One-step electrospinning of carbon nanowebs on metallic textiles for high-capacitance supercapacitor fabrics

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Supporting information

1. Experimental section

Preparation of conductive cotton fabric current collectors by polymer-assisted metal deposition (PAMD)

The Ni-coated cotton fabric was fabricated by using polymer-assisted metal deposition (PAMD) method as published in the previous papers.[1, 2] In this typical experiment, commercially available cotton fabrics were firstly dipped into an ethanol solution of poly[2-(methacryloyloxy)ethyl trimethylammonium chloride-co-3-(trimethoxysilyl)propy methacrylate] (P(METAC-co-MPTS)), and then dried at 80°C for 10 min. After that, the fabrics were incubated in an ammonia (95% humidity) atmosphere for about 4 h at room temperature followed by being baked at 80°C for 2 h. Subsequently, the samples were immersed into an aqueous solution of Ammonium Tetrachloropalladate(II) ($(NH4)_2PdCl_4$) (5 mM) for 15 min and then rinsed by deionized (DI) water for several times. Finally, the $PdCl_4^{2-}$ moieties-loaded fabrics were immersed into the electroless deposition (ELD) bath of nickel and the Ni-coated cotton fabric (Ni-Cotton) was obtained. The detailed recipe and procedures for electroless deposition of nickel can be found in the literature.[3, 4]

Preparation of cotton fabric electrodes by electrospinning

In order to form a uniform suspended solution for the electrospinning process, multi-wall carbon nanotubes (MWCNTs) were firstly treated in a mixed H_2SO_4/HNO_3 (v/v=3:1) solution with continues sonication at a low temperature of 45°C for 5 h. Then the treated MWCNTs were dispersed into a Polyacrylonitrile (PAN, Mw=150,000) dissolved *N*,*N*′-dimethyl-formamide (DMF) solution. The weight ratio of MWCNTs and PAN was kept at 20/80, 40/60, 60/40, 70/30 and 80/20, respectively. For the electrospinning process (TL-Pro, Tong Li Tech), Ni-Cotton fabrics were placed on the cylindrical collector as the collecting substrates. Then the

electrospinning process was conducted at an electrical potential of 25kV applied between the spinneret and the collector with a suspension feeding rate of 1 mL/h and the gap between spinneret and the collector was kept at 25 cm. The electrospinning time was controlled accordingly. Finally, the fabric electrodes were obtained with a compact carbon nanofiber web covering on the surface of Ni-Cotton (C-Web@Ni-Cotton).

Assembly of the fabric supercapacitors

For the liquid device, two pieces of C-Web@Ni-Cotton as electrodes were separated by a piece of clean pristine cotton fabric. They were wrapped by Polytetrafluoroethylene (PTFE) tape and immersed in 1M Sodium sulphate (Na_2SO_4) aqueous electrolyte. For the solid device, two electrodes were immersed into Lithium chloride (LiCl) aqueous solution and the separator (pristine cotton fabric) was soaked with Polyvinyl Alcohol (PVA)/LiCl gel electrolyte, respectively. After that, they were assembled into a fabric supercapacitor dried in air to remove excess water in the electrolyte. Finally, the device was encapsulated with plastic tape or waterproof fabrics for electrochemical testing. PVA/LiCl was prepared by dissolving LiCl (6.3g) and PVA (3g) in DI water (30mL) and stirring at 85°C for 1 h.

Characterization Method

The morphologies of treated CNTs and as-made fabric electrodes were observed by scanning electron microscope (SEM, TM3000, Hitachi) and transmission electron microscope (TEM). Their chemical composition information was characterized by Fourier transform infrared spectroscopy (FTIR, Spectrum 100, PerkinElmer) and X-ray photoelectron spectroscopy (XPS), respectively. XPS measurement was carried out with a Sengyang SKL-12 spectrometer using $Mg_{K\alpha}$ radiation. A homemade four-probe measurement method was applied to obtain the electrical resistance of the Ni/cotton fabric. The detailed procedure of preparing the four-probe electrodes and its testing method can be found in the literature.[5] For the electrochemical performance testing, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were performed on a CHI600e electrochemical workstation. The electrochemical impedance spectra (EIS) were recorded using a Solartron 1255 frequency response analyzer coupled with Solartron 1287 electrochemical interface. The areal capacitance

C (mF/cm^2) of the fabric supercapacitor was calculated from the GCD curve by using the equation: $C = It/(VS)$, where I (mA) is the discharging current, t (s) is the discharging time, V (V) is the potential window during discharging process and S (cm^2) stand for the contact surface area of the electrodes.

