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A NiAl layered double hydroxide@carbon nanoparticles hybrid electrode for high-

performance asymmetric supercapacitors<sup>†</sup>

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A NiAl layered double hydroxide (LDH)@carbon nanoparticles (CNPs) hybrid electrode was fabricated *via* a facile and cost-effective approach and displays excellent pseudocapacitive behavior in asymmetric supercapacitors.

Recently, a significant amount of effort has been devoted to producing flexible, lightweight and environmentally friendly energy storage devices, as a result of the urgent need for sustainable and renewable power sources.<sup>1,2</sup> Supercapacitors (SCs) represent a type of emerging energy storage device that has attracted increasing attention due to their high power density, fast charging/discharging rate and excellent cycling stability.<sup>3-6</sup> Such outstanding properties make them promising in a wide range of applications from day-to-day electrical and portable electronics to industrial energy management, where high power density and long cycle-life are imperative. So far, pseudocapacitive transition-metal oxides/hydroxides have been extensively exploited in SCs and have the advantages of high capacitance, low cost and environmental friendliness.7-9 However, the main obstacle for these materials is that they suffer from poor electrical conductivity and severe aggregation in particulate form, which consequently results in inferior highrate performance and lower energy output.

To solve these problems, one effective approach is to anchor electroactive materials onto a specific substrate in order to fabricate an ordered array electrode as well as to improve the conductivity *via* the incorporation of highly conductive polymers or carbon materials (*e.g.*, carbon nanotubes, activated carbon and graphene). For instance,  $MnO_2/CNT$  array,  $Ni(OH)_2/$ graphene nanoplate,  $V_2O_5/carbon$  nanotube and  $MnO_2/$ conductive polymer coaxial nanowire hybrid electrodes with improved electrochemical capacitive behavior have all been explored.<sup>1,10-13</sup> Even though progress has been made in improving the capacitance and durability, there are still challenges for the application of these materials in modern power sources in a real supercapacitor manufacturing environment because of their high cost and complicated fabrication procedures. Therefore, it is of great importance to develop new hybrid electrodes *via* facile routes so as to obtain supercapacitors with high electrochemical performance.

Layered double hydroxides (LDHs), also known as anionic clays,<sup>14,15</sup> have been intensively explored as pseudocapacitive materials due to their high redox activity, low cost and long cycle life.<sup>16-20</sup> Herein, we report the design and fabrication of NiAl-LDH nanoplatelet arrays (NPAs)@carbon nanoparticles (CNPs) hybrid electrodes on a conductive fabric (CF) substrate for high-performance pseudocapacitors through a cost-effective process. Firstly, LDH nanoplatelet arrays (NPAs) were fabricated on the surface of the conductive fabric substrate via an in situ growth method, which was followed by the incorporation of carbon nanoparticles (CNPs) onto the LDH nanoplatelets. The resulting NiAl-LDH@CNPs electrode exhibits a high specific capacitance and rate capability, resulting from its enhanced electrochemically active surface area and electrical conductivity. In addition, a practical application of this new material has been demonstrated in an asymmetric all-solid-state SC, in which LDH@CNPs serves as a positive electrode and activated carbon (AC) as a negative electrode.

The synthesis of the LDH@CNPs hybrid electrode involves the growth of vertically aligned LDH NPAs *via* a hydrothermal reaction followed the addition of a CNP coating through a vacuum filtration process, as illustrated in Fig. 1a. The wellinterlaced conductive fabric, which has a relatively smooth surface and a diameter of ~9.5 µm provides an electrically conductive network (Fig. 1b). Using a hydrothermal synthesis, large-scale NiAl-LDH NPAs were grown vertically on each fiber of the textile with a uniform structure (Fig. 1c and d). The obtained LDH NPAs provide a porous network structure with a thickness of ~6 nm. The XRD pattern (Fig. 1e) shows a series of reflections at 11.7°, 23.5°, 34.8°, 59.7° and 60.9°, corresponding to the

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**Fig. 1** (a) Schematic illustration showing the fabrication of the LDH@CNPs hybrid electrode; (b) SEM image of the conductive fibers (CFs); (c) and (d) top-view SEM images of the NiAl-LDH NPAs on the surface of CFs; (e) XRD pattern of as-prepared LDH NPAs on CFs.

[003], [006], [012], [110] and [113] reflections of the layered LDH phase. A TEM image shows the hexagonal morphology of a single LDH microcrystal, and the corresponding selected-area electron diffraction (SAED) pattern exhibits hexagonally arranged bright spots, indicating its single-crystal nature (ESI, Fig. S1†).

