Supporting Information

Alternating Assembly of Ni-Al Layered Double Hydroxide and Graphene for High-Rate Alkaline Battery Cathode

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Experimental detail

Synthesis and exfoliation of Ni-Al LDH

Ni-Al LDH was prepared using the hydrothermal method. Definitely, 0.009 mol $Ni(NO_3)_2.6H_2O$ and 0.003 mol $Al(NO_3)_3.9H_2O$ were dissolved in 100 ml deionized water. Then 0.04 mol urea was added as a precipitating agent. The solution was stirred for 30 min at room temperature to form a homogeneous solution. The aqueous suspension was then transferred into a Teflon-lined autoclave, followed by hydrothermal treatment at a temperature of 100 °C for 24 h. The resultant green dispersion was filtered and washed subsequently with deionized water and anhydrous ethanol for several times. The Ni-Al-CO$_3$ LDH was obtained by drying the precipitate at 60 °C. The exfoliation of Ni-Al LDH was carried out in formamide. Typically, 1.0 g of the above obtained Ni-Al-CO$_3$ LDH was dispersed into 1 L of an aqueous solution containing 1.5 M NaNO$_3$ and 0.005 M HNO$_3$. The vessel was sealed after purging with nitrogen gas, and was shaken for 3 days at room temperature to substitute CO_3^{2-} for NO_3^-. Through this process, NaNO$_3$-HNO$_3$ exchanged Ni-Al-NO$_3$ LDH was obtained. The exchanged product was obtained using the same procedure as described for the pristine material. The Ni-Al-NO$_3$ LDH was redispersed into formamide and formed a concentration of 1.0 g/L. This dispersion was stirred vigorously under nitrogen protection for 3 days at room temperature. The resultant translucent colloidal suspension

was centrifuged at 2000 rpm for 10 min to remove the thicker Ni-Al LDH sheets. After centrifugation, a green transparent solution composed of delaminated Ni-Al LDH platelets was obtained.

Synthesis of graphene oxide (GO)

GO was synthesized from natural flaked graphite using a modified Hummers method in our groups.[1,2] Definitely, 18 3.00 g flake graphite and 1.50 g $NaNO_3$ were added into 69 mL of concentrated H_2SO_4 (98%, w/w) and cooled to 0 °C in an ice bath. 9.01 g $KMnO_4$ was added slowly into the mixture under vigorous stirring. The reaction temperature was maintained below 20 °C for 4 h, then 35 °C for 24 h. The mixture gradually became thick and appeared dusty green. Additional 9.01 g $KMnO_4$ was added slowly and stirred for 4 h, then 69 mL H_2SO_4 (98%, w/w) was mixed in and stirred for 36 h. The reaction mixture was cooled to the room temperature and poured onto ice (400 mL) with 10 mL H_2O_2 (30%, w/w). The color of the mixture turned into light yellow. The centrifugal product was washed with HCl (10%, w/w) and water, and dialyzing, filtering and drying under vacuum for 24 h. The exfoliated GO was obtained under ultrasonication process with an ultrasonic bath. An aqueous suspension of GO flakes (0.6467 mg/mL) was achieved by dispersing graphene oxide in deionized water.

Preparation of Ni-Al LDH/graphene composites

20 ml of GO suspension (0.6467 mg/ml) was added to 500 ml of the Ni-Al LDH nanosheet suspension (1 g/L formamide) and rested overnight. The flocculent Ni-Al LDH/GO composites were self-assembled by electrostatic forces. The floccules were centrifuged and washed subsequently with deionized water and anhydrous ethanol for several times. The dried Ni-Al LDH/GO composites were transferred into a tubular furnace, and treated thermally at 200 °C for 6 h under Ar atmosphere to harvest more conductive Ni-Al LDH/graphene materials (183.6 mg). During the whole processes of the assembly of the composite, the Ni-Al LDH was ensured excessive. Thus, the content of graphene in the Ni-Al LDH/graphene composite could be estimated about 7% by neglecting oxygen loss of the surface groups.

