

## Supporting Information

### **Hierarchical carbon nanofibers-based hybrid film on ultralight magnesium foil for ultrahigh energy density supercapacitors**

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## **Text S1**

### **Preparation of CNF/Ni<sub>3</sub>P-Ni@Mg**

Generally, the synthesis method of this composite material mainly consists of two steps. The first step is to immerse the processed magnesium foil in a chemical plating solution at a temperature of 80 °C for 20 minutes to form a highly conductive nickel phosphide layer (named as Ni<sub>3</sub>P-Ni@Mg). To facilitate the growth of CNFs, the Ni<sub>3</sub>P-Ni@Mg composite sample was subjected to treatment within a thermal chemical vapor deposition (TCVD) system (Type: YG-120610, Shanghai Yuzhi Technology Co., Ltd., China) by using Acetylene (C<sub>2</sub>H<sub>2</sub>) gas as a carbon source. The operation pressure and temperature were fixed at 10 kPa and 550 °C, respectively. The duration for growth of CNFs is fixed at 2 h based on the previous experiments (Fig. S8). To clarify the influence of current collector from different material, we used Al foil to replace Mg for energy density calculation (named as CNF/Ni<sub>3</sub>P-Ni@Al).

## **Text S2 Characterization**

### **Characterization methods**

X-ray diffraction (XRD, Ultima IV, Japan) analyses were carried out over a  $2\theta$  range of 20–80°, incrementing by 0.02° per minute. Cu K $\alpha$  radiation was employed for the measurements. The examination of the structure and surface morphology was conducted via scanning electron microscopy (SEM, Phenom, Phenom XL, Netherlands) operated at 5-10 kV. The samples were investigated in SEM chamber without the application of Au sputtering. This SEM equipment is coupled with an EDX detector for reviewing the elemental makeup of the samples. The phase composition of the active hybrid material deposited on the Mg substrate was ascertained using a high-resolution transmission electron microscope (FEI-TecnaiG2F30, USA), which was employed to investigate the crystal structure and morphology. The composition and valence states of CNFs/Ni<sub>3</sub>P-Ni@Mg were investigated by X-ray photoelectron spectroscopy (XPS, Thermo SCIENTIFIC ESCALAB Xi<sup>+</sup>, UK).

### **Electrochemical measurements/characterization**

An electrochemical workstation (model CHI660, Shanghai Chenhua Co., Ltd., China) was utilized to perform the electrochemical measurements, which employed a conventional three-electrode setup. The reference electrode consisted of Ag/AgCl (saturated with 3 M KCl), while the counter electrode was made of Pt sheet (99% pure, with a thickness of 1 mm). Cyclic voltammetry (CV) and corresponding galvanostatic charge/discharge (GCD) tests on the CNFs/Ni<sub>3</sub>P-Ni@Mg composite capacitor electrodes were carried out at different scan rates and current densities in 3 M KOH electrolyte solutions. The working electrode's geometric active surface area was maintained at a constant 1 cm<sup>2</sup>. Furthermore, the cyclic service life of the composite-based supercapacitor was assessed at a current density of 50 mA cm<sup>-2</sup>.

For a three-electrode system, the specific capacitance ( $C_s$ , mF cm<sup>-2</sup>) can be determined using the following equation:

$$C_s = \frac{\int I_r dV}{2au} \quad (1)$$

Where  $I_r$  represents the response current (mA),  $dV$  is the applied potential window (V),  $a$  denotes the electrode testing area (cm<sup>2</sup>), and  $u$  is the scan rate (V s<sup>-1</sup>).

To determine the energy density (E) and power density (P) of the CNFs/Ni<sub>3</sub>P-Ni@Mg capacitor electrode, a symmetric two-electrode system was employed for the supercapacitor. A pair of CNFs/Ni<sub>3</sub>P-Ni@Mg electrodes were positioned in opposition to each other and evaluated in a 3 M KOH solution. The specific capacitance, energy density (E, Wh kg<sup>-1</sup>), and power density (P, W kg<sup>-1</sup>) of these supercapacitors were computed using the following equation:

$$E = \frac{1}{2 \times 3.6} C_s (\Delta V)^2 \quad (2)$$

$$P = \frac{E_d \times 3600}{\Delta t} \quad (3)$$

Where  $V$  is the potential window (v),  $\Delta t$  is the discharge time (s), and  $m$  is the total mass of the active material (g). The mass loading of the active materials is calculated by the equation of [active area] x [thickness] x [density] x [exposed ratio]. For CNFs, the density, thickness, active area and exposed ratio are 2.1 g cm<sup>-3</sup>, 8.1 μm, 1 cm<sup>2</sup> and 50% (due to the intertwined open structure), respectively. For Ni<sub>3</sub>P-Ni, using nickel with higher density as the calculation (8.9 g cm<sup>-3</sup>), 2.1 μm, 1 cm<sup>2</sup> and 100 %, respectively.

