Electronic Supporting Information

Preparation of Two-Dimensional Assembled Ni-Mn-C Ternary Composite for High-Performance All-Solid-State Flexible Supercapacitor

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Experimental Section

Synthesis of Ni-MOF crystals

In a typical procedure, 1.3 g NiCl$_2\bullet$6H$_2$O and 3 g K$_2$C$_2$O$_4$ were dissolved in 20 mL deionized water (refer to as dispersion A). 1.5 mL ethylenediamine (C$_2$H$_8$N$_2$) was added to 1.3 g NiCl$_2\bullet$6H$_2$O to form a dispersion B. Then, dispersion B was added dropwisely into dispersion A under stirring. After reaction at ambient condition for 48 h, the formed Ni-MOF crystals were collected by centrifugation followed by washing using methanol several times, and drying in a vacuum oven at 40 °C.

Preparation of Ni(OH)$_2$-MnO$_2$/C, MnO$_2$/C, Ni(OH)$_2$/C and Ni-MOF-derived porous carbon (NPC) composites

First, the prepared Ni-MOF crystals were annealed under N$_2$ protection at 300 °C for 1 h, and then 700 °C for another 2 h to obtain the Ni@C composite. After that, 20 mg Ni@C composite and 6 mg potassium permanganate (KMnO$_4$) were dispersed in 36 mL deionized water. The mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and then heated at 150 °C for 24 h. The Ni(OH)$_2$-MnO$_2$/C composites were collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C. Ni-MOF-derived porous carbon (NPC) was obtained by etching Ni@C composite using an aqueous mixture of 3 M FeCl$_3$ and 3 M HCl at 80 °C for 8 h, followed by washing with deionized water until PH=7, and then drying in a vacuum oven at 60 °C.

The preparation of MnO$_2$/C composites is similar to that of the Ni(OH)$_2$-MnO$_2$/C composites. Briefly, Ni-MOF-derived porous carbon and potassium permanganate (KMnO$_4$) (mass ratio of 3:1) was dispersed in 36 ml deionized water. The obtained solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and then heated at 150 °C for 1 h. The MnO$_2$/C composites were collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C.

The Ni(OH)$_2$/C composite was prepared by mixing 30 mg NPC, 32 mg NiCl$_2$·6H$_2$O and 50 mg Urea in 20 mL distilled water. Then the mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 180 °C for 2 h. The Ni(OH)$_2$/C composites were

collected and washed with distilled water several times, and then dried in a vacuum oven at 60 °C.

Material characterizations

The field emission scanning electron microscope (FESEM, Hitachi SL8010) and transmission electron microscopy (TEM, JEM-100CXⅡ) were used to characterize morphology, microstructure and element compositions of the samples. The structures of the samples were identified by a X-ray powder diffractometer (XRD, PNAlytical X'Pert PRO) with Cu Kα radiation (I = 1.54056 Å) operating at 40 kV and 250 mA, and a Raman spectroscopy (LabRAM HR800 Horiba JobinYvon) with a 531.95 nm laser. The surface chemical states of samples were investigated using a X-ray photoelectron spectroscopy (XPS, Shimadzu Co., Ltd. Hongkong) with a Kratos Axis Ultra-DLD system.

Electrochemical measurements

The $Ni(OH)_2$-MnO_2/C composites electrode was fabricated by coating a slurry, which is composed of $Ni(OH)_2$-MnO_2/C composites, acetylene black and polyvinylidene difluoride (weight ratio is 8:1:1) dispersed in N-methyl-2-pyrrolidone (NMP), on a carbon paper. Then, the prepared electrodes were dried in a vacuum oven at 80 °C for overnight. Measurements of CV, galvanostatic charge/discharge, electrochemical impedance spectroscopy were carried out on a CHI 760E electrochemistry workstation. The electrochemical measurements of individual working electrodes were performed in 6 M KOH aqueous solution using three-electrode configuration. A platinum foil was used as counter electrode, and an Ag/AgCl was served as reference electrode. The all-solid-state symmetric supercapacitor was constructed by using $Ni(OH)_2$-MnO_2/C composites as cathode and anode, and KOH/poly(vinyl alcohol) (PVA) gel as solid electrolyte. The KOH/PVA gel electrolyte was prepared by mixing 0.5 g PVA and 0.5 g KOH in 5 mL distilled water at 80-90 °C to form a homogeneous gel.