An ideal supercapacitive material should have excellent electrical conductivity to support fast electron transport, especially at high charge–discharge rates. In order to enhance the conductivity of the as-grown LDH NPAs electrode, a thin layer of conductive CNPs was integrated onto the surface of the LDH nanoplatelets *via* a vacuum filter in order to fabricate a hybrid LDH@CNPs structure. The CNPs (size: 12–18 nm) used in this study were obtained from candle soot using a simple, low-cost process (for details, see ESI, Fig. S2†).

The well-defined and interconnected 3D network of the resulting structure was revealed using typical SEM images (Fig. 2a–c). The numerous CNPs are densely coated onto both sides of each LDH nanoplatelet, which maintains its original porous structure. The XPS spectrum of NiAl-LDH (Fig. 2d) shows two peaks located at 856.7 and 869.9 eV, corresponding to the  $2p_{3/2}$  and  $2p_{1/2}$  levels of Ni<sup>2+</sup>, respectively. After deposition of the CNP layer, both peaks shift to lower energy levels (856.2 and 869.5 eV, respectively), as a result of the interaction between the LDH NPAs and CNPs. Moreover, the Raman spectrum (Fig. 3e) of the LDH@CNPs sample exhibits absorption peaks (478, 546 and 1054 cm<sup>-1</sup>) originating from NiAl-LDH and two signals (1347 and 1603 cm<sup>-1</sup>) that can be attributed to CNPs, further verifying the formation of the LDH@CNPs hybrid material.

In order to optimize the electrochemical performance of the LDH@CNPs electrode, cyclic voltammetry (CV) of electrodes with various CNP content were investigated using a three-electrode system (Fig. 3a). A pair of anodic/cathodic peaks are observed in all of the CV curves as a result of the Faradic capacitive behavior, corresponding to the reversible redox reaction of Ni<sup>2+</sup>/Ni<sup>3+</sup> that is associated with OH<sup>-</sup>. The specific capacitance of the bare LDH NPAs was calculated to be 627 F  $g^{-1}$ based on the CV curve at a scan rate of 2 mV s<sup>-1</sup>. After addition of the CNP coating, the specific capacitance of the LDH@CNPs electrode (obtained from CV measurements) increased at first to a maximum (1146 F  $g^{-1}$ ) with the increase in the CNPs : LDH weight ratio from 0 to 6.8%, but it then decreased upon a further increase in CNPs loading. Moreover, the galvanostatic charge-discharge curves (ESI, Fig. S3<sup>†</sup>) is consistent with the results of the CV analysis. Therefore, the LDH@CNPs sample with  $m_{\rm CNPs}/m_{\rm LDH} = 6.8\%$  was chosen as the optimum electrode for further evaluation of its electrochemical performance. The overall mass loading of the LDH@CNPs hybrid material was  $0.25 \text{ mg cm}^{-2}$ . With respect to the rate capability, the pristine LDH NPA electrode shows a specific capacitance of 208 F  $g^{-1}$  at a scan rate of 200 mV s<sup>-1</sup>, which means it retains only 31% of the initial capacitance at 2 mV  $s^{-1}$ . In comparison, the LDH@CNPs hybrid electrode exhibits a specific capacitance of 478 F  $g^{-1}$  at 200 mV  $s^{-1}$ , which is a retention of 42% (Fig. 3b), thus demonstrating its superior high-rate capability. In addition, electrochemical impedance spectroscopy (EIS) was applied



Fig. 2 (a-c) SEM images of the LDH@CNPs hybrid material at different magnifications; (d) Ni 2p XPS spectra of pristine LDH and LDH@CNPs; (e) Raman spectra of the LDH, CNPs and LDH@CNPs samples.



Fig. 3 (a) CV curves of the LDH@CNPs hybrid electrodes with various  $m_{\rm CNPs}/m_{\rm LDH}$  ratios obtained using a three-electrode system in 1.0 M KOH solution; (b) the specific capacitance of the LDH and LDH@CNPs electrodes at different scan rates.

in order to study the ion diffusion and electron transfer properties of the obtained hybrid electrode (Fig. S4†). The equivalent series resistance (ESR) was only 1.4  $\Omega$  for the LDH@CNPs sample (area: 1 cm<sup>2</sup>), which is much lower than that of pure LDH NPAs (3.62  $\Omega$ ; 1 cm<sup>2</sup>), indicating that the LDH@CNPs electrode has better electrical conductivity. The enhanced capacitance and high-rate capability of the LDH@CNPs electrode can be attributed to an improvement in the electrical conductivity of the electrode after being coated with CNPs.

