Supporting Information

Graphene-Wrapped CoNi-Layered Double Hydroxides Microspheres as a New Anode Material for Lithium-ion Batteries

Liluo Shi, Yaxin Chen, Renyue He, Xiaohong Chen and Huaihe Song*.

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing, 100029, PR China

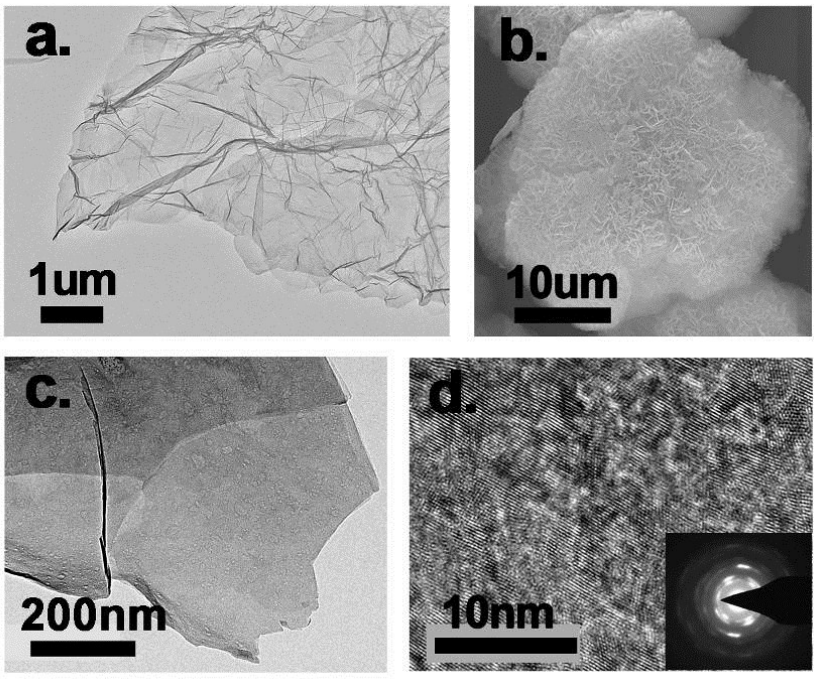

Fig. 1 (a) TEM image of GNS; SEM image (b), TEM image (c) and HRTEM image (d) (inset: SAED pattern) of CoNi-LDHs.

