Supporting Information

Conductive membrane of EVA filled by carbon black for flexible energy-storage devices

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Experiment section

Materials and preparation

Ethylene-vinyl acetate (EVA) copolymer containing 32% vinyl acetate (melt flow rate: 3.2 g/10 min at 230 °C and 2.160 kg) was supplied by Sinopec Group, Maoming petroleum Chemical Industry Limited Company, China. Carbon black (particle diameter: 40~60 nm) was obtained from Dongzheng Chemical Industry Limited Company, China. Carbon (CB) and carbon nanotube (CNT) filled EVA composites membranes were prepared in the following procedure:

All the materials were adequately dried in a vacuum oven at appropriate temperatures. In order to improve the dispersion of carbon black (CB) and carbon nanotubes (CNT) in EVA, solution mixing process was used to prepare EVA/CB/CNT composites. X mass of EVA, y mass of CB and z mass of CNTs were dissolved in toluene, and they were mixed in a beaker. The resultant mixture was thoroughly homogenized using ultrasound and finally casted into thin sheets.

Anodic electrodeposition of MnO_2 was carried out in a conventional three-electrode glass with a constant current density of 1mA cm^{-2} from a solution containing 0.01 M manganese acetate ($MnAc_2$) and 0.02 M ammonium acetate (NH_4Ac). The working electrode is the as-prepared $E_{50-x/2}B_{50-x/2}C_x$ (x= 1, 3, 5, 0) conductive substrates (0.5*1.5 cm^2), while a graphite rod of about 4.0 cm^2 was used as the auxiliary electrode, and a saturated Ag/AgCl was used as the reference electrode. Prior to electrodeposition, the working electrode was cleaned ultrasonically in distilled water, ethanol, and acetone and then rinsed in distilled water again. The reaction temperature and deposition time are at 70 ^oC and 20 min, respectively.

Assembly of the solid-state Supercapacitor

The solid-state supercapacitor was assembled by two piece of $MnO_2/E_{49.5}B_{49.5}C_1$ electrodes with a separater (Whatman 8 μm filter paper) sandwiched in it. The PVA/H_3PO_4 gel was used as solid electrolyte and binder between the electrodes and separater. PVA/H_3PO_4 electrolyte was

simply made as follows: 6 g PVA powder was added to a mixed solution of 6 g H_3PO_4 and 60 ml deionized water. The whole mixture was heating up steadily to ~ 85 °C under vigorous stirring until the solution became clear. Then the solution was kept at 85 °C without stirring. Prior to the assembling, the $MnO_2/E_{49.5}B_{49.5}C_1$ electrodes were immersed into the PVA/H_3PO_4 solution for 10 minutes and kept the bare substrate part without samples above the solution. And then, they were assembled and kept at room temperature. At last, the solid-state supercapacitor was prepared succesfully after the PVA/H_3PO_4 gel solidified.

Mechanical testing

Before testing, all specimens were conditioned at 25 °C and 50 % relative humidity for 5 days. Tensile properties were characterized using a Hounsfield THE 10K-S testing machine according to ASTM D 638.Five samples were tested from each compound and the average results were recorded.

Characteriazation

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The resistivity of $E_xB_yC_z$ substrates is measured by a standard four-probe method using a homemade ST2253 digital and intelligent four-probe probe. The morphologies, chemical composition of the products were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F), X-ray diffraction (XRD, D8 ADVANCE), respectively. The electrochemical properties of the products were investigated with cyclic voltammetry (CV), charge-discharge measurements and electrochemical impedance spectroscopy in a conventional three-electrode cell employing a CHI 760D electrochemical workstation (Chenhua, Shanghai).

Data analysis

The power density and energy density were calculated by using the following equations:

$$P = V^2 / [4RS] \quad (1)$$

$$E = 0.5CV^2/S \quad (2)$$

where V is the applied voltage, R is the internal resistance calculated by equation (3), S is the total area of active electrode materials, and C is the measured total areal capacitance

of electrode calculated by equation (4):

$$R = \Delta V_{iR} / 2I \quad (3)$$

$$C = I\Delta t / [SV] \quad (4)$$

where I is the applied current, ΔV_{iR} is the voltage drop between the first two points from its top cut-off of discharge curve, Δt is the discharge time after the initial iR drop.

Table S1. Tensile properties of EVA, EVA/CB, and EVA/CB/CNTs composites

Sample EVA/CB/CNTs	Young's modulus / MPa	Elongation at break / %	Tensile strength / MPa
100/0/0	5.1±1.4	663.9±62	3.1±0.7
90/10/0	9.0±0.8	624.5±36	3.3±0.3
80/20/0	15.7±1.6	453.6±31	2.5±0.3
70/30/0	60.7±31	141.8±70	2.8±0.2
60/40/0	104.4±12	166.9±30	3.7±0.5
50/50/0	134.2±42	23.0±4	1.9±0.4
49.5/49.5/1	156.2±19	22.0±3	2.1±0.2
48.5/48.5/3	210.8±19	12.0±2	3.1±0.3
47.5/47.5/5	211.5±14	10.0±2	3.2±0.3

Table S2. Conductivity of FTO, PETI, EVA, and EVA/CB/CNTs composites

Substrates	Conductivity (S cm^{-1})
FTO	7.74×10^{-1}
PETI	6.02×10^{-3}
Ti	4.00×10^{3}
$E_{50}B_{50}C_0$	4.38×10^{-2}
$E_{49.5}B_{49.5}C_1$	1.67×10^{-1}
$E_{48.5}B_{48.5}C_3$	1.72×10^{-1}
$E_{47.5}B_{47.5}C_5$	2.34×10^{-1}