The capacitive contribution from surface- and diffusion-controlled processes was analyzed according to Dunn's method.[47] The current response (i) in a fix potential (V) were calculated according to the following equation:

$$i(V) = k_1 v + k_2 v^{1/2}$$

Where v is the sweep rate, k_1v and $k_2v^{1/2}$ presents capacitive effects and diffusion-controlled insertion effects, respectively.
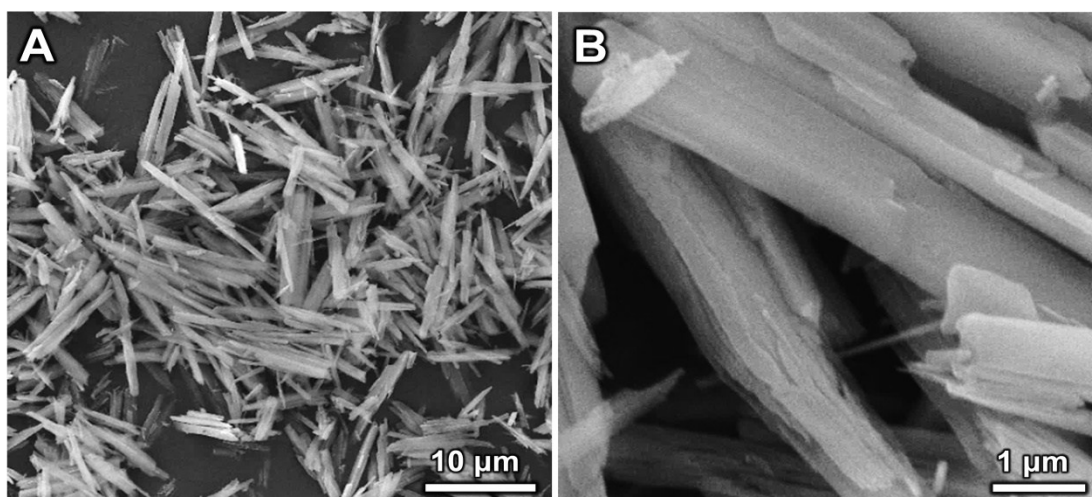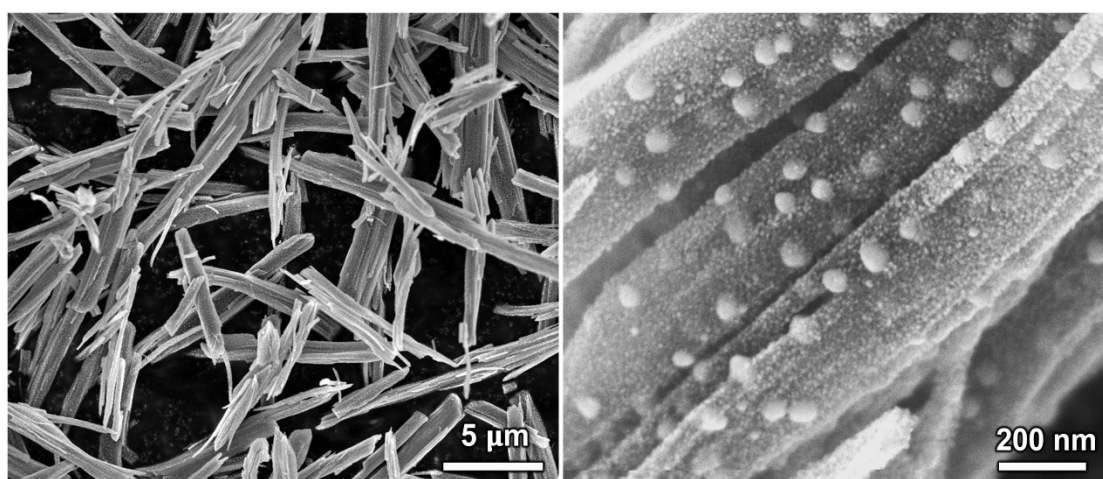
Fig. S1. SEM images of Ni-MOF crystals.