Physical and electrochemical characterization

The microstructure of the samples was investigated by a JEOL 6300F field-emission scanning electron microscopy (JEOL, Tokyo, Japan) and transmission electron microscopy (JEOL, JEM-2100F). The crystalline structure of the samples was characterized by X-Ray diffraction (XRD, JEOL-D/ruax2550PC) using Cu Kα radiation at 40 kV, 250 mA and λ=1.5406 Å. Raman spectra were recorded on a LabRAM HR800 Raman spectrometer using a 632 nm excitation laser. Fourier-Transform IR (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR Spectrometer using KBr pellet technique. Zeta-potential measurements were conducted on a Malvern Zetasizer NanoZS system.

The prepared active materials, conductive acetylene black, and poly(tetrafluoroethylene) binder were mixed uniformly with a mass ratio of 80:15:5, and were coated onto a nickel foam to form the working electrode (1x1 cm^2). The loading weight at the working electrode was 10.6 ±0.5 mg. The platinum foil and the Hg/HgO in 6M KOH were used as the counter and reference electrodes, respectively. The cyclic voltammetry (CV) were measured by a CHI660D electrochemical workstation at different scan rates of 5, 10, 20, and 50 mV s^{-1}. Galvanostatic charge-discharge measurements were performed on a LAND-CT2001A test system. Electrochemical impedance spectroscopy (EIS) measurements were performed on a PARATAT 2273-type electrochemical system. The frequency range applied was from 100 kHz to 0.01 Hz at the open circuit potential with amplitude of 5 mV.

Data analysis

Fig. S1 shows the FT-IR spectra of GO, Ni-Al LDH and Ni-Al LDH/graphene. For GO, the absorption band for C=O stretching vibration appear at 1729 cm^{-1}, and the absorption bands at 1399–1064 cm^{-1} are ascribed to the epoxy C–O-C stretching vibration and the alkoxy C–O-H stretching vibration, respectively.[3,4] The peaks at 3508 cm^{-1} correspond to the O-H and the stretching vibrations at 1365 and 738 cm^{-1} are attributed to CO_3^{2-} in the Ni-Al LDH. Compared to the Ni-Al LDH, the Ni-Al LDH/graphene has weaker CO_3^{2-} stretching vibrations, further indicating that the decarbonation was effective after ion exchange. The Ni-Al LDH/graphene composite has a higher relative intensity of peak at 1615 cm^{-1} compared with pure Ni-Al LDH, which may be caused by the C=C stretching vibration of graphene. The bands below 800 cm^{-1} are

ascribed to the bending vibrations of metal-oxygen (M-O).[5]
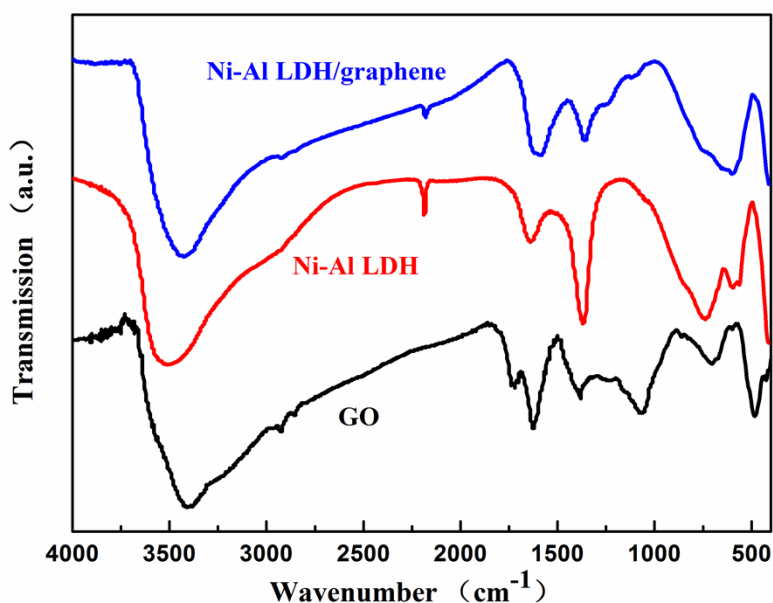
Fig. S1 FT-IR spectra of GO, Ni-Al LDH and Ni-Al LDH/graphene composite