2. Characterization of acid-treated MWCNTs

The FTIR spectra (Fig. S1a) indicates the existence of carboxylic acid (-COOH) groups, where the vibrational modes at 3467, 1637 and 1400 cm^{-1} represents the O-H stretching, carbonyl stretching and out of plane O-H bending, respectively.[6] Fig. S1b shows the C1s core level XPS spectrum of this treated CNTs sample. The C1s peak can be deconvoluted into three peaks attributed to C-C (284.3 eV), C-OH (285.7 eV) and –COOH bonds, respectively.[7-9] By calculation from the XPS spectra, the oxygen ratio is 15%.

TEM images (Fig. S1c and S1d) clearly show the morphology of MWCNTs. The MWCNTs are typical multiwall carbon nanotube with the wall thickness of averagely 13nm, which is consistent with the specification provided by the manufacturer (10-15 nm). The interlayer distance in the MWCNTs can be estimated at 0.37 nm. In addition, shortcut MWCNTs with length less than 5μm are found, which was due to the acid treatment.

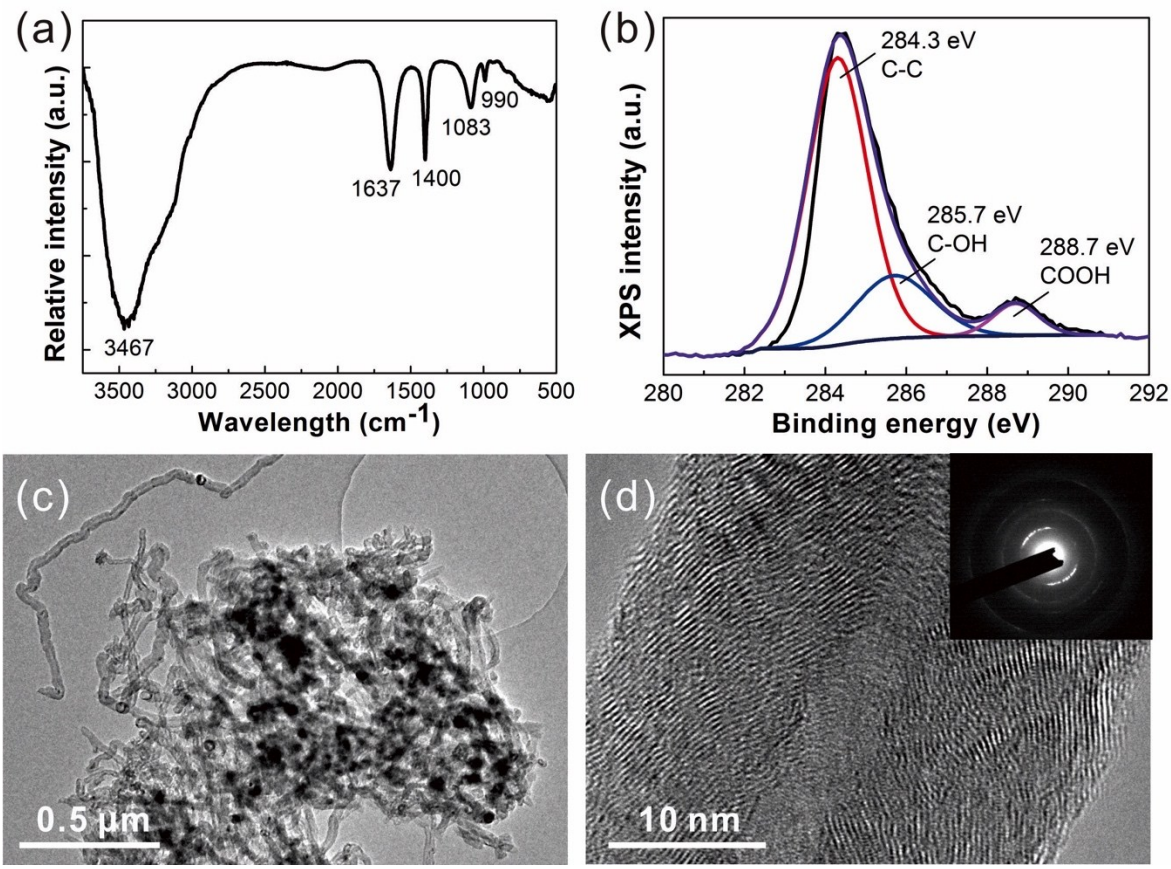

Fig. S1 (a) IR spectra and (b) C1s core level XPS spectrum of the treated MWCNTs. (c) TEM image and (d) HRTEM image of the treated MWCNTs. The insert graph in (d) is the electron diffraction pattern.

