Electronic Supplementary Material (ESI) for ChemComm.

Facile preparation of free-standing rGO paper-based Ni-Mn LDH/graphene superlattice composites as pseudocapacitive electrode

Wei Quan, Zilong Tang*, Shitong Wang, Ye Hong and Zhongtai Zhang

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China.

**Corresponding author. E-mail address: tzl@tsinghua.edu.cn, tel/fax: 86-10-62783685.*

Experimental Section

Preparation of rGO solutions for assemble of rGO paper

Graphite oxide in the form of powder was prepared using the Hummers method.[1] 100 mL homogeneous brown colloidal GO solutions containing 100 mL de-ionized water and 10 mg graphite oxide sheets was prepared after ultrasonic treatment under 35 kHz for 1h. Then it was centrifuged at 10000 rpm for 10 min to remove unexfoliated material, and the supernatant being the final graphene oxide dispersion. To reduce GO, 20 mM of hydrazine monohydrate ($N_2H_4 \cdot H_2O$) was added into above solution, which was then reacted in a water bath at 95 °C for 15 min under constant stirring. Before reduction, the pH of the dispersions was adjusted to 9-10 with 25% ammonia solution (2 μL per ml of dispersion) to promote the colloidal stability of the graphene oxide sheets through electrostatic repulsion.

Preparation of Ni-Mn LDH composite film

The composite film prepared by the filtration process consists of rGO paper and functional Ni-Mn LDH/graphene layer. The rGO paper was filtrated first through the Anodisc membrane filter (47 mm in diameter, 0.2 mm pore size, Whatman), and when the solution was about to be used up, another suspension solution mentioned above (about 50 mL) containing flocculated LDH/G composites was added sequentially, followed by sufficient ethanol to clean extra formamid. Finally, the film was peeled off from the filter after air drying for a whole night. A pure rGO paper was also prepared for mass calculation of functional layer and performance comparison.

Preparation of Ni-Mn LDH powders

All the chemicals are of analytical grade and were used without further purification. Ni-Mn LDH powders were prepared by a simple solvothermal process as follows: a homogeneous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (0.8 mmol,), $MnCl_2 \cdot 4H_2O$ (0. 8mmol), H_2O (3.0 g), and methanol (12 g) was prepared first before transferred into a 80 mL PTFE vessel coated by a stainless autoclave. Then, the reactor was put in an oven at 180 °C for 24 h. The precipitated powders were collected by filtration and washed thoroughly with DI water, ethanol and acetone. The obtained powder was dried at 60 °C for 8 h.

Preparation of Ni-Mn LDH/graphene composites

The preparation of Ni-Mn LDH/graphene with superlattice structure was based on a previous report by Sasaki.[2] Briefly, 0.1 g Ni-Mn LDHs were dispersed in a formamide-water binary solution (250 mL, 1:4 v/v), which was then heated in a water bath at 80 °C for 8 h under continuous magnetic stirring and a nitrogen gas protection until it turns completely translucent. A brown colloidal suspension of exfoliated GO nanosheets (0.2 mg mL^{-1}) was obtained by dispersing the as-prepared GO sheets from Hummers method in water under 35 kHz for 1 h. After 50 ml of above suspension was mixed with 50 mL formamide, 8 μL of hydrazine monohydrate was added into the solutions, followed by heated in a water bath at 80 °C for 3 h. A dark black suspension was obtained, indicating the reduction into rGO nanosheets. Electrostatic heteroassembly experiments were carried out by dropwise addition of above anionic rGO nanosheets into 100 mL cationic LDH nanosheets solution under constant stirring. Then a suspension solution containing the flocculated products was obtained.

Material Characterization

Nitrogen adsorption and desorption experiment of the composite film was carried out by a specific surface area analyzer (Autosorb-iQ2-MP, Quantachrome Instruments). The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation based on the mass of functional layer. Atomic force microscope (AFM, SPI400, NSK) was employed to test the thickness of exploited Ni-Mn LDH and graphene nanosheets. The crystalline structure of the film electrode was characterized by X-ray diffraction patterns (XRD, D/max-V2500, Rigaku) from 10° to 60° at 6° min^{-1}, using Cu Kα radiation (λ=1.5406 Å) as source. Field-emission scanning electron microscope

(SEM, LEO-1530, Zeiss) and transmission electron microscopy (TEM, TECNAI G220, FEI) were used to investigate the morphology and crystal structure of the as-prepared samples. The pure Ni-Mn LDH electrode was prepared by mixing active materials, carbon black, and poly-vinylidene fluoride (PVDF) (85:10:5) in ethanol. The mixture was then stirred overnight and the slurry was loaded on the nickel foam (1 cm × 1 cm in area) and dried in air at 80 °C overnight. The electrode was pressed under 40 MPa and dried for 3 h.