Fig. S2 shows the HRTEM images and the corresponding SAED patterns of the prepared GO, Ni-Al LDH/GO, and Ni-Al LDH/graphene. The GO presented coexistence of non-crystalline and crystalline carbon structures. The non-crystalline structures were majorly originated from the destruction of the hexagonal carbon rings in terms of introduction of oxygen atoms. In the crystalline areas, the hexagonal lattices of graphene with the spacing of 0.35 nm could be clearly distinguished (Fig. S2(a)). Both the Ni-Al LDH/GO and the Ni-Al LDH/graphene demonstrated well-crystalline Ni-Al LDH nanostructures that exposed (012) lattices with the spacing of 0.24 nm (Fig. S2(b) and Fig. S2(c)). Because most of the graphene base was coated with LDH platelets, it was difficult to find the graphene lattices at the basal surfaces of the composites. However, in the edged areas the extended graphene layer could be resolved. The lattice of GO with less-crystalline graphene was not examined for the Ni-Al LDH/GO composite. The lattice spacing of 0.33 nm in the Ni-Al LDH/graphene composite could be ascribed to the restored sp^2 carbon under thermal treatment.
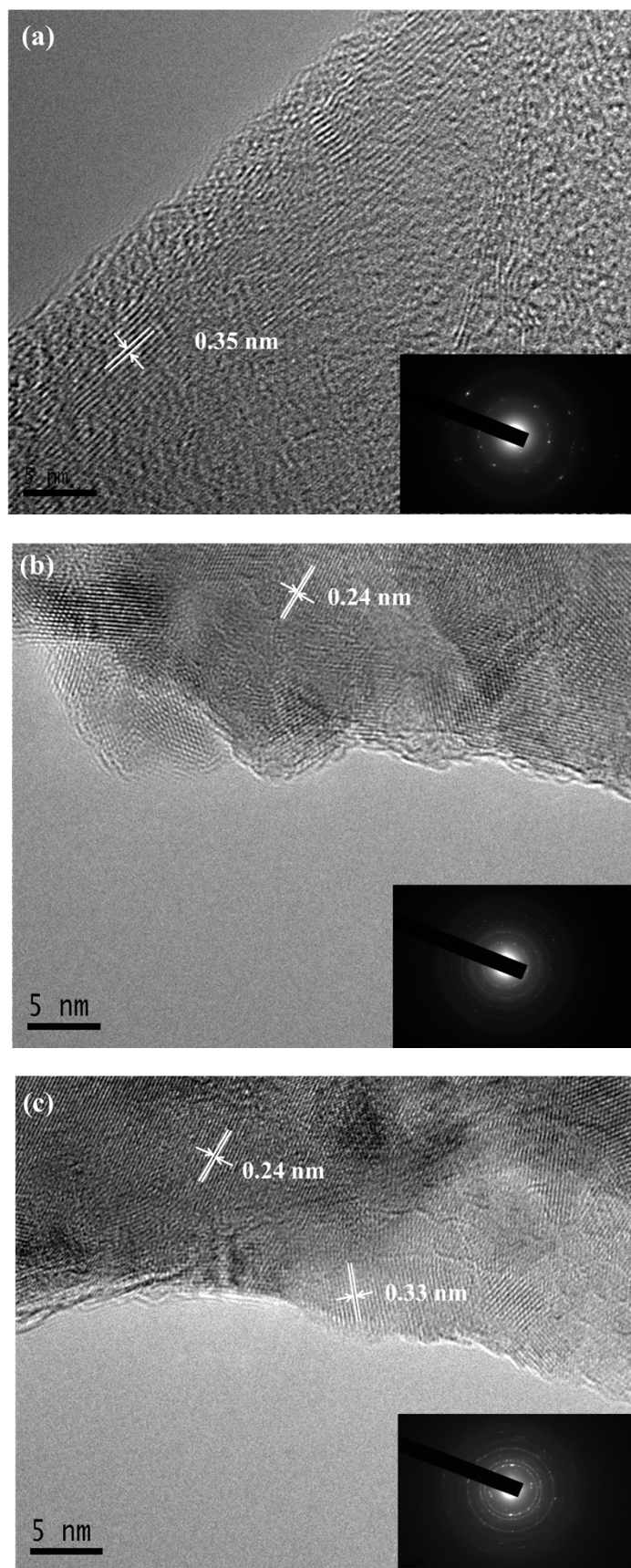
Fig. S2 HRTEM images of the prepared (a) GO, (b) Ni-Al LDH/GO, (c) Ni-Al LDH/graphene, and insets are the corresponding SAED patterns.
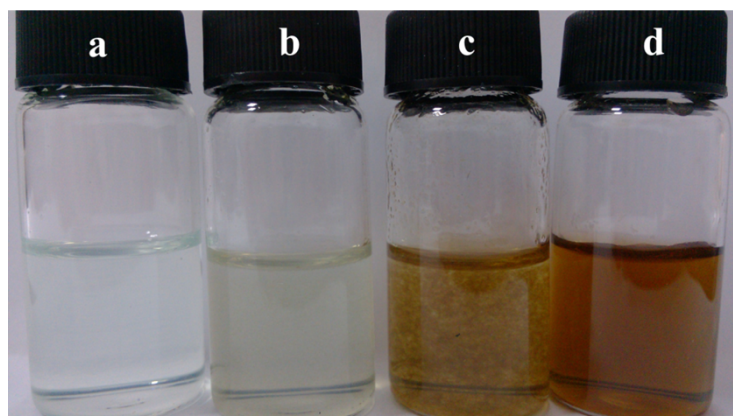
Fig. S3 Digital photographs of dispersions of delaminated Ni-Al LDH (a), Ni-Al LDH (excessive)/GO (b), Ni-Al LDH/GO (excessive) (c), and GO (d).