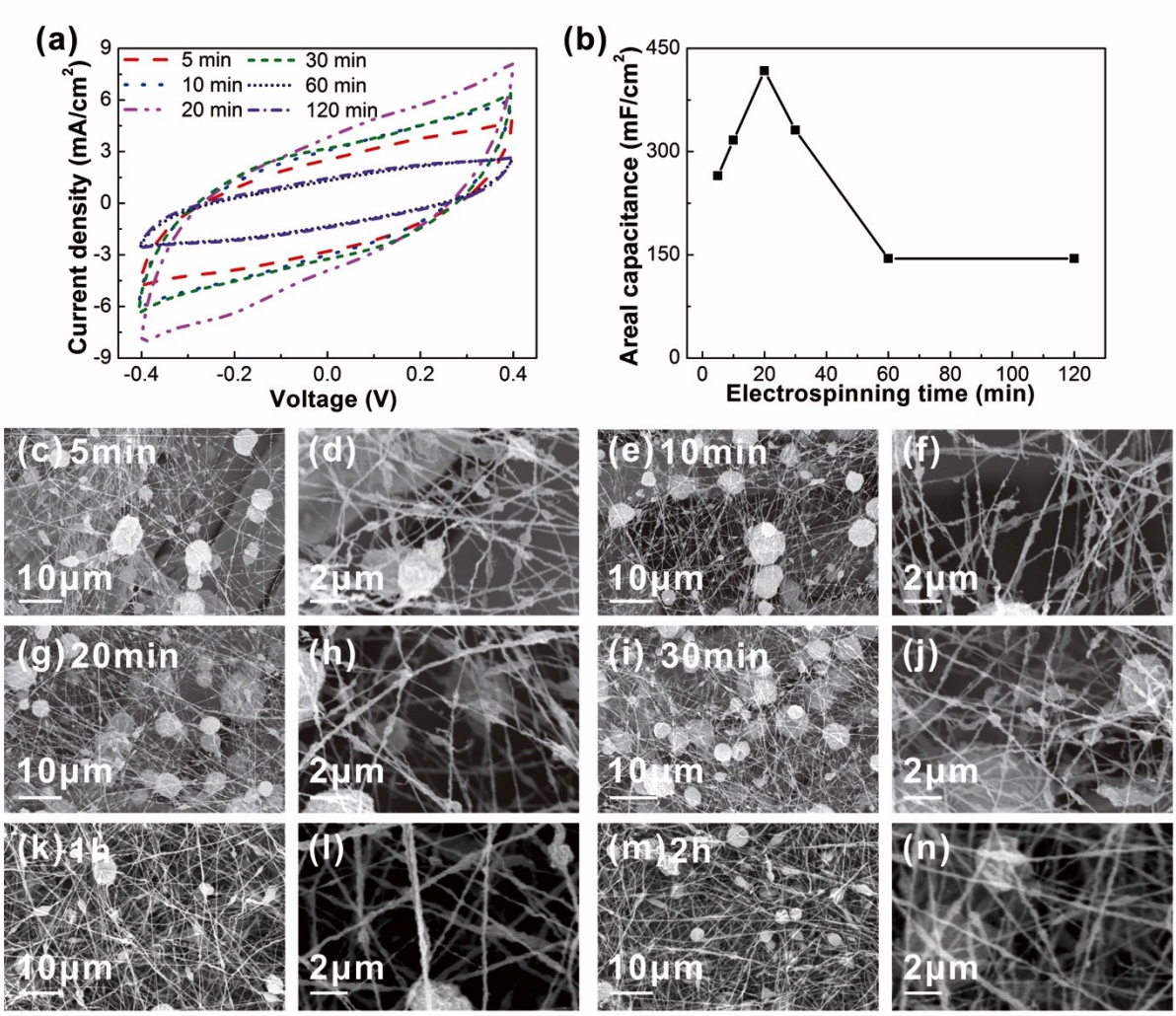

Fig. S2 CV (a) curves and the summary real capacitance (b) of the C-Web@Ni-Cotton supercapacitor fabrics obtained by using different lengths of electrospinning time and tested in 1M Na_2SO_4 liquid electrolyte. The scan rate is 10 mV/s. SEM images of the carbon nanoweb obtained by using different lengths of electrospinning time from 5 min (c) (d), 10 min (e) (f), 20 min (g) (h), 30 min (i) (j), 1 h (k) (l) to 2 h (m) (n).

