Supporting Information for
Layered Assembly of Graphene Oxide and Layered Double Hydroxide Nanosheets as Electrode Materials for Supercapacitor

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Materials and equipments

60 wt% water suspension of polytetrafluoroethylene was purchased from Aadams Beta. Other chemicals used in this work were purchased from Sigma-Aldrich. Ni foam (100 ppi, 95 % porosity, 1.8±0.1 mm thick) was purchased from Kunshan Bitaixiang Electronics., Ltd. SEM was measured on a Quanta 400 FEG field-emission scanning electron microscope. TEM was measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. AFM was imaged on a dimension 3100 atomic force microscope. XRD was collected on a X'Pert-Pro MPD. XPS was conducted on a ESCALAB 250 (Thermofisher scientific, Inc).

1. Synthesis and Characterizations of Co-Al Layered Double Hydroxide Nanosheets (Co-Al LDH-NS)

1) Preparation of Co-Al layered double hydroxide (Co-Al LDH)

Co-Al LDH were prepared using Sasaki's method.[1] Briefly, $CoCl_26H_2O$, $AlCl_36H_2O$, and urea were dissolved in 1 L of Milli-Q water to give the final concentrations of 10, 5, and 35 mM, respectively. Then, the mixed solution was heated at reflux temperature under continuous magnetic stirring for 2 days. The resulting pink, solid product was filtered, washed with, and finally air-dried at room temperature. SEM image of Co-Al LDH shows uniform and thin hexagonal platelets (Figure S1a). XRD pattern (Figure S1b) shows strong diffraction peaks. It suggests that the Co-Al LDH was highly crystallized and no peaks of impurities were discerned.

2) Preparation of Co-Al LDH-NS

1.0 g of the above obtained Co-Al LDH was dispersed into 1 L of an aqueous solution containing 1 M NaCl and 3.3 mM HCl. The vessel was sealed after purging with nitrogen gas, and then shaken for 12 h at ambient temperature. Through this process, NaCl-HCl exchanged Co-Al LDH was obtained. The exchanged product was filtered, washed with Milli-Q water and anhydrous ethanol several times. The exchanged product (0.5 g) was mixed with 500 ml of formamide in a conical beaker, which was tightly capped after purging with nitrogen gas. Then, the mixture was agitated vigorously in a mechanical shaker at a speed of 160 rpm for 2 days. To remove the unexfoliated parts, the resulting pink, translucent colloidal suspension was further treated by centrifugation at 2000 rpm for 10 min. After centrifugation, a pink, transparent solution (Co-Al LDH-NS) was obtained. The Co-Al LDH-NS suspension was very stable as shown in Figure 1b.

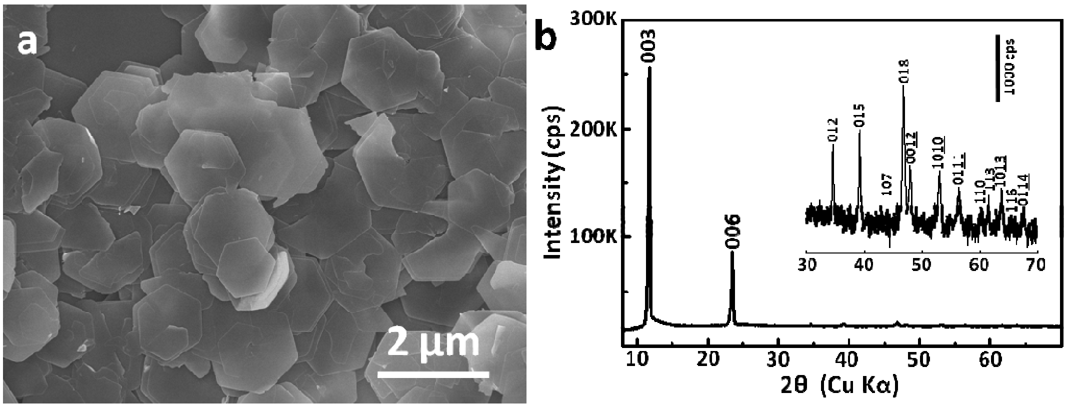

Figure S1 SEM image (a) and XRD pattern (b) of Co-Al LDH sample. Enlarge view of the pattern in high angles (Inset in b).

