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Supporting Information

NiAl layered double hydroxide@carbon nanoparticles hybrid electrode for high-performance asymmetric supercapacitors

Xiaoxi Liu, Chong Wang, Yibo Dou, Awu Zhou, Ting Pan, Jingbin Han,* and Min Wei

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

*Corresponding author. Tel: +86-10-64412131; Fax: +86-10-64425385.

Email address: hanjb@mail.buct.edu.cn

1. Experimental section

Synthesis of the LDH@CNPs electrode: The LDH nanoplatelet arrays (NPAs) were synthesized by a homogeneous hydrothermal method. Typically, 15 mmol of $Ni(NO_3)_2·6H_2O$, 5 mmol of $Al(NO_3)_2·9H_2O$, 20 mmol of NH_4F and 50 mmol of urea were dissolved in 100 ml of water, and afterwards the solution was transferred into a Teflon-lined stainless steel autoclave. The conductive fabric substrate (thickness: ~60 µm) was carefully cleaned with acetone, ethanol and distilled water for 30 min. A piece of clean conductive fabric (size: 2 cm×6 cm) was immersed into the solution. Subsequently, the autoclave was sealed and maintained at 110 °C for 8 h. After the reaction, the substrate was rinsed thoroughly and LDH nanoplatelet array was obtained on the substrate.

The LDH NPAs grown on the conductive fabrics can serve as a robust scaffold for the loading of additional conductive material. In this study, carbon nanoparticles (CNPs) were employed as conductive coating to improve the supercapacitor performance of LDH NPA electrode. A common candle in a room without apparent cross-ventilation was used to produce CNPs. The candle soot was collected by placing a glass slide on top of a smoldering candle.[1] After collection, 100 mg of the soot was refluxed in 50 mL of 5 M HNO_3 for 8 h to form a stable colloidal suspension. Oxidative acid treatment not only improves the dispersibility of CNPs in water, but also introduces OH^- groups to the CNPs surface, thus making the particles negatively charged and hydrophilic.

The NiAl-LDH@CNPs hybrid electrode was fabricated by a vacuum filter process: the LDH NPAs on conductive fabrics acts as the filter cloth and the CNPs suspension act as filter paste. After that a thin layer of CNPs can wrap on the surface LDH nanoplatelets to achieve LDH@CNPs hybrid structure. The loading content of CNPs on LDH nanoplatelets was controlled by the filtration time. The LDH@CNPs hybrid electrode was used as positive electrode to construct asymmetric all-solid-state supercapacitor.

Fabrication of All-Solid-State Supercapacitor: In a typical procedure, the negative electrode was prepared by mixing 80 wt% activated carbon, 10 wt% acetylene black and 10 wt% polytetrafluoroethylene (PTFE). The mixture was coated on a square-shaped conductive fabric substrate. The PVA/KCl gel electrolyte was prepared as follows: 3.36 g of KCl was added into 60 mL of deionized water, and then 6 g of powdered PVA was added. The whole mixture was heated to 85 °C under stirring until the solution became clear. A strip of the obtained fabric with LDH@CNPs and another with AC were floated on the PVA/KCl solution for 10 min, keeping the bare side of substrate above the solution. Subsequently, the electrode with a thin electrolyte coating was air-dried at room temperature for 4 h to vaporize excess water. The two electrodes were pressed together under a pressure of ~5 MPa for 10 min. Under this pressure, the PVA/KCl gel electrolyte layer on each electrode surface was combined into one thin separated layer. After these steps, the LDH@CNPs//AC asymmetric all-solid-state supercapacitor was obtained. The LDH//AC, LDH@CNPs//LDH@CNPs and AC//AC supercapacitors for comparison were assembled through a similar approach.

Characterization: X-ray diffraction (XRD) measurement was performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.15418 nm) at 40 kV, 30 mA, with a scanning rate of 10° min^{-1}. The morphology of the products was investigated using a Zeiss Supra 55 scanning electron microscope (SEM). Transmission electron microscopy (TEM) images were recorded with Philips TECNAI-20 and JEOL JEM-2010 high resolution transmission electron microscopes. Raman spectroscopy was obtained on a Renishaw instrument (inVia-Reflex, 633 nm). X-ray photoelectron spectra (XPS) were recorded on a Thermo VG Escalab 250 X-ray photoelectron spectrometer at a pressure of about 2×10^{-9} Pa with Al 193 Kα X-rays as the excitation source. The cyclic voltammetry and galvanostatic charging/discharging measurements were conducted with an electrochemical workstation (CHI 660C). A three-electrode system was applied to determine the optimal content of CNPs on LDH nanoplatelets. The LDH@CNPs hybrid electrode (1 cm × 1 cm), Hg/$HgCl_2$ (SCE) and platinum wire were used as working electrode, reference electrode and counter electrode, respectively. Electrochemical impedance spectra (EIS) measurements were performed by applying an alternating current voltage with 5 mV amplitude in a frequency range from 0.01 to 100 kHz by using a three-electrode system in 1.0 M KOH solution. The all-solid-state devices were measured in two-electrode system.

