Supporting Information

Large Scalable Nickel phosphide/Nickel@Carbon Cloth based Flexible Composite Electrodes for Symmetric Supercapacitors

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Text S1 Preparation

Prior to the experiments, the carbon cloth (purchased from Taiwan Carbon Energy Company) was ultrasonically cleaned by using deionized(DI) water and ethanol. After drying, the as-obtained CC was firstly activated in 0.2 g/L $NaBH_4$ solution for 5 min, and then immersed in nickel phosphide plating solution. Briefly, the standard plating solution contains 20 g/L $NiSO_4 \cdot 6H_2O$, 20 g/L NaH_2PO_2, 20 mL/L $C_3H_6O_3$, 10 g/L $C_4H_6O_4$, 2 mg/L CS $(NH_2)_2$ and 5 g/L $C_6H_5Na_3O_7$. Diluted ammonia and sulfuric acid were used to keep the pH value of 5 during the plating solution. All the chemicals are analytical grade. The plating temperature was maintained at 65 ℃. For standard growth of nickel phosphide layer, the planting duration was 20 min. After the electroless plating, the samples were subsequently annealed at 350 ℃ for 1 h with a heating/cooling rate of 5 ℃ min^{-1}.

For preparation of pure nickel coating on CC (namely Ni@CC), transitional electro-plating method was applied, where the pure nickel plate and CC used as anode and cathode, respectively. The galvanic solution was 240 g/L $NiSO_4 \cdot 6H_2O$ and 30 g/L H_3BO_3. Other parameters were kept constant: pH value (4), temperature (45℃) and current density (2 A cm^{-2}), deposition time (3min).

Text S2 Characterization

Characterization methods

The surface morphology of Ni_3P/Ni@CC was explored by using a scanning electron microscope (SEM, Phenom, Phenom XL, Netherlands) with an accelerating voltage from 5-10 kV. The SEM is equipped with a energy-dispersive X-ray spectrometer (EDX) was utilized to identify the elemental composition of these samples. High resolution transmission electron microscope (HR-TEM) images of Ni_3P/Ni@CC were examined using (HRTEM, FEITF20, USA) at an accelerating voltage of 200 kV. The structure and phase distribution of the synthesized of Ni_3P/Ni@CC samples and CC were performed by X-ray diffraction technology (XRD, Ultima IV, Japan) coupled with the Cu Kα radiation. A micro-controlled electronic universal tensile testing machine (TSE104B, Wance Technologies Ltd., China) was employed to characterize the mechanical property in the abovementioned SEM chamber. The quantitative amount of Ni and P element in Ni_3P/Ni@CC were detected by Inductively Coupled Plasma Mass Spectrometry (ICP-MS NexION 2000, USA). Their superficial chemical states (namely Ni_3P/Ni layer) were measured with an X-ray photoelectron spectroscopy (XPS, Thermo scientific ESCALAB Xi+, USA).

The survey of X-ray photoelectron spectroscopy (XPS, Thermo scientific Xi+, USA) (Fig. 1h-k) of Ni_3P/Ni@CC confirm the presence of P, Ni, and C elements. For C1s spectrum, the characteristic peaks at binding energies ~284.4 and 288.6 eV correspond to C–C and C=O bonds, respectively.[s1] The P_{2p} peaks centered at ~128.9 and ~132.8 eV attributed to metal-phosphide (Ni-P) and phosphate (PO_4^{3-}) species, respectively. The presence of P in a negative valence state further confirms the formation of nickel phosphide. Ni_{2p} peaks at 856.1, 873.8 eV and 852.6, 869.7 eV indicated the coexistence of Ni^{2+} and Ni^0 in the Ni_3P/Ni@CC composite.[S2]"

EC measurements

An CHI660E electrochemical workstation (Chenhua, China) was applied for EC investigations of Ni_3P/Ni@CC with a standard three-electrode system in an Ag/AgCl/3 M KCl and a Pt sheet (0.5cm x0.5cm) as reference and counter electrode, respectively. All the galvanostatic charge/discharge (GCD) as well as cyclic voltammetry (CV) curves were recorded in 3 M KOH aqueous electrolyte under various scanning rates and current densities, respectively. For calculation, the mass of active materials is estimated to about 1 mg. The geometric area of the capacitor electrode was fixed at 1.0 cm^2.