2. Synthesis and Characterizations of Graphene Oxide

Graphenen oxide (GO) was prepared using Hummer's method with a little modified by Zhang.[2-4] Commercial graphite was preoxidized according to the following method: Native graphite flake (0.5 g) was mixed with concentrated H_2SO_4 (0.75 mL), $K_2S_2O_8$ (0.25 g, 0.925 mmol), and P_2O_5 (0.25 g, 1.76 mmol), and then incubated at 80 °C for 6 hours. After filtered and washed with Milli-Q water repeatedly, the product was dried in air at room temperature overnight. This preoxidized graphite was then subjected to oxidation by Hummer's method. The preoxidized graphite powder (0.5 g) was placed in concentrated H_2SO_4 (11.5 mL) at 0 °C. $KMnO_4$ (1.5 g, 9.5 mmol) was added gradually with stirring while keeping the temperature of the mixture below 20 °C. The mixture was then stirred at 35 °C for 2 h, followed by the addition of distilled water (23 mL). Distilled water (70 mL) was then added to terminate the reaction. Subsequently, 30 % H_2O_2 (1 mL) was added and the color of the mixture changed to bright yellow. The mixture was centrifuged and washed with 10% HCl solution (125 mL) to remove residual metal ions. The precipitate was then washed with Milli-Q water and centrifuged repeatedly until the solution became neutral. To exfoliate the oxidized graphite, the product was treated with an ultrasonic probe at 400 W for 30 min, followed by centrifuging at 30 000 rpm for 30 min. The exfoliated GO was obtained in the supernatant. The precipitate was exfoliated repeatedly. Finally, a total of 350 mL supernatant was obtained. 10 ml of supernatant was dry at 100 °C for 2 days, and the mass was determined by electrode balance. The concentration of GO dispersion is 1.22 mg/ml.

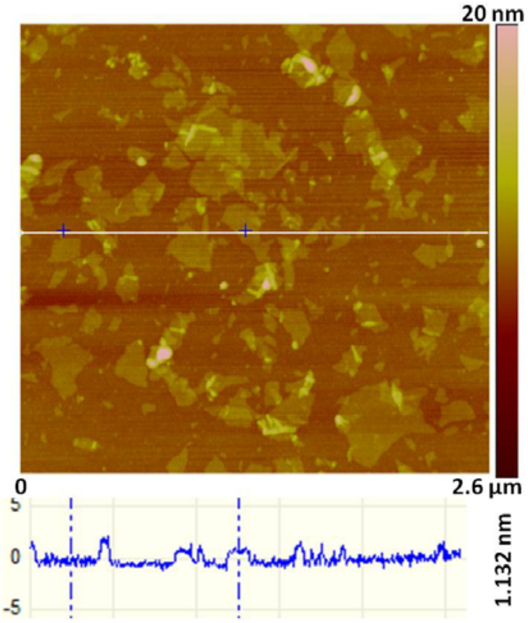

Figure S2 AFM image of GO

3. Synthesis of Co-Al LDH-NS/GO composite and determination of mass ratio of Co-Al LDH-NS and GO in the composite

Co-Al LDH-NS/GO composite was synthesized by mixing Co-Al LDH-NS dispersion and GO dispersion. 4.1 ml of GO dispersion in a concentration of 1.22 mg/ml was added into 400 ml Co-Al LDH-NS dispersion. The precipitation was centrifuged under 2000 rpm for 10 min, followed by washing with Milli-Q water and anhydrous ethanol repeatedly to remove water and formamide completely. After drying at 100 °C for two days, the obtained percipitation was ready for the use of electrochemical measurement. To determine the mass ratio of Co-Al LDH-NS and GO in the composite, the above obtained percipitation was weighted. The total weight is 10.4 mg. As the amount of Co-Al LDH-NS dispersion is largely excessive to GO dispersion (The supernatant of Co-Al LDH-NS and GO mixed solution is pale pink similar to the color of Co-Al LDH-NS dispersion, which proves Co-Al LDH-NS is excessive. See Fig. S3), all GO was thought to form percipitation and surplus Co-Al LDH-NS was left in the solution. Therefore, the weight of GO in the composite is equal to that of GO in dispersion to be 5.0 mg. After subtracting the weight of GO from the total weight of composite, we obtained the weight of Co-Al LDH-NS of 5.4 mg. Thus the mass ratio of GO and Co-Al LDH-NS is 0.926.