2. Supplementary Figures

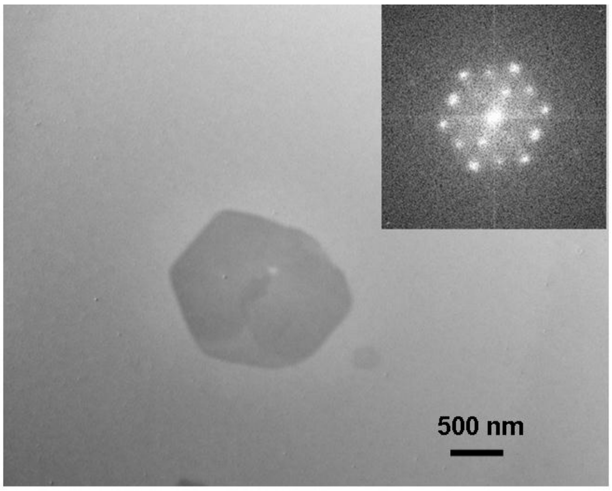

Fig. S1 TEM image of a single-crystalline NiAl-LDH nanoplatelet with corresponding selected-area electron diffraction pattern.

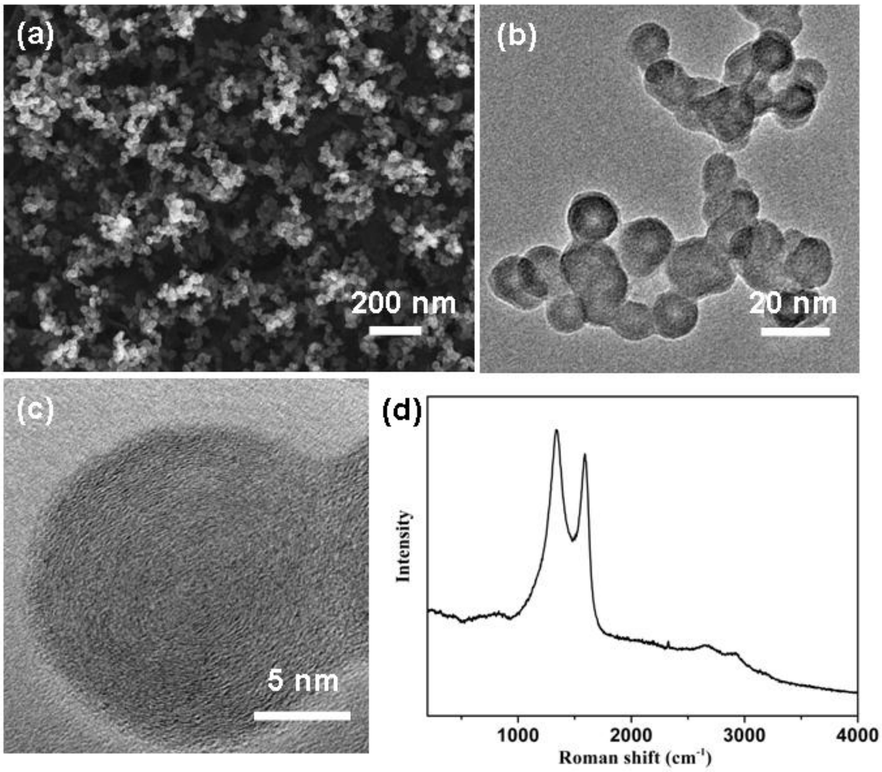

Fig. S2 (a) SEM image of the CNPs collected on glass slide; (b) low- and (c) high-magnification TEM images of CNPs; (d) Raman spectrum of CNPs.