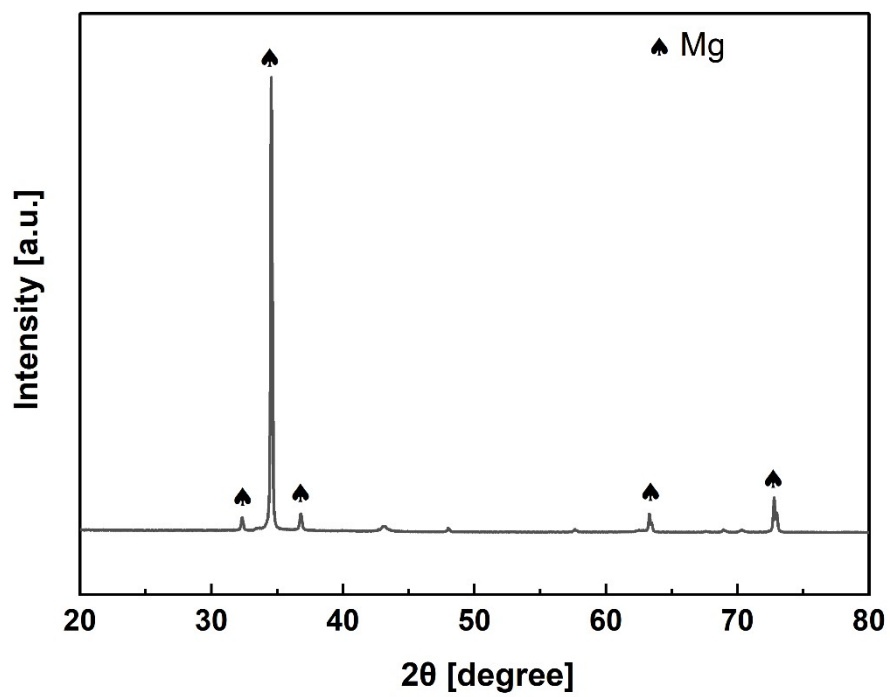
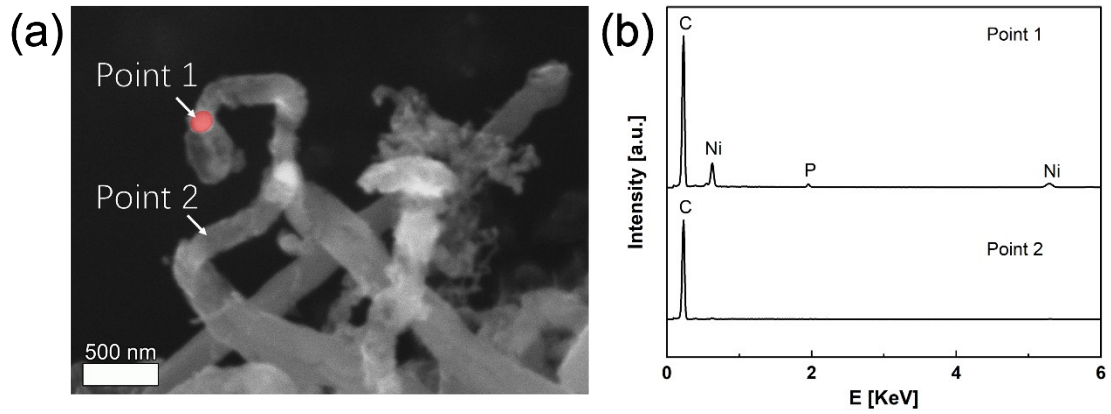
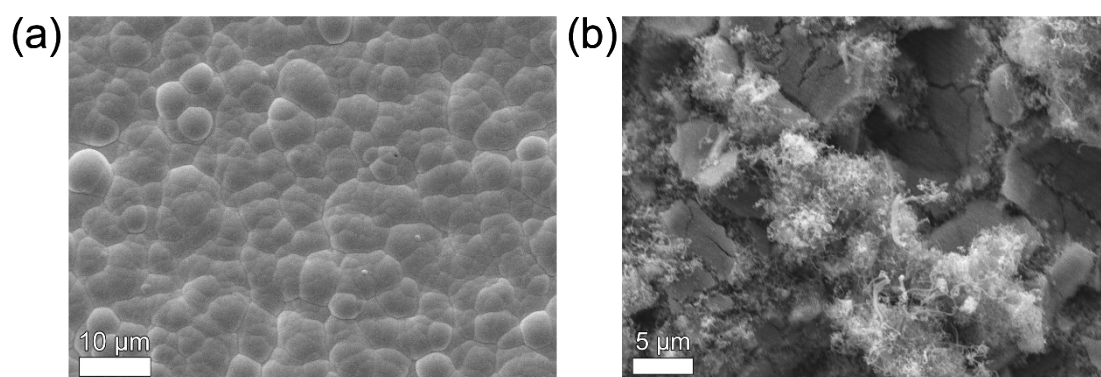