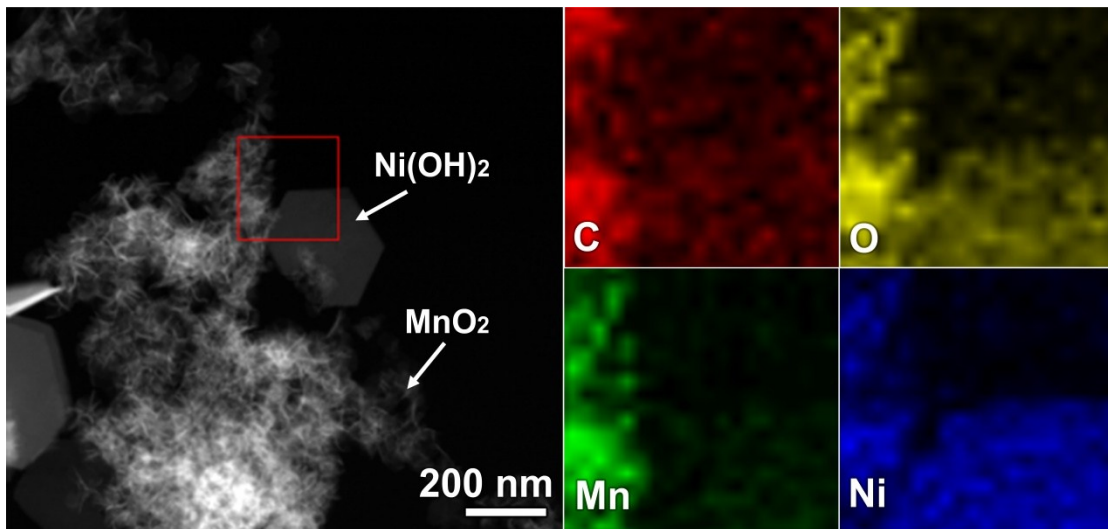**Fig. S2.** SEM images of the Ni@C composite derived from Ni-MOF.

Fig. S3. TEM image of the Ni(OH)$_2$-MnO$_2$/C composite after a strong sonication to separate the components, and corresponding EDX element mapping images of the region indicated by the red box.
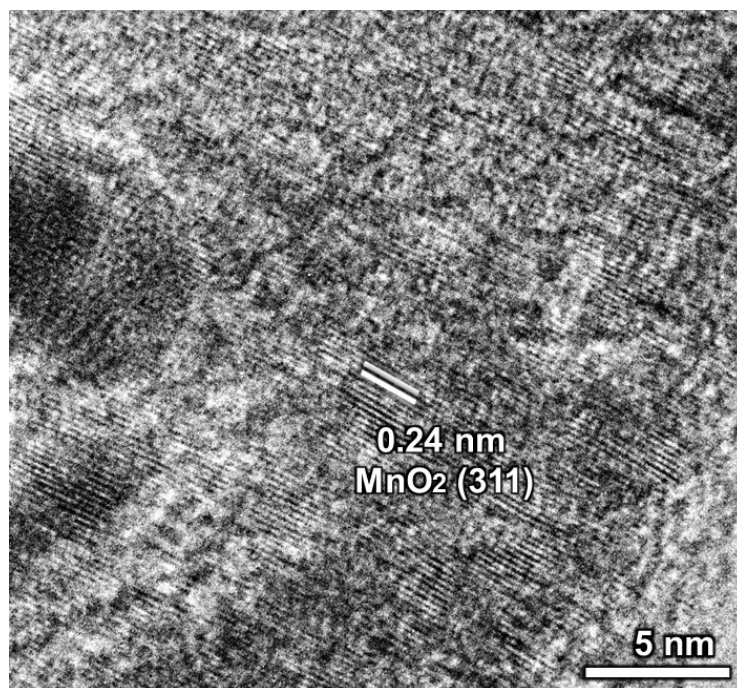

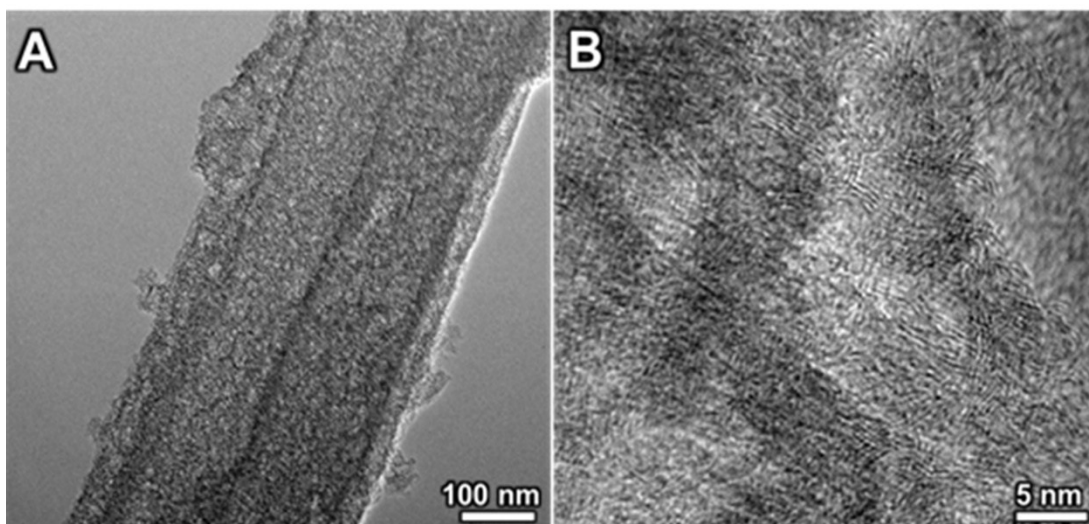**Fig. S4.** HRTEM image of a MnO$_2$ nanosheet within obtained Ni(OH)$_2$-MnO$_2$/C composite.