Before electrochemical measurements, the film was cut into a circular platelet (diameter 1.2 cm) loaded with about 0.4 mg LDH/graphene composites. Then it was investigated under a three-electrode cell configuration at 25 °C. The composite film was acted directly as the working electrode, which was soaked in a 1 M KOH solution and degassed in a vacuum for 5 h before tests. Platinum foil and HgO/Hg (1M KOH) were used as the counter and reference electrode, respectively. The cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation (IM6, Zahner), while galvanostatic charge-discharge tests were carried on a supercapacitor test instrument (BT2000, Arbin). Unit of F cm^{-2} is employed in the capacitance evaluation, due to its more practical meaning for ultrathin film electrode.[3]

Calculated of specific capacitance of the electrode

The specific capacitance of each sample was calculated from galvanostatic charge-discharge curves as follows:

$$C_s = I \times \Delta t/(\Delta V \times S) \tag{1}$$

$$C_m = I \times \Delta t/(\Delta V \times m) \tag{2}$$

where C_s (F cm^{-1}) and C_m (F g^{-1}) all indicate the specific capacitance of the electrode base on different unit of measurements; I (A) is the discharge current; Δt (s) is the discharge time; ΔV (V) corresponds to the voltage change after a full charge or discharge process; S (cm^2) and m (g) indicates the surface area of the film electrode tested and m (g) is the mass of Ni-Mn LDH/graphene composites loaded on the rGO paper.