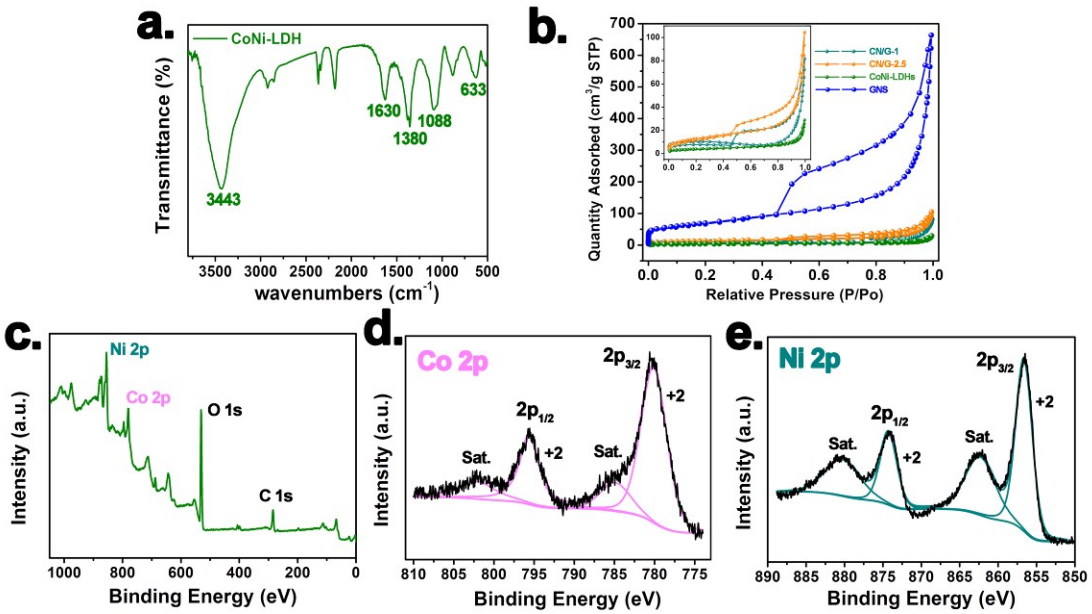

Fig. 2 (a) FT-IR spectrum of CoNi-LDHs; (b) Nitrogen adsorption–desorption isotherms of LDHs/Gs, CoNi-LDHs and GNS, inset: the enlargement of the isotherms of LDHs/Gs and CoNi-LDHs; XPS spectra of (c) CoNi-LDHs and its (d) Co 2p and (e) Ni 2p spectra.

The XRD patterns of GNS and CoNi-LDHs are shown in Fig. 3a, the peak which appearing around 26° shows a dispersive state of low intensity, indicating that GNS has a relatively low crystallinity. The (003), (006) and (009) characteristic peaks of CoNi-LDHs are sharp and strong which means that the LDHs layers present good crystallinity. The functional groups can be tested from the FT-IR spectrum in Fig. S2a. The band at ca. 3443 cm^{-1} exhibits the O-H stretching vibration from the interlayer H_2O molecules and metal-hydroxyl groups. The bands at ca. 1634cm^{-1}, 1388cm^{-1}, and 1088cm^{-1} are associated to the bending vibration of the water molecule, the vibration of interlayer CO_3^{2-} and NO_3^{2-} and non-symmetric stretching vibration of C-O-C bond,

respectively. At the low wavelength range of ca. 633 cm^{-1}, the bond is correspond to the M-O, O-M-O, M-O-M vibrations (M= Co and Ni) [1, 2]. From the XPS spectrum in Fig. S2c, CoNi-LDHs are composed of Co 2p, Ni 2p, C 1s and O 1s. Two accompanying peaks show the spin–orbit splitting into the satellite peaks (named as 'Sat'). Both Ni 2p and Co 2p curves are consist of two spin–orbit doublets and two shake-up 'Sat'. For the high-resolution spectra of Co 2p, the binding energy values of 780.9 and 796.4 eV are observed for the Co $2p_{1/2}$ and Co $2p_{3/2}$ regions which correspond to the Co^{2+} valence state of cobalt hydroxide as shown in Fig. S2d. Meanwhile, for the Ni 2p curve of Fig. S2e, the binding energy values of 872.6 and 855.1 eV correspond to the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ with spin–orbit characteristics of Ni^{2+} in nickel hydroxide.

For the CV curves of GNS in Fig. 5a, the distinct peak around 0.5~0.8 V at the first cathodic scan corresponds to Li^+ irreversible intercalation into the graphene sheets and the SEI film formation. As a typical carbon material, the potential of reversible lithium intercalation of GNS remains at ca. 0.1V. The peaks of ca. 0.2 and 1.2 V at the anodic scan represent the Li+ deintercalation from the graphene sheets and the defective sites, respectively [3]. The galvanostatic charge-discharge curves of GNS (Fig. 5d) correspond well to the CV curves.

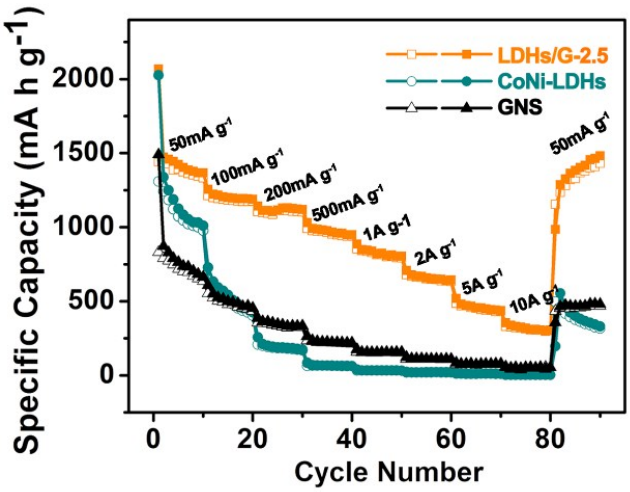

Fig. 3 the rate performances of LDHs/Gs and GNS electrodes at different current densities from 0.05 A g^{-1} to 10 A g^{-1} then back to 0.05 A g^{-1} and CoNi-LDHs electrode at different current densities from 0.05 A g^{-1} to 2 A g^{-1} then back to 0.05 A g^{-1}.