Fig. S5. TEM images of a porous carbon structure, which was obtained by the treatment of Ni(OH)$_2$-MnO$_2$/C composite in 1 M HCl for 8 h to completely remove Ni(OH)$_2$, MnO$_2$ and Ni.

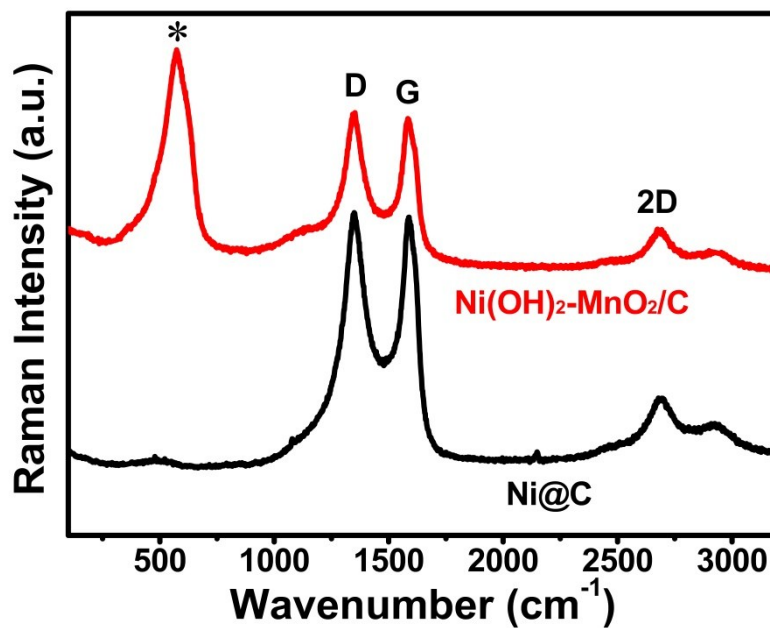**Fig. S6.** Raman spectra of the Ni(OH)$_2$-MnO$_2$/C and