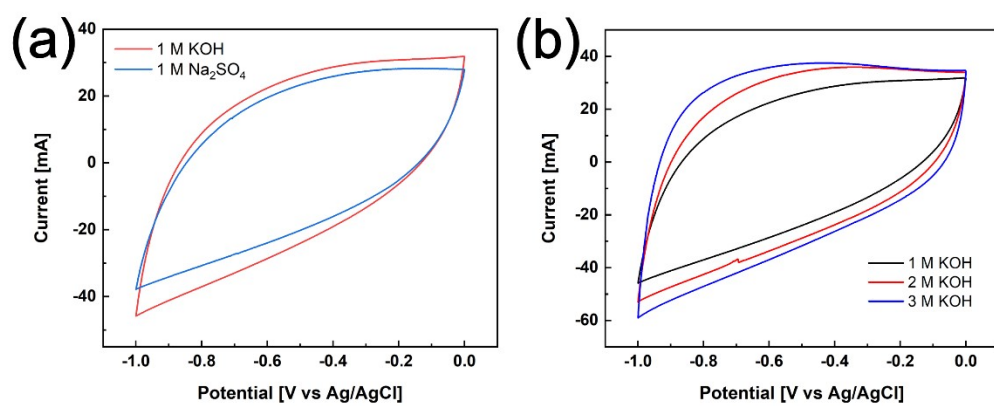
Fig. S1 XRD spectra of an applied magnesium foil.



**Fig. S2** (a) Enlarged SEM image of a CNF that grown on a nickel phosphide nanoparticle, (b) EDX spectra of the “point 1” and “point 2” in (a). A representative nanoparticle is colored with red.

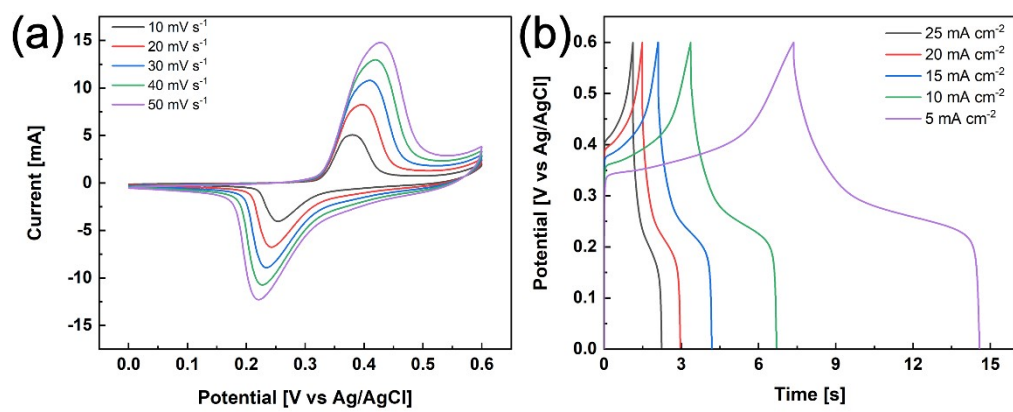


**Fig. S3** (a) SEM images of Mg after chemical nickel plating, (b) and subsequently treated in TCVD at initial growth stage.