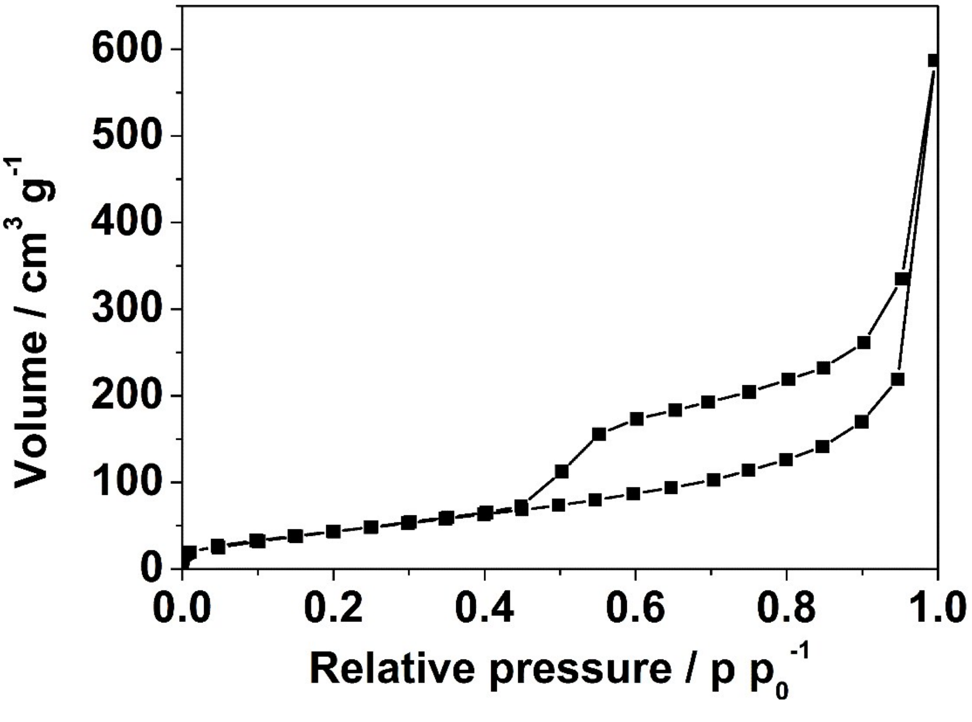

Fig. S1 Nitrogen adsorption/desorption isotherm of the composite film

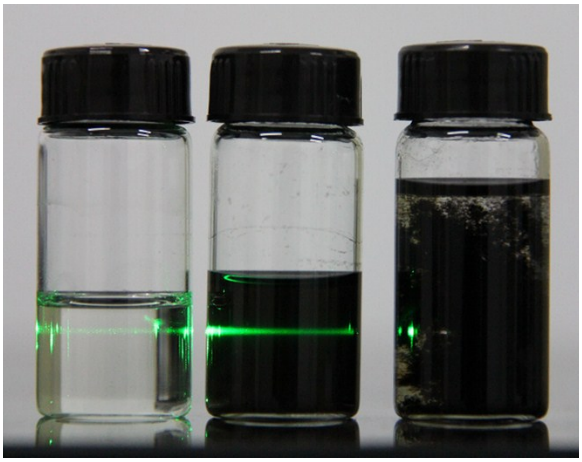

Fig. S2 Tyndall effects of exploited LDH and graphene nanosheets

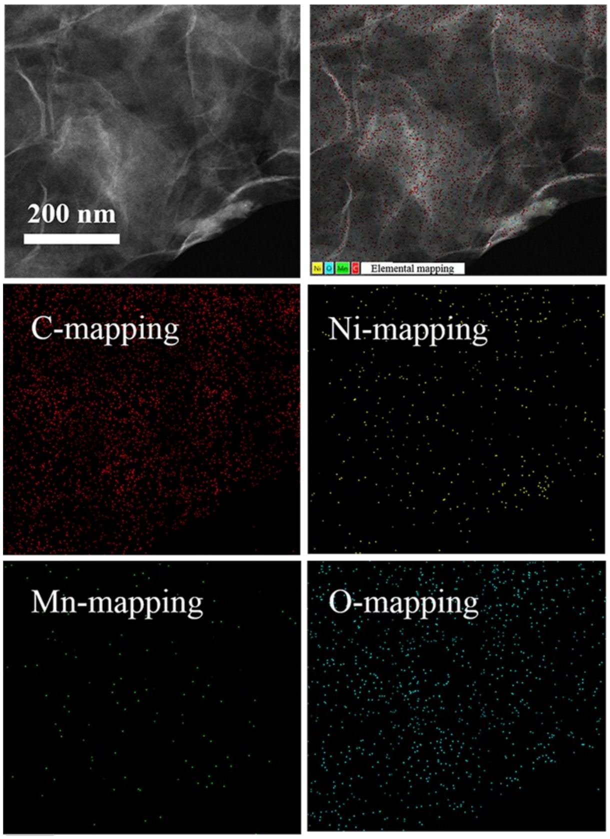

Fig. S3 Elemental mapping of LDH/G composites with superlattice structure.

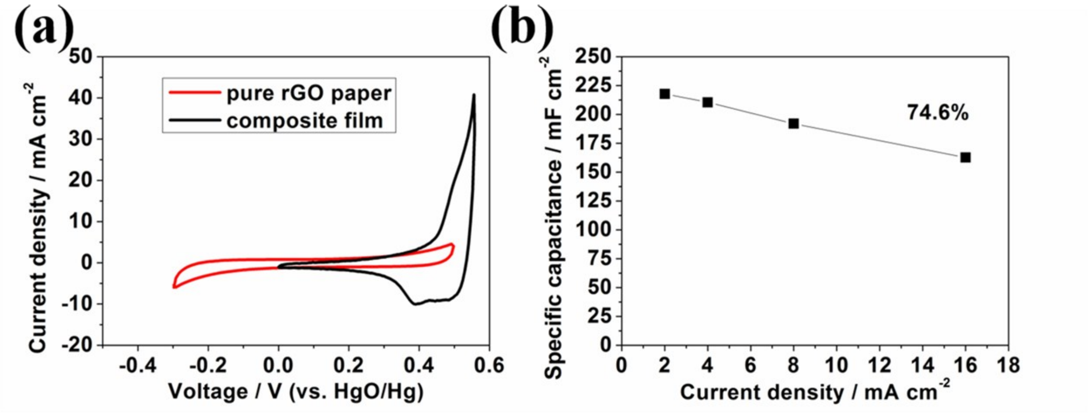

Fig. S4 CV curves of pure rGO paper and the composite film at the scan rate of 40 mV·s^{-1} (a) and calculated specific capacitance of the composite film at different current densities (b).