Ni@C composites. * indicates the peak which can be assigned to M-O (M = Ni, Mn) stretching vibrations from Ni(OH)$_2$ and/or MnO$_2$.
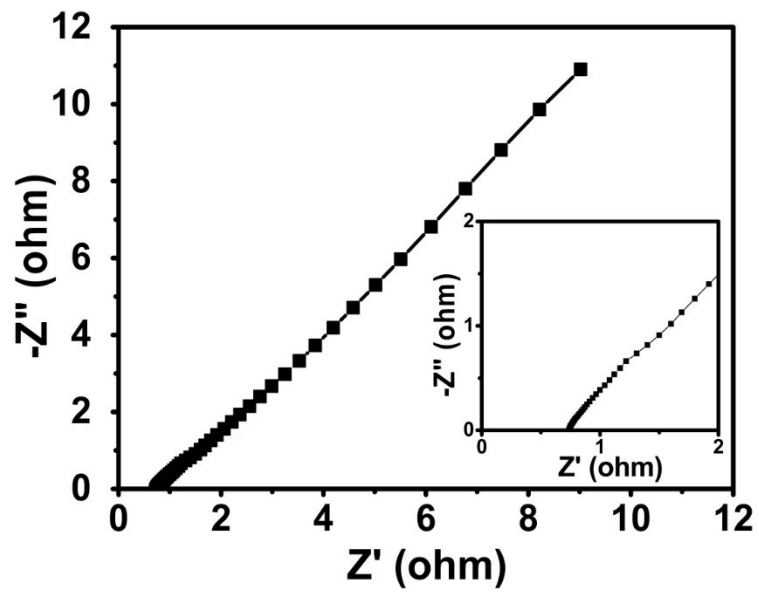
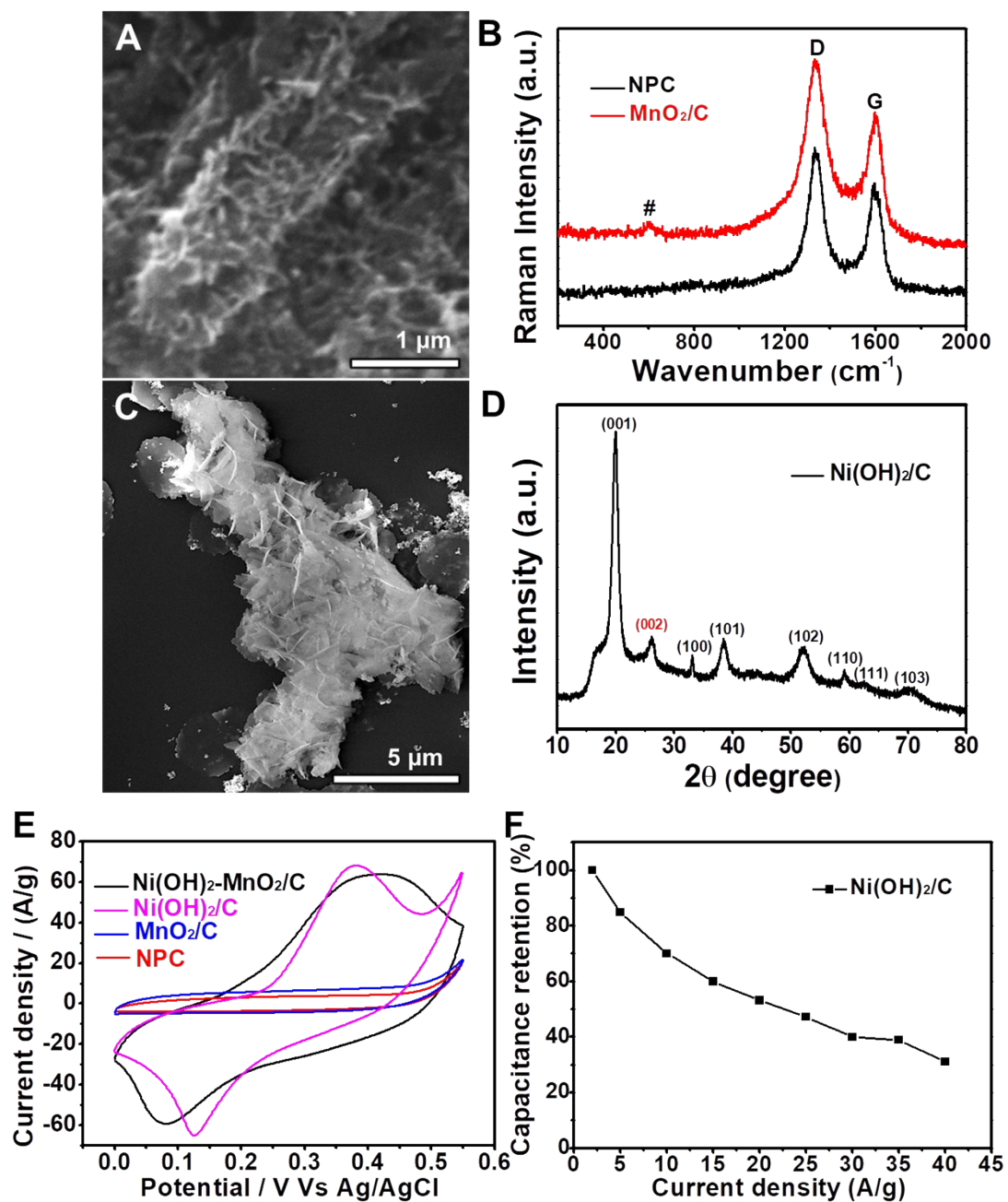**Fig. S7.** Nyquist plot of the obtained Ni(OH)$_2$-MnO$_2$/C composite.