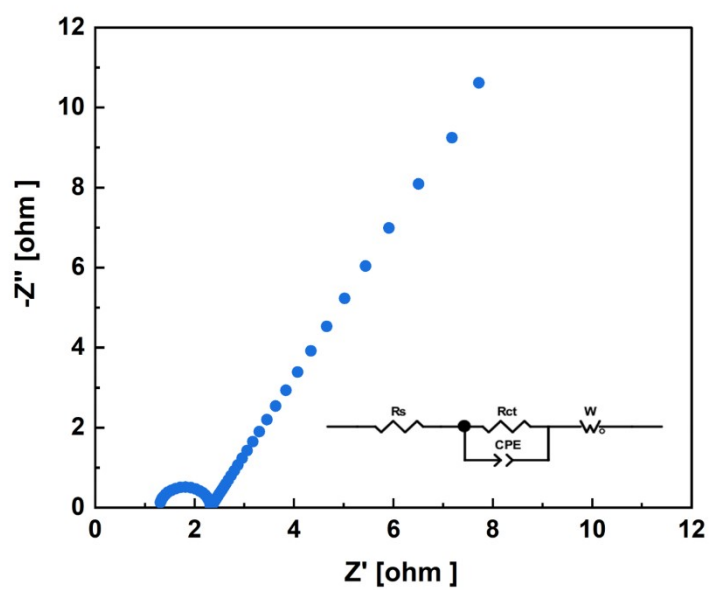


**Fig. S4** Cyclic voltammograms of CNFs/Ni<sub>3</sub>P-Ni@Mg that measured in (a) KOH and Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte, respectively, (b) in different concentrations of KOH electrolytes.