Figure S3. Digital photograph of Co-Al LDH-NS dispersion (left) and Mixture of Co-Al LDH-NS and GO (right**).**

4. Zeta potential of GO and Co-Al LDH-NS

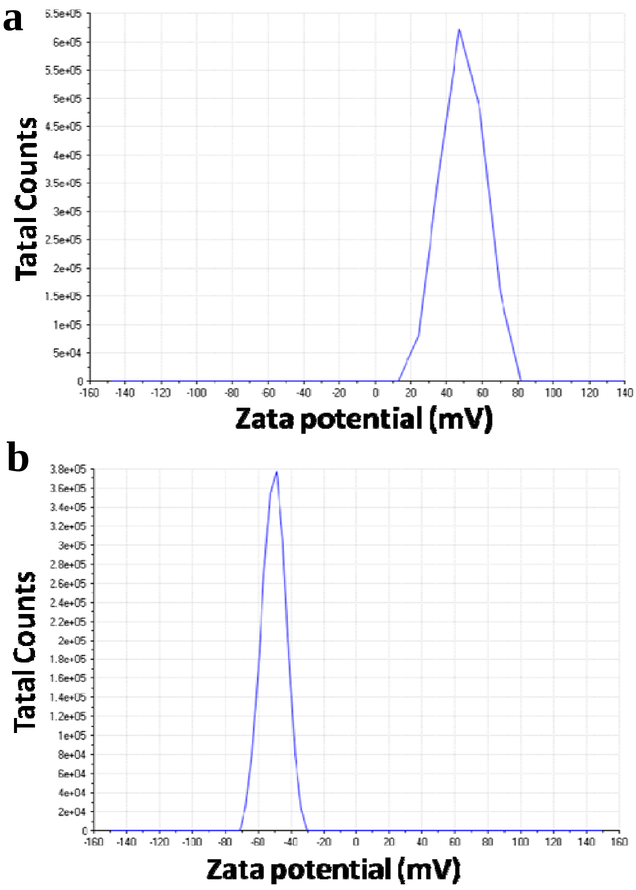

Figure S4 Zeta potential of GO in water (a), Co-Al LDH-NS in formamide (b).

5. Electrochemical measurement

Electrochemical measurement was carried out on a CHI 660D electrochemistry workstation. To prepare electrode, 1 mg of Co-Al-LDH-NS/GO composite was mixed with polytetrafluoroethylene in a mass ratio of 50:1, and then, a few drops of ethanol was added. The suspension was drop-dried into 1 cm^2 Ni foam at 80 °C overnight. The foam with sample was pressed at 5 MPa before measurement. Electrochemical measurements were carried out in 1 M aqueous KOH in a shielding box at room temperature. A platinum wire and a Ag/AgCl served as a counter electrode and reference electrode, respectively. The specific capacitance, average capacitance, power density (P) and energy density (E) were calculated by following equations.

$$C = \frac{\int I dt}{m \Delta V}$$

Where C is average capacitance, I is the oxidation or reduction current, dt is time differential, m is the mass of the active electrode material, and ΔV indicates the voltage range of one sweep segment.

$$C = I \times \triangle t / (\triangle V \times m)$$

$$E = C \times (\triangle V)^2 / 2 = P \times \triangle t$$

Where C is specific capacitance, I is constant discharging current, $\triangle t$ is discharge time, $\triangle V$ is voltage change after a full discharge and m is mass of active material.

6. CV curves of Ni foam, Ni foam coated with Co-Al LDH and GO mixture and Ni foam coated with Co-Al LDH-NS/GO composite at scan rate is 50 mV/s.

In control experiments, the CV curves of Co-Al LDH and GO mixture and bare Ni foam were measured as shown in Figure S5. The CV performance of Co-Al LDH and GO mixture is much lower than that of Co-Al LDH-NS/GO composite. The background signal duo to Ni foam was so small that it was negligible.

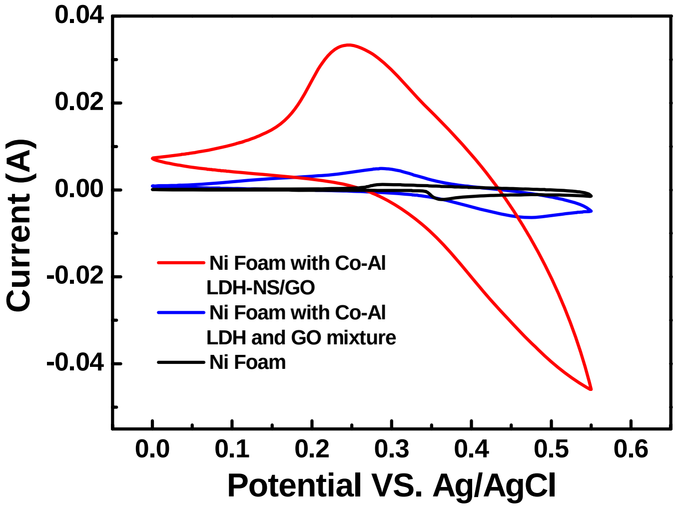

Figure S5 CV curves of Ni foam, Ni foam coated with Co-Al LDH and GO mixture and Ni foam coated with Co-Al LDH-NS/GO composite under a scan rate of 50 mV/s.

References

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