## **Electronic Supplementary Information**

# The improved electrochemical performances of MOF-derived Ni-Co layered double hydroxide complexes using distinctive hollow-in-hollow structures

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#### **1. Supplementary Figures**



**Fig. S1** TEM image of HCS@ZIF-67s synthesized without introduction of carboxylic groups to HCS surfaces.



Fig. S2 TEM images of (a) SiO<sub>2</sub> microsphere and (b, c) micro-sized HCS.

Sample	C (At%)	O (At%)	Si (At%)
SiO <sub>2</sub> @C	42.7	45.4	11.9
HCS	81.9	18.1	-

Table S1 Elemental composition data of SiO<sub>2</sub>@C and HCS obtained by EDX measurements.



Fig. S3 SEM images of (a) HCS, (b) HCS@ZIF-67-2, (c) HIH-LDH-2, and (d) HIH-LDH-1.



Fig. S4 TEM images of (a) pristine ZIF-67 and (b) H-LDH.



**Fig. S5** (a) STEM image, (b) STEM-EDX line analysis result, and (c) EDX spectrum of HIH-LDH-2. The inset in (c) indicates the elemental composition of HIH-LDH-2.



Fig. S6 XRD spectra of H-LDH, HIH-LDH-1, and HIH-LDH-2.



Fig. S7 Raman spectra of H-LDH and HIH-LDH-2.



**Fig. S8** (a) Nitrogen adsorption/desorption plots and (b) pore-size distribution curves of H-LDH, HIH-LDH-1, and HIH-LDH-2.



Fig. S9 CV curves of (a) H-LDH, (b) HIH-LDH-1, and (c) HIH-LDH-2 with different scan rates.



Fig. S10 GCD curves of (a) H-LDH, (b) HIH-LDH-1, and (c) HIH-LDH-2 with different current densities.



Fig. S11 Schematic diagram of the assembled HSC device (HIH-LDH-2//MPRGO).

#### 2. Structural characteristics and electrochemical results of negative electrode material (MPRGO).

As a negative electrode material for our HSC device, MPRGO was synthesized according to our previous work.<sup>s1</sup> Briefly, MPRGO was the graphene material with large surface area, which was prepared by combined process of lyophilization of graphene oxide (GO) solution and plasma reduction. As a result of above process, several morphological features were introduced into the MPRGO sheets, which included web-like configuration (Fig. S12a), numerous crack-shaped mesopores (Fig. S12b), and corrugated surfaces (Fig. S12c). Based on these characteristics, MPRGO demonstrated large BET surface area as high as 606.8 m<sup>2</sup> g<sup>-1</sup>. In addition, the mesoporosity of MPRGO was further confirmed by its type-IV hysteresis loop (Fig. S13a) and a pore-size distribution curve centered near 2.95 nm (Fig. S13b).

Owing to its large ion accessible area with abundant mesopores, MPRGO was expected to offer excellent electrochemical performances. The electrochemical properties of MPRGO were measured in a 1 M KOH electrolyte with a three-electrode system. Initially, the CV curves were acquired at various scan rates in the potential range from -1 to 0 V (vs. Ag|AgCl) (Fig. S14a). MPRGO showed rectangular CV curve, whose shape was not distorted even at a high scan rate of 400 mV s<sup>-1</sup>, indicating that the charge storage of MPRGO arose from fast ion adsorption/desorption process (EDLC). For further investigation, GCD tests were implemented with different current densities in the same potential range with CV tests. As shown in Fig. S14b, MPRGO displayed capacitive behavior with linear discharging curves, which was in aggrement with CV data. According to the calculation of specific capacitance using GCD results, the capacitance of MPRGO was 300.3 F g<sup>-1</sup> at 5 A g<sup>-1</sup>, and it was still 247.8 F g<sup>-1</sup> when the current density increased to 80 A  $g^{-1}$  (83% retention) (Fig. S14c). The high specific capacitance and reliable rate performance of MPRGO can be attributed to a couple of factors. First, the large surface area of MPRGO not only provided increased ion accessible sites but also decreased the diffusion length of electrolyte ions. Second, carbon-based capacitive materials were known to render high rate capability since the electrostatic charge storage process was theoretically much faster than the faradaic reaction.<sup>s2</sup> Additionally, MPRGO showed a low  $R_{ct}$  value (10.64  $\Omega$ ) and steep slope in its Nyquist plot, demonstrating the ideal capacitive behavior (Fig. S14d). Take these results into consideration, MPRGO was suitable for the application as a negative electrode material for our HSC device.



Fig. S12 (a, b) SEM images and (c) TEM image of MPRGO.



Fig. S13 (a) Nitrogen adsorption/desorption plot and (b) pore-size distribution curve of MPRGO.



**Fig. S14** Electrochemical performance of MPRGO: (a) CV curves at various scan rates. (b) GCD results with different current densities. (c) specific capacitance as a function of current density. (d) Nyquist plot in the frequency range from 10 mHz to 100 kHz, the inset exhibits the high frequency region of the plot.

### 3. References.

S1. G. Lee, C. Lee, C. –M. Yoon, M. Kim and J. Jang, ACS Appl. Mater. Interfaces, 2017, 9, 5222–5230.

S2. T. Liu, L. Zhang, B. Cheng, W. You and J. Yu, Chem. Commun., 2018, 54, 3731-3734.