In order to demonstrate the potential of the LDH@CNPs electrode for practical application, a sandwich-shaped asymmetric all-solid-state supercapacitor was assembled using LDH@CNPs and active carbon (AC) as the positive and negative electrode, respectively (Fig. 4a, see ESI, Fig. S5<sup>†</sup> for details). Fig. 4b shows CV curves of the LDH@CNPs//AC all-solid-state supercapacitor at different scan rates in the voltage window of 0-1.6 V, which display a quasi-rectangular geometry without any apparent redox peaks. This is related to the high conductivity of the LDH@CNPs hybrid electrode and the fast redox reaction that occurs with the PVA/KOH solid electrolyte. Galvanostatic charge-discharge curves obtained at different current densities (Fig. 4c) also exhibit typical pseudocapacitive behavior, with a coulombic efficiency of ~93%. The specific capacitance of the LDH@CNPs/AC and LDH//AC supercapacitors as a function of the current density were further investigated (Fig. 4d). The



Fig. 4 (a) Schematic illustration of the LDH@CNPs//AC asymmetric SC; (b) CV curves of the LDH@CNPs//AC supercapacitor at different scan rates; (c) charge–discharge curves of the LDH@CNPs//AC SC at different current densities; (d) specific capacitance of the LDH//AC and LDH@CNPs//AC asymmetric SCs at different current densities; (e) Ragone plots of the LDH@CNPs//AC, LDH//AC, AC//AC and LDH@CNPs//LDH@CNPs supercapacitors; (f) cycling stability of the LDH@CNPs//AC SC during a charge–discharge test at 10 A g<sup>-1</sup> (inset: a digital picture showing how two highly flexible devices in series can light a red light-emitting-diode).

LDH//AC capacitor exhibits a specific capacitance of 105 F  $g^{-1}$  at 1 A  $g^{-1}$  and 35 F  $g^{-1}$  at 10 A  $g^{-1}$ , demonstrating a ~67% loss of the initial capacitance. In contrast, the LDH@CNPs//AC capacitor exhibits a specific capacitance of 138 F  $g^{-1}$  at 1 A  $g^{-1}$ , and 79 F  $g^{-1}$  at 10 A  $g^{-1}$  with a retention of 57.2%. The better rate performance highlights the advantage of the improved electrical conductivity of the electrode after coating with CNPs, which would definitely facilitate electron transport. Fig. 4e shows plots of the specific energy vs. specific power for the four SCs (LDH@CNPs//AC, LDH//AC, AC//AC, LDH@CNPs// LDH@CNPs) as the charge-discharge current is increased from 1 to 10 A g<sup>-1</sup>. The specific energy values for LDH@CNPs// LDH@CNPs, AC//AC, LDH//AC are 35.3, 21.0 and 30.2 W h kg<sup>-1</sup>, respectively, at 1 A g<sup>-1</sup>. In contrast, the LDH@CNPs//AC supercapacitor exhibits a largely enhanced specific energy, achieving the highest specific energy of 47.7 W h kg<sup>-1</sup> (1 A g<sup>-1</sup>) and the maximum specific power of 51 kW kg<sup>-1</sup> (10 A g<sup>-1</sup>). Furthermore, the energy density of the LDH@CNPs//AC supercapacitor is superior to previously reported graphene hydrogel//  $MnO_2$  (23.2 W h kg<sup>-1</sup>),<sup>21</sup>  $MnO_2$  nanowire@graphene composite//graphene (30.4 W h kg<sup>-1</sup>),<sup>22</sup> and NiO//reduced graphene oxide  $(39.9 \text{ W h kg}^{-1})^{23}$  asymmetric SCs.

Cycling capability is one of the key requirements for practical applications. A cycling life test on the LDH@CNPs//AC supercapacitor was carried out at a current density of 10 A g<sup>-1</sup> using a galvanostatic charge–discharge technique, and the results show a capacitance retention of 88.9% over 2000 cycles (Fig. 4f). To further demonstrate the prospective application of this asymmetric supercapacitor, two single units were connected in series in order to light a red light-emitting-diode (Fig. 4f), which exhibits an enhanced potential window of up to 2.8 V (Fig. S6†). In addition, the change in the CV curves that were collected at different bending angles is subtle and acceptable (Fig. S7†), and the LDH@CNPs//AC supercapacitor exhibits a low leakage current and good self-discharge performance (for details see ESI, Fig. S8†), demonstrating its suitability as a flexible energy storage device for practical applications.

In conclusion, a facile and cost-effective approach was developed to fabricate a high-performance asymmetric supercapacitor based on a LDH@CNPs//AC hybrid structure. The resulting supercapacitor exhibits excellent capacitive performance, including a high specific capacitance, good cycling capability and a high energy density. The improved capacitance and rate capability can be attributed to the enhanced electrical conductivity that results from the incorporation of CNPs combined with the facile ion diffusion pathways provided by the 3D macroporous structure. Therefore, this asymmetric supercapacitor holds great promise for application in flexible and lightweight energy storage devices.

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