Fig. S3 shows the digital photographs of dispersions of delaminated Ni-Al LDH, Ni-Al LDH (excessive)/GO, Ni-Al LDH/GO (excessive), and GO. Zeta potential of of the exfoliated LDH platelets dispersed in formamide was measured to be 52.3 mV. The positive charges were produced in the exfoliated process due to the loss of the interlayered anions. The zeta potential of the GO was determined to be -54.2 mV, which can be attributed to the presence of oxygenated functional groups on the surface. It is known that zeta potential with an absolute value larger than 30 mV means a stable dispersion.[6] This means the dispersions of delaminated LDH and GO are stable due to the strong electrostatic repulsion. The zeta potential of the Ni-Al LDH (excessive)/GO and the Ni-Al LDH/GO (excessive) were measured 37.5 mV and -40.3 mV, respectively. It implies sediments could be formed via mixing positively charged Ni-Al LDH dispersions and negatively charged GO solutions that reduced surface charges of nanosheets.

Shown in Fig. S4 are EIS profiles of Ni-Al LDH and Ni-Al LDH/graphene composite electrodes. They include a high-frequency semicircle corresponding to the charge transfer process on the electrode/electrolyte interface and a low-frequency sloped line associated with mass transfer of ions. Obviously, the semicircle of the Ni-Al LDH/graphene composite is smaller than that of the pristine Ni-Al LDH, indicating the smaller charge-transfer resistance. The improved charge-transfer ability is attributed to the graphene interlayer which provides high speed electronic networks in meeting the needs of Ni-Al LDH redox reactions.
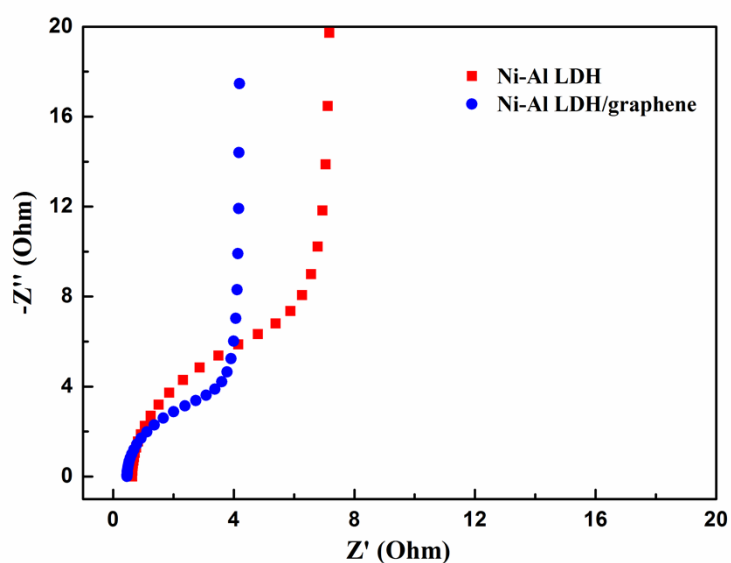
Fig. S4 EIS profiles of Ni-Al LDH and Ni-Al LDH/graphene composite electrodes.

References

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