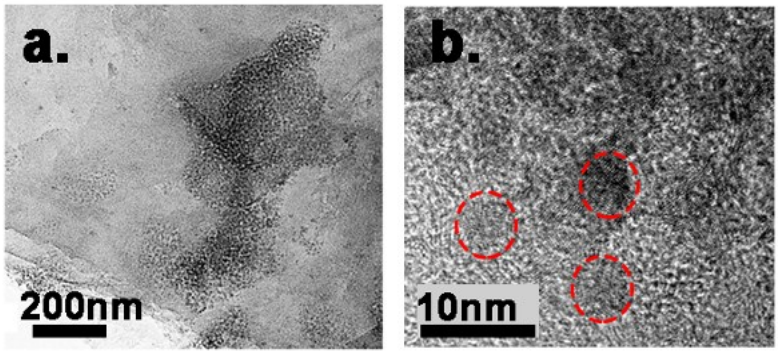

Fig. 4 (a, b) TEM images of LDHs/G-2.5 electrode material after long cycling.

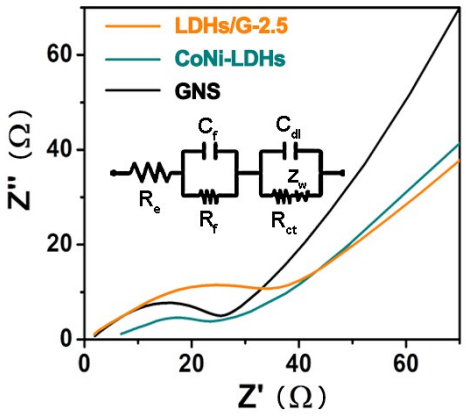

Fig. 5 EIS spectra of LDHs/G-2.5, CoNi-LDHs and GNS electrodes after 10 cycles at current density of 100 mA g-1, inset: randles equivalent circuit for the electrodes.

Table 1 SSAs and pore parameters of CN/G-1, CN/G-2.5, CoNi-LDHs and GNS.

Sample	S_{BET}(m^2 g^{-1})	S_{mi}(m^2 g^{-1})	S_{me}(m^2 g^{-1})	V_t（cm^3 g^{-1}）	V_{mi}（cm^3 g^{-1}）	V_{me}（cm^3 g^{-1}）
LDHs/G-1	31.0	0.6	30.4	0.126	0.0039	0.1221
LDHs/G-2.5	46.3	0.0	46.3	0.161	0.0001	0.1609
CoNi-LDHs	13.7	11.9	1.8	0.044	0.0009	0.0431
GNS	248.8	25.2	223.6	1.026	0.0100	1.0160

Table 2 Kinetic parameters of the electrodes at the potential of 2.3 V after 10 cycles.

Sample	R_f (Ω)	R_{ct} (Ω)	R_e (Ω)
CN/G-2.5	9.23	9.24	2.24
CoNi-LDHs	4.67	12.77	3.71
GNS	6.45	6.79	5.26

References

[1] G. Nagaraju, G.S.R. Raju, Y.H. Ko, J.S. Yu, Hierarchical Ni-Co layered double hydroxide nanosheets entrapped on conductive textile fibers: a cost-effective and flexible electrode for high-performance pseudocapacitors, Nanoscale 8 (2016) 812-825.

[2] R. Li, Z. Hu, X. Shao, P. Cheng, S. Li, W. Yu, W. Lin, D. Yuan, Large Scale Synthesis of NiCo Layered Double Hydroxides for Superior Asymmetric Electrochemical Capacitor, Sci. Rep. 6 (2016) 18737.

[3] L. Shi, Y. Chen, H. Song, A. Li, X. Chen, J. Zhou, Z. Ma, Preparation and Lithium-Storage Performance of a Novel Hierarchical Porous Carbon from Sucrose Using Mg-Al Layered Double Hydroxides as Template, Electrochim. Acta 231 (2017) 153-161.