By keeping a glass plate on top of smoldering candle for several minutes, a layer of tightly packed CNPs was collected on the surface of the glass slide (Fig. S2a). Low-magnification TEM image (Fig. S2b) indicates the uniform scale (12−18 nm) of the CNPs. High-magnification TEM image (Fig. S2c) displays that one carbon nanoparticle is composed of many curved carbon lamellas, forming onion-like structures. It has been reported that the annual ring-like CNPs stacked with several curved grapheme layers have a graphitic structure with good conductivity.[2] The typical Raman spectrum (Fig. S2d) further indicates that the CNPs possess a structure analogous to graphite with some degree of disordering.

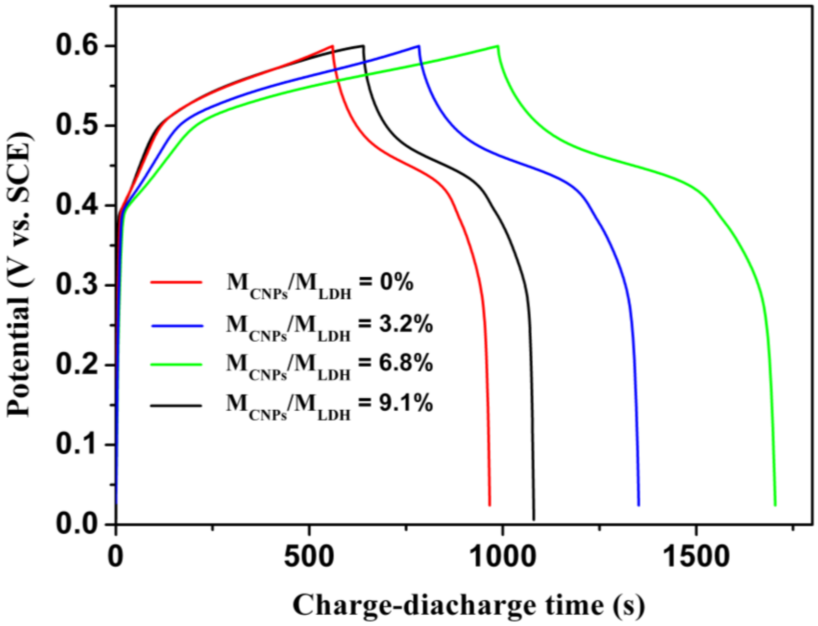

Fig. S3 Galvanostatic charge–discharge curves of the LDH@CNPs hybrid electrodes with various CNPs content using a three-electrode system in 1.0 M KOH solution.

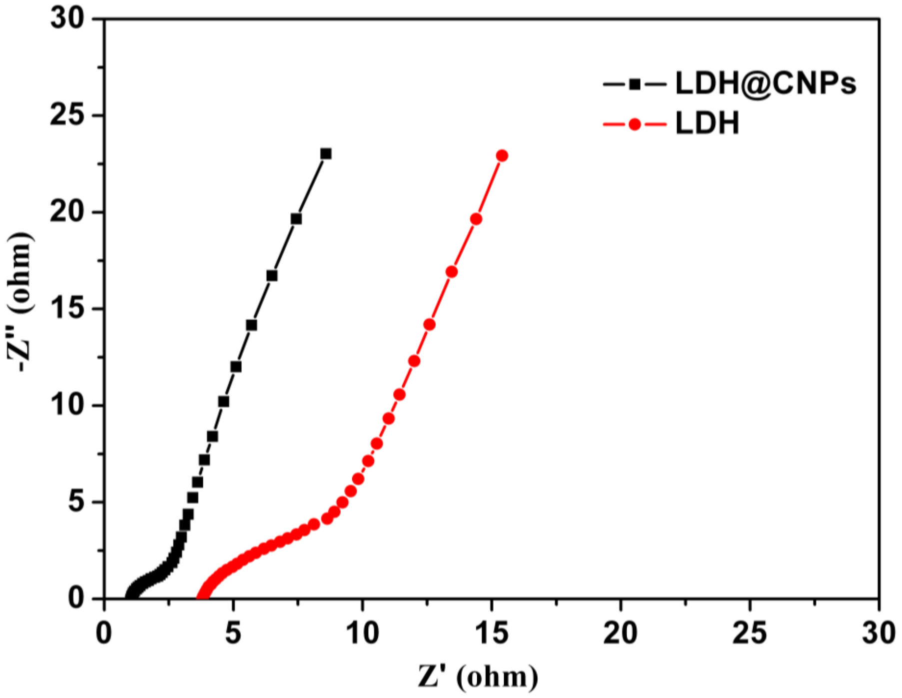

Fig. S4 Nyquist plots of the electrochemical impedance spectroscopy (EIS) for the LDH@CNPs and pristine LDH electrodes by using a three-electrode system in 1.0 M KOH solution performed from 0.01 to 100 kHz.