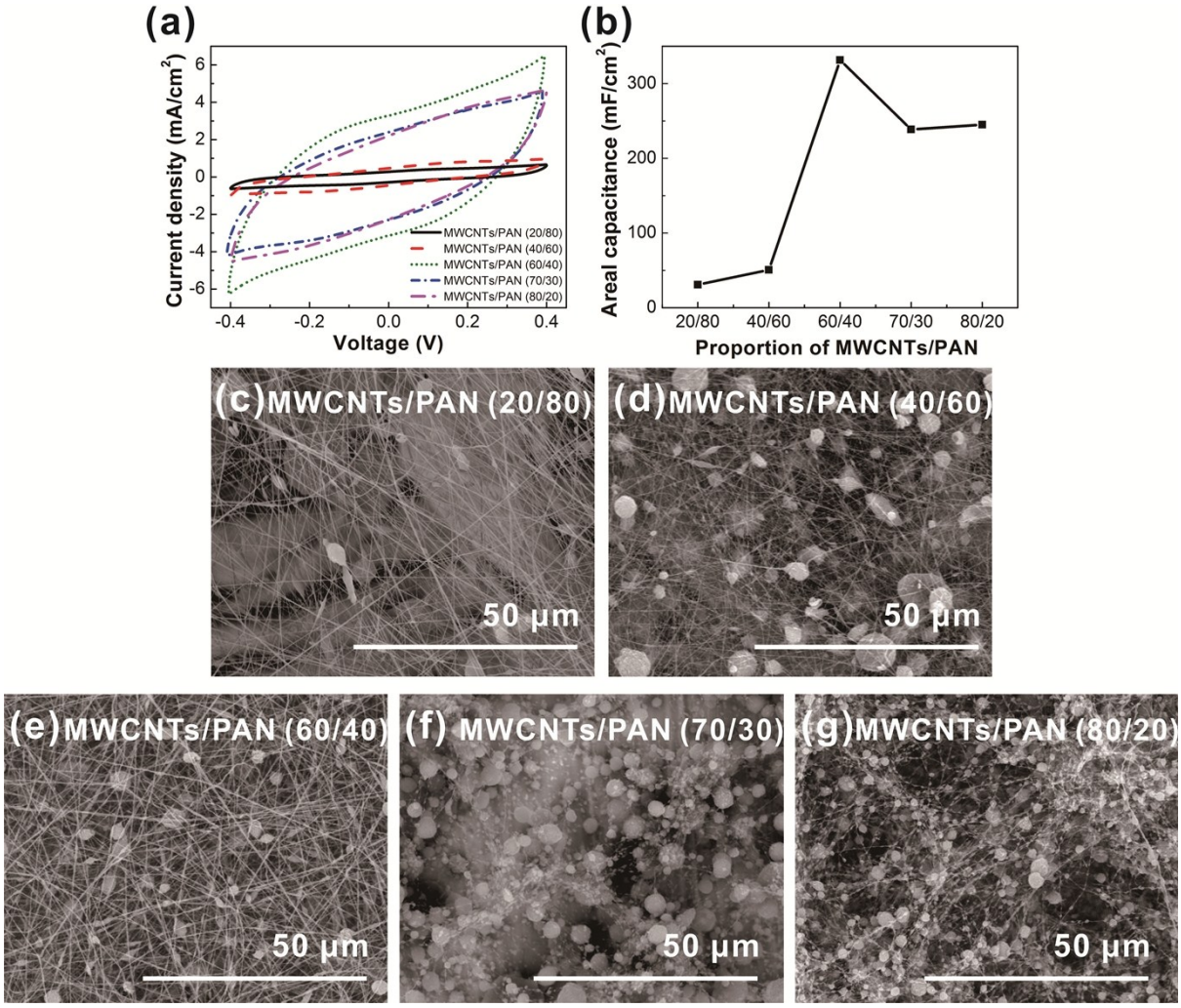

Fig. S3 CV curves (a) and the summary of areal capacitance (b) of C-Web@Ni-Cotton supercapacitor fabrics obtained by using different MWCNTs/PAN proportions of electrospinning solutions and tested in 1M Na_2SO_4 liquid electrolyte. The scan rate is 10 mV/s. SEM images (c)-(g) of the carbon nanofiber webs by using different MWNTs/PAN proportions.