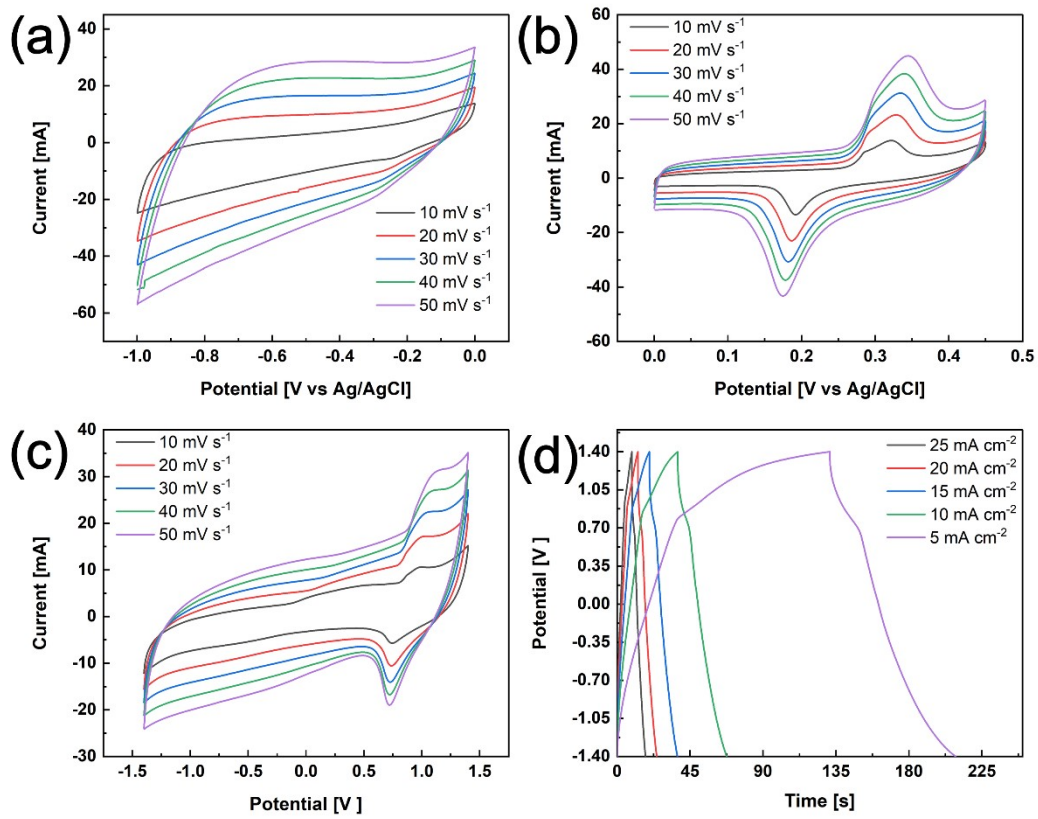




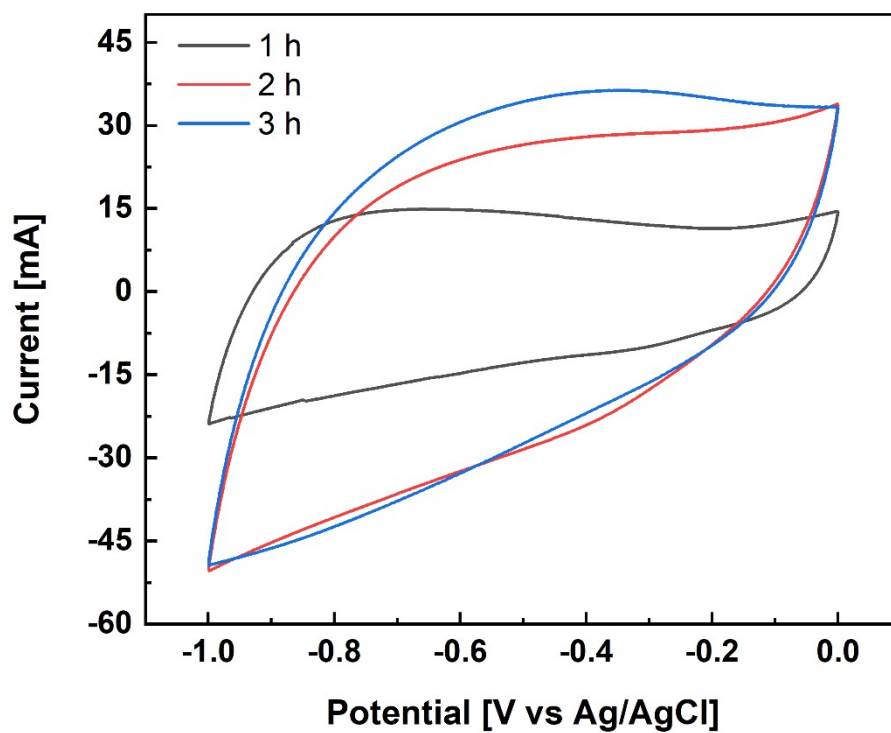
**Fig. S5** (a) CV and (b) GCD curves of Ni<sub>3</sub>P-Ni@Mg.



**Fig. S6** Nyquist plot of a CNFs/Ni<sub>3</sub>P-Ni@Mg.



**Fig. S7** (a, b) CV curves of a CNFs/Ni<sub>3</sub>P-Ni hybrid based on a Aluminium (Al) foil in a three-electrode system at various potential ranges, (c, d) the related CV and GCD curves recorded using two electrode system. For all the measurements, the used electrolyte was 3 M KOH.



**Fig. S8** Cyclic voltammograms of CNFs/Ni<sub>3</sub>P-Ni@Mg composite film with a TCVD treatment time of 1, 2 and 3 h. The scan rate was 100 mV s<sup>-1</sup>.

## Tables

**Table S1.** Chemical composition of used solution for electroless plating process on Magnesium/Aluminium foil.

Chemicals	Concentration (g/L)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	25
$\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$	30
$\text{C}_8\text{H}_{14}\text{O}_4$	4
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	5
$\text{CH}_3\text{COONa}$	8
$\text{F}_2\text{H}_5\text{N}$	0.6
$\text{CH}_4\text{N}_2\text{S}$	0.02
$\text{NH}_2\text{CH}_2\text{COOH}$	0.1

**Table S2.** Comparison of EC performance with similar transition metal/carbon composite based supercapacitors

Electrode Material	Electrolyte	Energy density(Wh/kg)	Power density(W/kg)	Ref.
Co <sub>x</sub> Ni <sub>1-x</sub> P/CNF	2 M KOH	32.20	3500	[S1]
GO@NiCoP//AG	3 M KOH	27.71	788	[S2]
Co <sub>2</sub> P@N&P/CNF	4 M KOH	22.31	225	[S3]
NiCoP@NF//AC	6 M KOH	27.00	647	[S4]
Ni <sub>2</sub> P-CNFs	6 M KOH	8.50	353	[S5]
Ni(OH) <sub>2</sub> /MWCN T/CNF	2 M KOH	47.50	750	[S6]
CNFs/Ni <sub>3</sub> P- Ni@Mg	3 M KOH	52.10	2534	This work

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