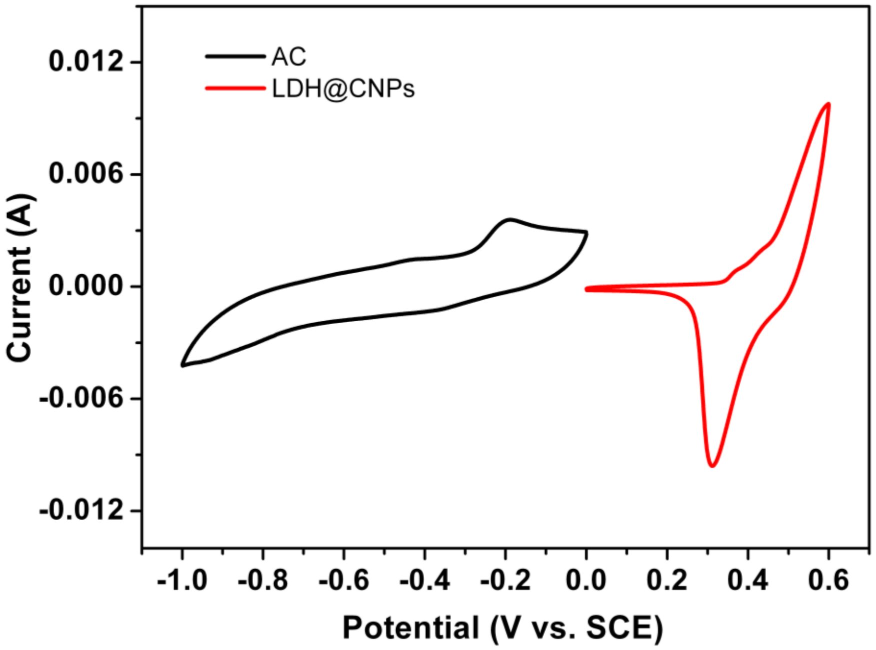

Fig. S5 Cyclic voltammograms of AC electrode and LDH@CNPs electrode in a three-electrode system in 1.0 M KOH solution.

Before the assembly of LDH@CNPs//AC asymmetric supercapacitor, the mass ratio between positive and negative electrode materials should be fixed according to the equation: Q+=Q-, where Q+ and Q- are the charges stored in the positive and negative electrodes, respectively. Based on the integral area of the CV curves (Fig. S5), the mass ratio of AC and LDH@CNPs was quantified as $m_{\mathrm{AC}}/m_{\mathrm{LDH@CNPs}}=7.25$.

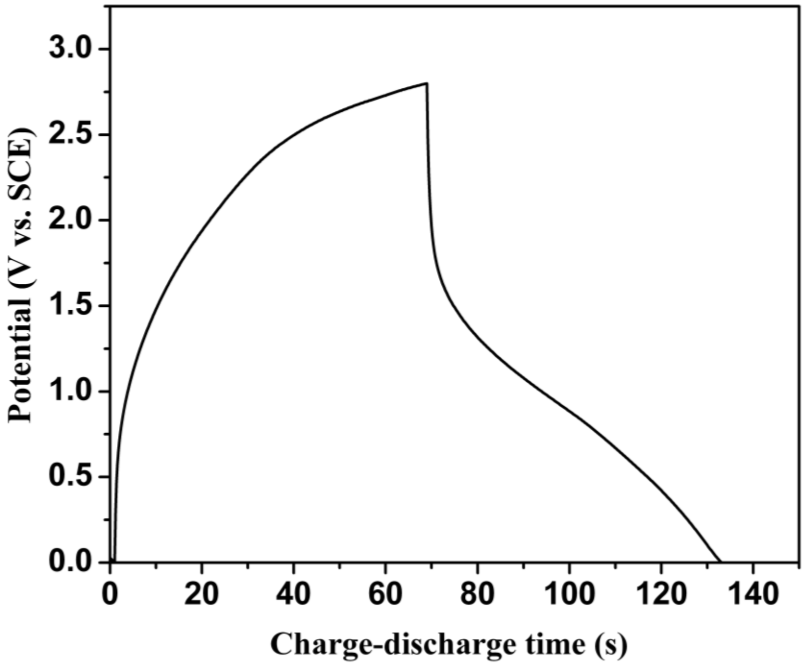

Fig. S6 Galvanostatic charge-discharge curve of the two in-series supercapacitor group.

