides or cobalt oxides precursor.[S3] Therefore, we expect it could overcome the difficulty. As our reviewers have found the clues, it’s necessary for us to point out that our hope for the optimmal performance is spinel $NiCo_2O_4$.

[S1] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.

[S2] X. Wang, H. Bai, G. Shi, *J. Am. Chem. Soc.* **2011**, 133, 6338.

[S3] W. Chen, S. Li, C. Chen and L. Yan, *Adv. Mater.*, **2011**, 23, 5679-5683.

[S4] C. Z. Yuan, J. Y. Li, L. R. Hou, X. G. Zhang, L. F. Shen and X. W. Lou, *Adv. Funct. Mater.*, 2012, **22**, 4592-4597.