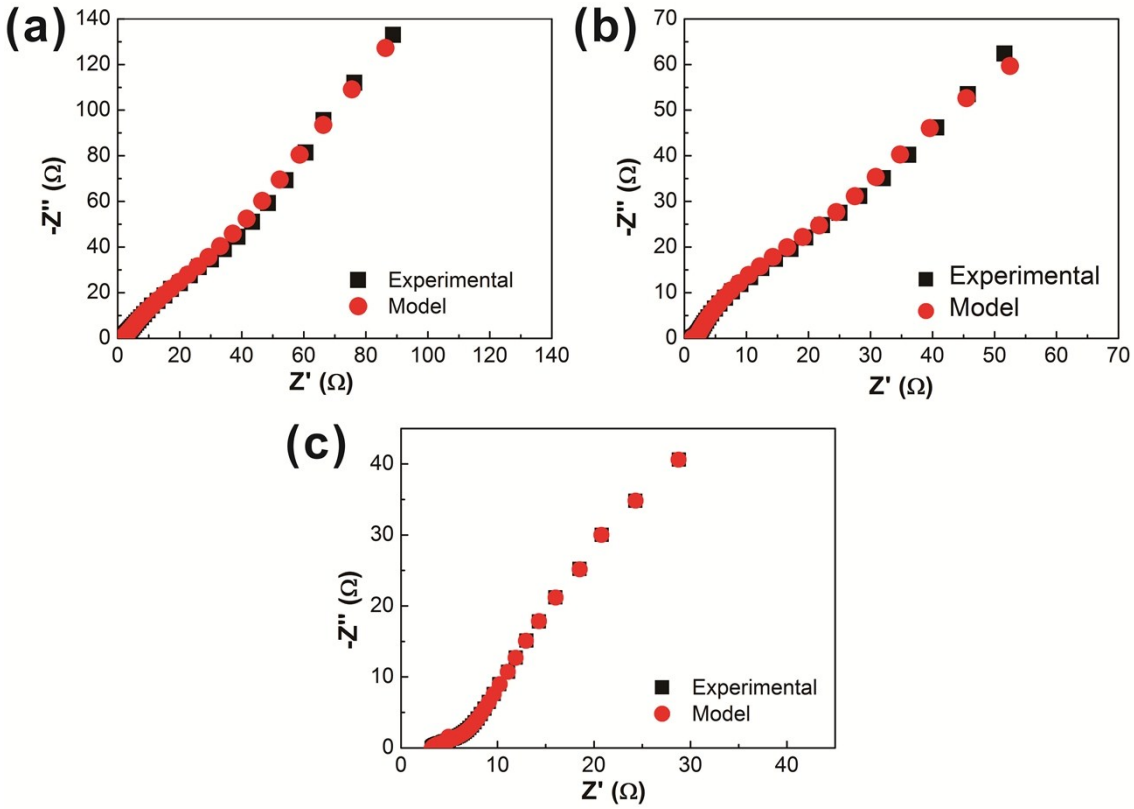

Fig. S4 Experimental (black curve) and modeled EIS plots for the samples (a) before and (b) after 3000 cycles tested in liquid electrolyte and the (c) solid-stated supercapacitor fabric.

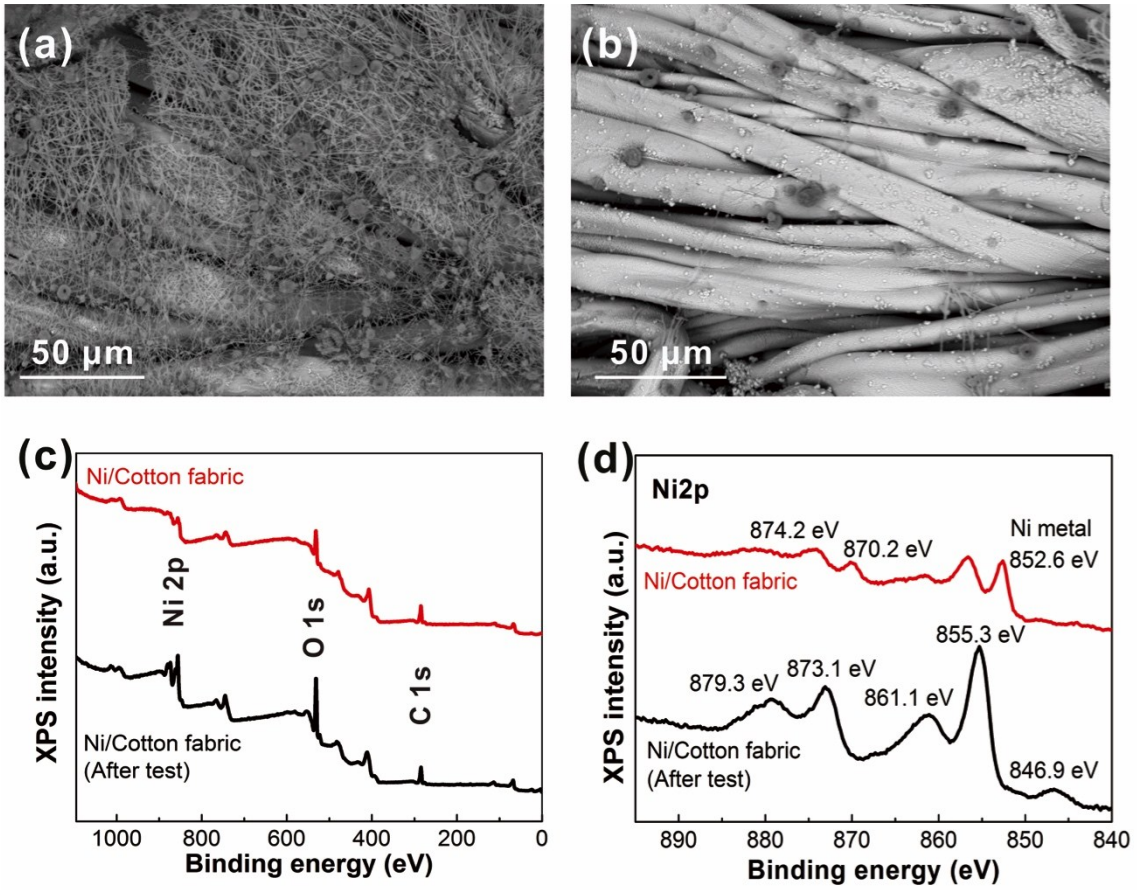

Fig. S5 SEM images of the C-Web@Ni-Cotton fabric electrode (a) and the Ni-Cotton current collector (b) after electrochemical retention test. XPS spectra across a wide scan (c) and Ni2p XPS spectra (d) of the Ni-Cotton fabric before (red line) and after (black line) electrochemical test.