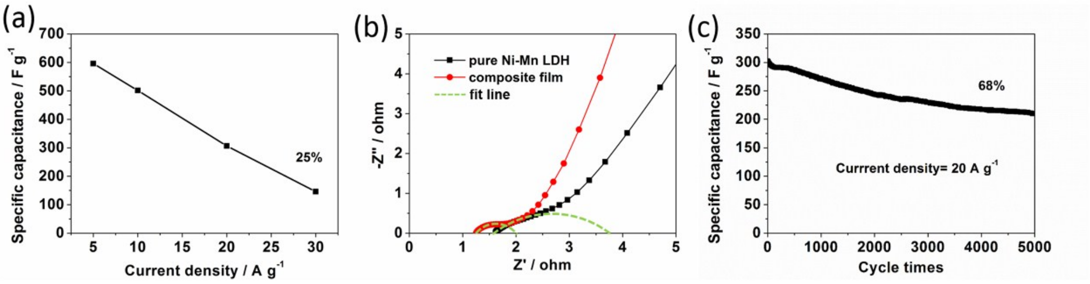

Fig. S5 Rate property of pure Ni-Mn LDH electrode (a), EIS comparison between composite film and pure LDH electrode (b), and cycle stability of pure LDH electrode (c).

Table S1 Comparison of capacitances, cycle stability and assemble methods for some reported flexible rGO paper-based films and LDH/graphene composites electrodes.

Electrode materials	Capacitance (rate)	Retention (cycles)	Assemble method	Ref.
Graphene paper-based MnO_2 and PANI	380 F g^{-1} (20 A g^{-1})	85% (10000)	Filtration, electrodeposition and in situ polymerization	4
Graphene paper-based MnO_2	315 F g^{-1} (20 A g^{-1})	85% (10000)	Filtration and polymerization	5
Graphene nanofiber film-based	210 F g^{-1}	71%	Filtration	6

PANI	(0.3 A g^{-1})	(800)		
Flexible graphene/PANI composite paper	490 F g^{-1} (10 A g^{-1}g)	82% (1000)	Filtration and polymerization	7
Embossed rGO–MnO2 hybrid films	389 F g^{-1} (1 A g^{-1})	95% (1000)	Filtration and sacrificial template	8
Co_3O_4–rGO–CNTs hybrid paper	378 F g^{-1} (2 A g^{-1})	96% (700)	Filtration and hydrothermal treatment	9
NiO-graphene three-dimensional networks	816 F g^{-1} (5 mV s^{-1})	100% (2000)	CVD and sacrificial template	10
Ni-Al LDH/graphene composites	851 F g^{-1} (17.86 A g^{-1})	91% (500)	Traditional method using binder and Ni foam	11
Co-Al LDH/graphene 3D porous hybrid aerogel	305 F g^{-1} (20 A g^{-1})	97% (10000)	Traditional method using binder and Ni foam	12
Molecular-scaled Ni-Co LDH/ graphene composites	525 F g^{-1} (30 A g^{-1})	97% (2000)	Assembled onto ITO glass via binder	2
Our work	421 (36 A g^{-1})	95% (10000)	Filtration	

Reference

1 S. Park, R. S. Ruoff, Nat. Nanotechnol. 2009, 4, 217.

2 R. Z. Ma, X. H. Liu, J. B. Liang, Y. Bando and T. Sasaki, Adv. Mater., 2014, 26, 4173.

3 J. Come, V. Augustyn, J. W. Kim, P. Rozier, P. Taberna, P. Gogosti, J. W. Long and B. Dunn, J. Electrochem. Soc., 2015, 161, A718.

4 H. L. Li, Y. He, V. Pavlinek, Q. L. Cheng, P. Sahab and C. Z. Li, J. Mater. Chem. A, 2015, 3, 17165.

5 Y. M. Sun, Z. Fang, C. X. Wang, K. R. R. M. Ariyawansha, A. J. Zhou and Hongwei Duan, Nanoscale, 2015, 7, 7790.

6 Q. Wu, Y. X. Xu, Z. Y. Yao, A. R. Liu and Gaoquan Shi, ACS Nano, 2010, 4, 1963.

7 H. P. Cong, X. C. Ren, P. Wang and S. H. Yu, Energy Environ. Sci., 2013, 6, 1185.

8 B. G. Choi, M. Yang, W. H. Hong, J. W. Choi and Y. S. Huh, ACS Nano, 2012, 6, 4020.

9 C. Yuan, L. Yang, L. Hou, J. Li, Y. Sun, X. Zhang, L. Shen, X. Lu, S. Xiong and X. W. Lou, Adv. Funct. Mater., 2012, 22, 2560.

10 X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang and H. Zhang, Small, 2011, 7, 3163.

11 J. Xu, S. L. Gai, F. He, N. Niu, P. Gao, Y. j. Chen and P. P. Yang, J. Mater. Chem. A, 2014, 2, 1022.

12 A. L. Zhang, C. Wang, Q. J. Xu, H. M. Liu, Y. G. Wang and Y. Y. Xia, RSC Adv., 2015, 5, 26017.