Fig. S8. (A) SEM images of the MnO_2/C composite. (B) Raman spectra of the MnO_2/C composite and Ni-MOF-derived porous carbon (NPC). # indicates the peak corresponding to Mn-O stretching vibrations from MnO_2. (C) SEM images of the $Ni(OH)_2/C$ composite. (D) XRD pattern of the $Ni(OH)_2/C$ composite (the (002) peak is from graphitic carbon). (E) CV curves of the $Ni(OH)_2$-MnO_2/C, $Ni(OH)_2/C$, MnO_2/C and NPC at a scan rate of 100 mV/s. (F) Rate performance of the $Ni(OH)_2/C$ composite at different current densities.

Table S1. The electrochemical performance contribution of each component to the total performance of Ni(OH)$_2$-MnO$_2$/C composite.

Component	Weight percentage (%)	Performance contribution (%)
NPC	16	1.7
MnO$_2$	18	7.2
Ni(OH)$_2$	66	91.1

Based on the weight percentage of each component of Ni(OH)$_2$-MnO$_2$/C composite obtained from inductively coupled plasma-mass spectrometry (ICP-MS) measurements and corresponding result of electrochemical characterization, the performance contribution of each component can be roughly obtained, which indicates Ni(OH)$_2$ plays an essential role.
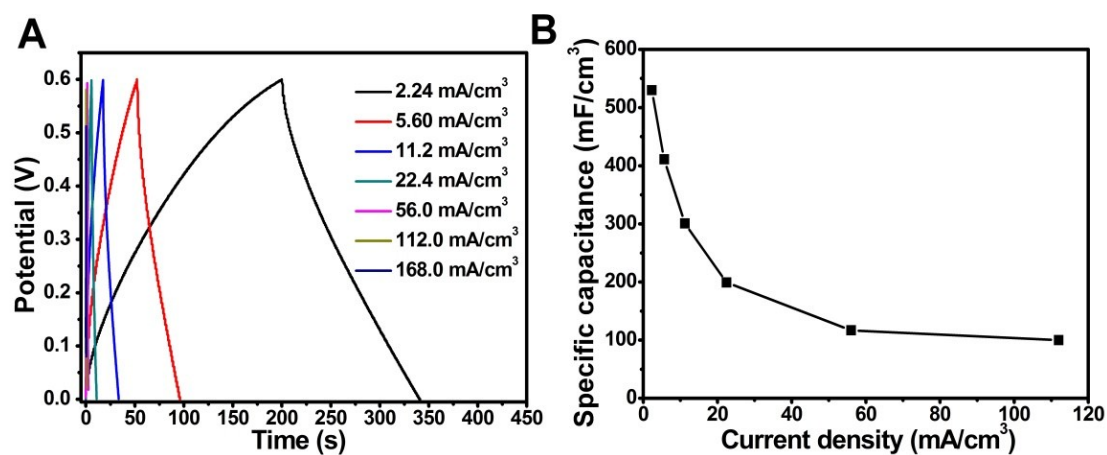

Fig. S9. Electrochemical measurements of the fabricated all-solid-state supercapacitors device based on obtained Ni(OH)$_2$-MnO$_2$/C composite. (A) Charge/discharge curves at different current densities. (B) Specific capacitances at different current densities.
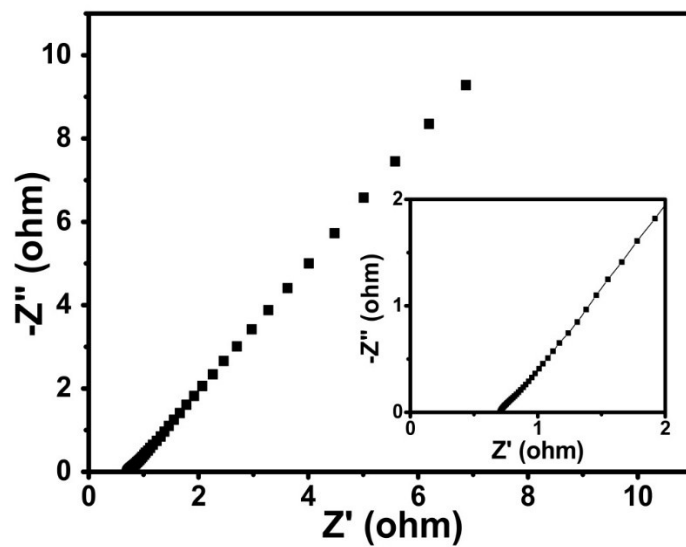
Fig. S10. Nyquist plot of the fabricated all-solid-state supercapacitors device based on obtained Ni(OH)$_2$-MnO$_2$/C composite, which shows an equivalent series resistance of 0.71 Ω.