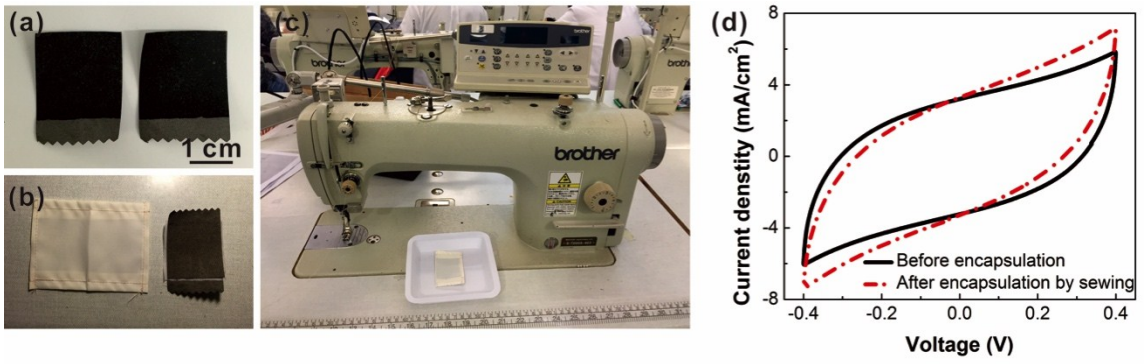

Fig. S6 Photographs of C-Web@Ni-Cotton fabric electrodes with large dimension (a), components for assembling the supercapacitor fabrics (b) and sewing machine (brand: Brother) that used for the integration of the fabric device into commercial fabrics (c). (d) CV curves of the supercapacitor fabrics before and after encapsulation by sewing technology.

Table S1 Summary of the performance of fabric-based supercapacitors.

Electrode materials	**Electrolyte material**	**Areal capacitance (mF/cm^2)**	**Flexibility**	**Source**
MnO_2/TiN@Carbon cloth//activated carbon cloth	5M LiCl	215.2 @6 mA/cm^2	-	[9]
GO@cotton cloth	6M KOH	194 @1 mA/cm^2	-	[10]
Activated carbon@Cotton fabric	1M Na_sSO_4	435 @5 mA/cm^2	-	[11]
SWCNT@Cotton fabric	1M LiPF6	480 @0.2 mA/cm^2	-	[12]
PANI/SWCNT@Wood fiber cloth	1M H_2SO_4	92 @0.2 mA/cm^2	-	[13]
Carbonized electrospun MWCNT (23%)-embedded PAN	6M KOH	144 @1 mA/cm^2	-	[14]
Ppy/MO@cotton fabric	2M NaCl	309 @0.6 mA/cm^2	-	[15]
C-Web@Ni-Cotton supercapacitor fabric	1M Na_sSO_4	973.5 @2.5 mA/cm^2	-	This work
Activated carbon@Knitted carbon fabric	Solid SiWA	440 @4.8 mA/cm^2	80% @11^{th} bending test	[16]
Co-based MOF/PANI@Carbon cloth	PVA/H_2SO_4	35 @0.05 mA/cm^2	-	[17]
Electrospun PEDOT@Carbon cloth	EMIBF4 and PVDF-co-HFP	80 @2 mA/cm^2	-	[18]
PANI/CNT@Au-Polyester fabric	PVA/H_3PO_4	103 @1 mA/cm^2	No decay after 1 bending test	[19]
Activated carbon cloth	PVA/H_2SO_4	28 @1 mA/cm^2	No decay after 1 bending test	[20]
MnO_2/ZnO@Carbon cloth	PVA/LiCl	26 @0.5 mA/cm^2	-	[21]
C-Web@Ni-Cotton supercapacitor fabric	PVA/LiCl	275.8 @1 mA/cm^2	No decay after 2000 cycles	This work

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