Energy density (*E*) and power density (*P*) of these Ni_3P/Ni@CC//Ni_3P/Ni@CC capacitor electrodes were evaluated by employed a symmetrical two-electrode system. The symmetrical SC device was separated by a membrane (Type: N-115, Dupont, USA). The *E* (Wh kg^{-1}) and the *P* (W kg^{-1}) were calculated based on followed equation[S3,4]：

$$c_s = \frac{I \times t}{m \times \Delta v} \quad (1)$$

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

$$P = \frac{3600E}{t} \quad (3)$$

Where C_s is the specific capacitance (F g^{-1}), I is current density (A g^{-1}) of the charge-discharge, t is the discharge time (s), and ΔV is the potential window range (V).

Figures

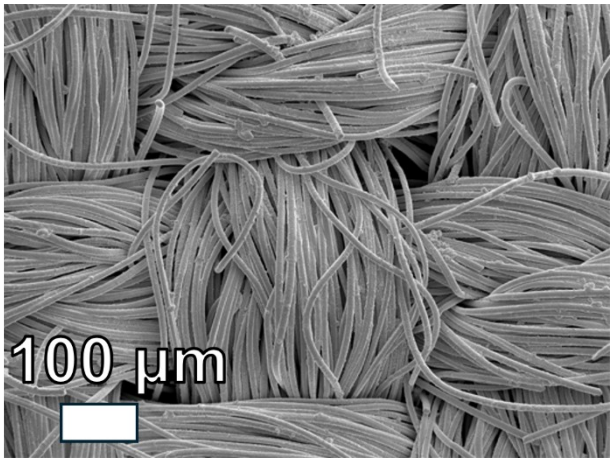

Fig. S1 SEM images of a Ni_3P/Ni @CC sample in low magnification.

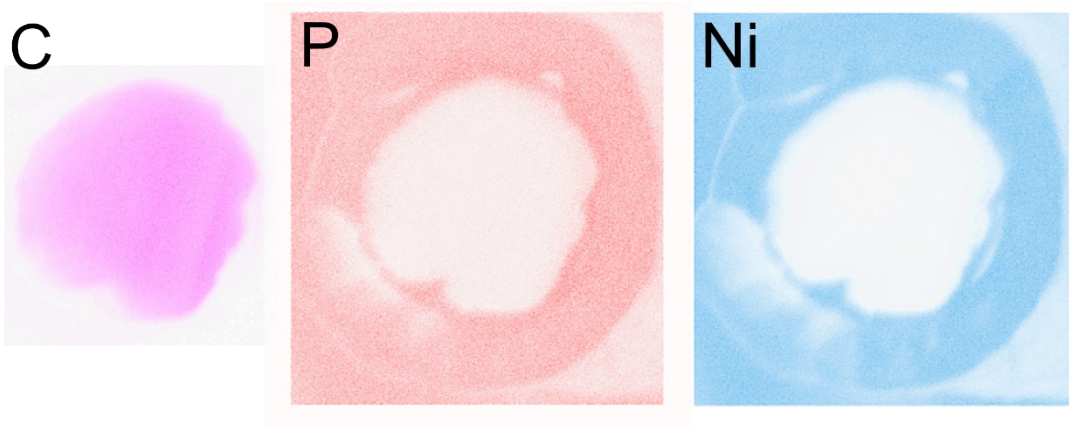

Fig. S2 EDX elemental mapping images of Ni, P and C, which recorded on a cross-section of an individual Ni_3P/Ni@CC fiber.