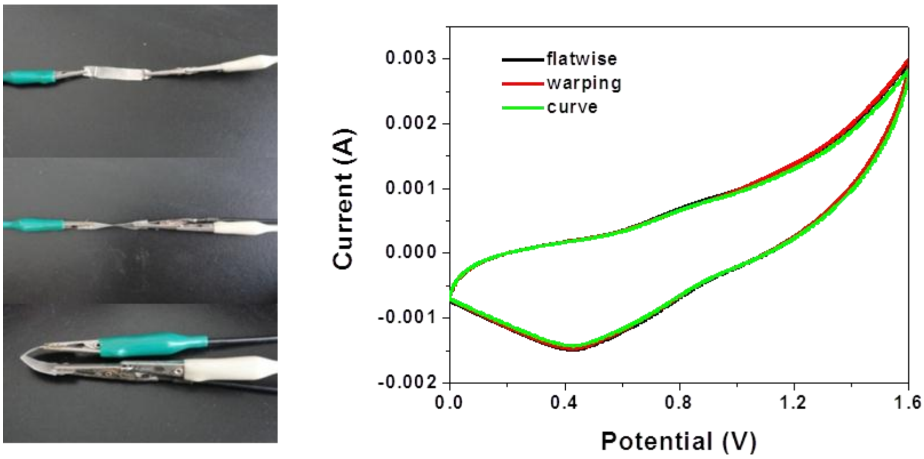

Fig. S7 Optical photographs of the all-solid-state supercapacitor device under different bending degrees and their CV curvers.

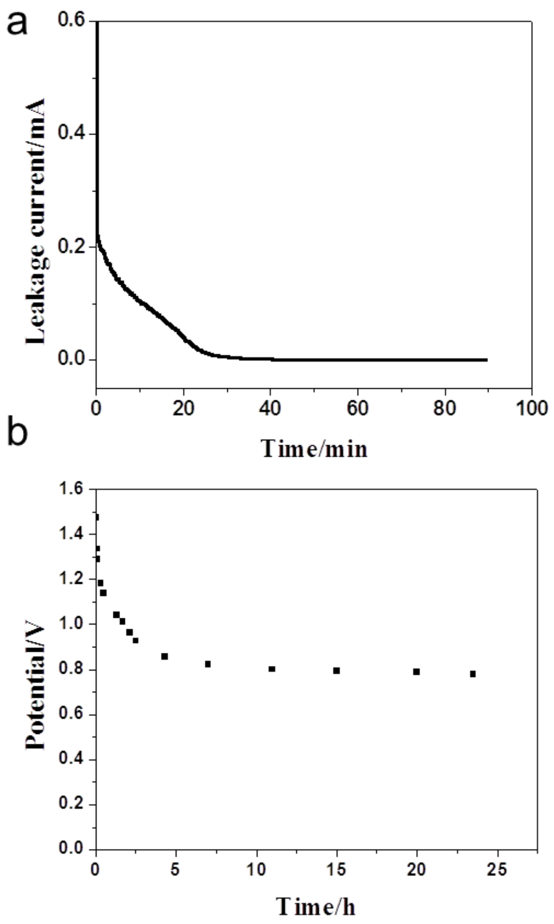

Fig. S8 (a) The leakage current curve of the LDH@CNPs//AC asymmetric supercapacitor charged at 2 mA to a floating potential of 1.6 V and kept at 1.6 V for 1.5 h; (b) self-discharge curve of the charged device at 1.6 V for 20 min.

With regard to the practical applications, leakage current and self-discharge of the energy storage device are main concerns. As shown in Fig. S8, the leakage current of LDH@CNPs//AC asymmetric supercapacitor dropped significantly at the beginning and then kept stable at 4.5 µA after 1.5 h. Such small value of leakage current indicates little shuttle reactions caused by the impurities in the electrode materials.[3] In addition, self-discharge curve undergoes rapid decrease in several hours, but the device shows a stable output voltage of ~0.8 V after 4.5 h and almost 50% of the initial charged potential was retained for 25 h. The low leakage current and good self-discharge performance of the LDH@CNPs//AC asymmetric supercapacitor are very desirable for its applications in wearable energy strage systems and sensor networks.

References

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