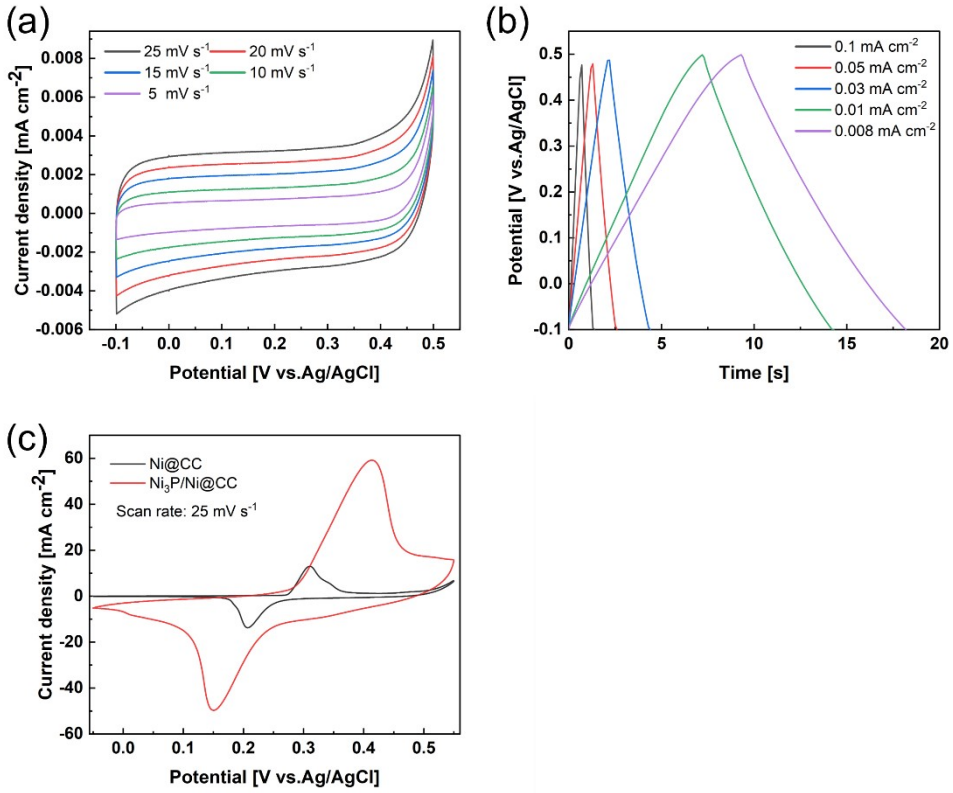

Fig. S3 CV curves and GCD curves of (a, b) a pristine CC and (c) comparative CVs of Ni@CC and Ni_3P/Ni@CC in 3 M KOH electrolyte.

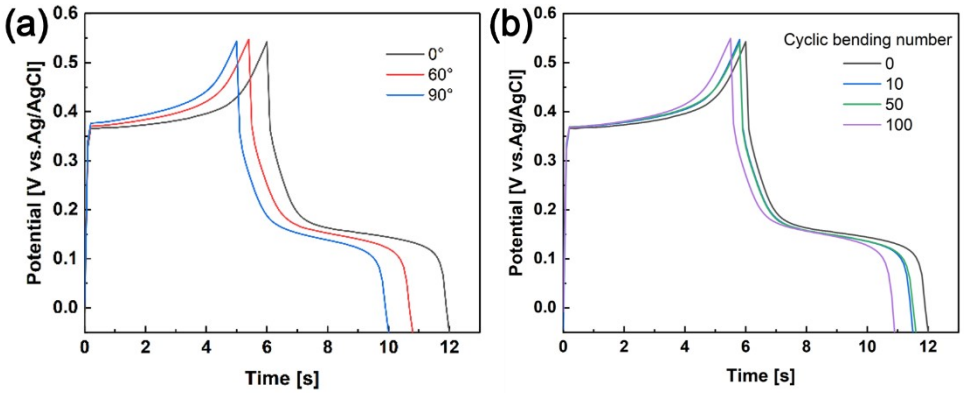

Fig. S4 (a) GCD curves under bonding state different bending angles. (b) GCD curves of the Ni_3P/Ni@CC based SCs after the periodic bending test (up to 60°) for different times.

Tables

Table S1. Deposition cost for fabrication of 1m^2 Ni_3P/Ni@CC.

Chemicals[2]/Item	Price (USD/kg)[1]	Dosage (g/m^2)	Cost (USD/m^2)
$NiSO_4$	5.10	200	0.42
NaH_2PO_2	22.03	200	4.40
$C_6H_5Na_3O_7$	0.75	50	0.04
C_3H_6O	1.01	200	0.20
$C_4H_6O_4$	1.79	100	0.18
		Subtotal[2]	1.05
Electricity[3]			0.8
		Total	1.85

*1. The prices of chemicals are obtained from the internet: https://china.chemnet.com/ For calculation, the currency exchange rate is 1 USD= 7.22 CNY.

2. Metal turn over (MTO) of the planting solution is estimated to 5.

3. Electricity for heating and maintain the planting solution at the temperature of 65 °C. For calculation, the price of electricity is fixed at 0.14 USD/kwh

Table S2. The ICP-MS test of Ni and P contents in Ni_3P/Ni@CC.

Element	Atomic percentage%
Ni	82.02
P	17.98

Table S3. Summary of nickel phosphide based SCs.

Electrode	Electrolyte	E (Wh kg^{-1})	P (W kg^{-1})	Ref.
Ni_3P//AC	6 M KOH	34.2	299.9	S5
Ni@NCP//rGO	1 M KOH	23.37	400.6	S6
Ni_2P@ CM//AC	3 M KOH	47.46	397	S7
Ni_2P/NCHT//ACF	2 M KOH	46.53	1125	S8
Ni_2P@C//AC	1 M KOH	44.0	800	S9
Ni_3P/Ni@CC	3 M KOH	51.1	3500	This work

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