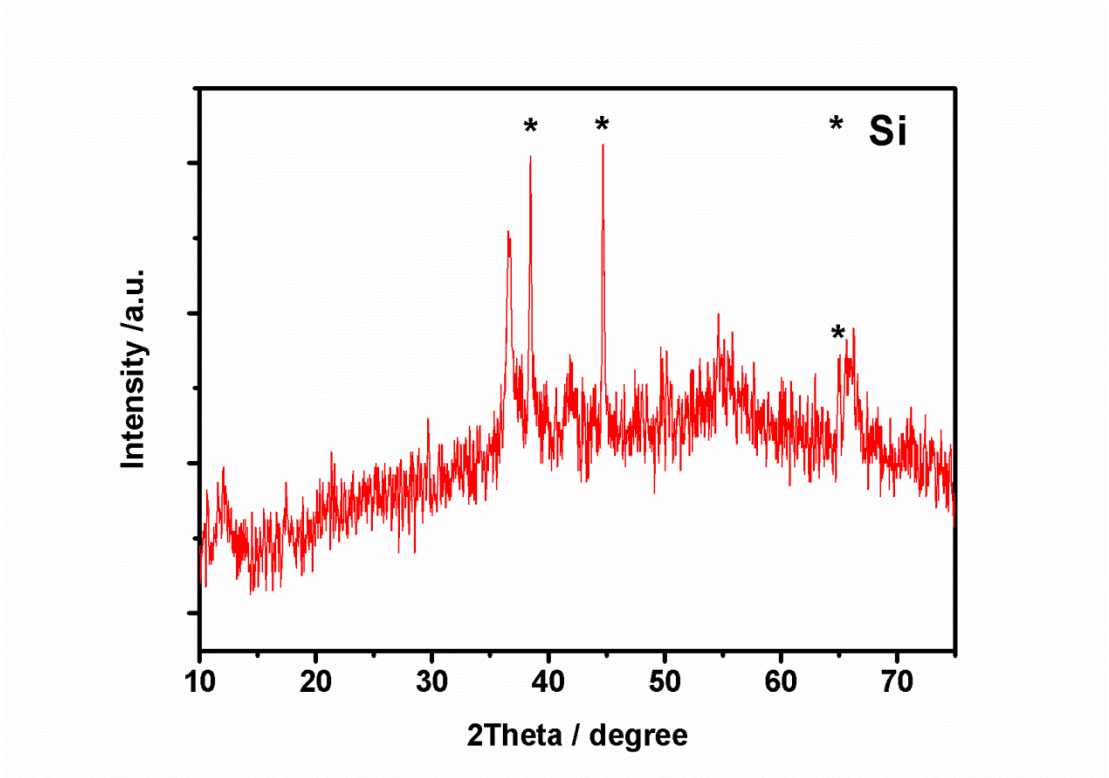

Fig. S1 XRD pattern of MnO_2 electrodeposited on the $E_{49.5}B_{49.5}C_1$ substrate.

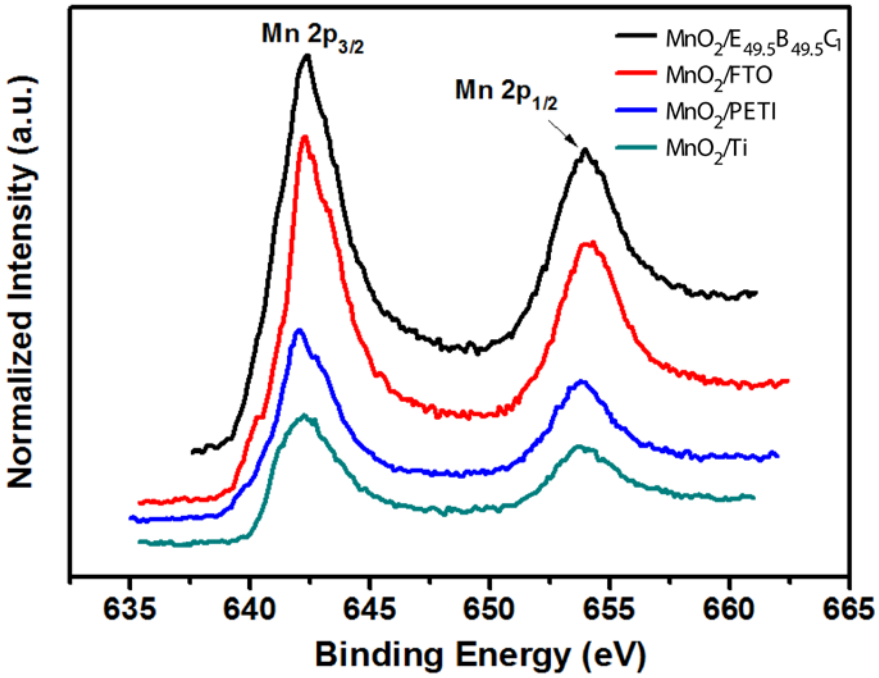

Fig. S2 Mn 2p XPS spectras of MnO_2 electrodeposited on the $E_{49.5}B_{49.5}C_1$, FTO, PETI, and Ti substrates.

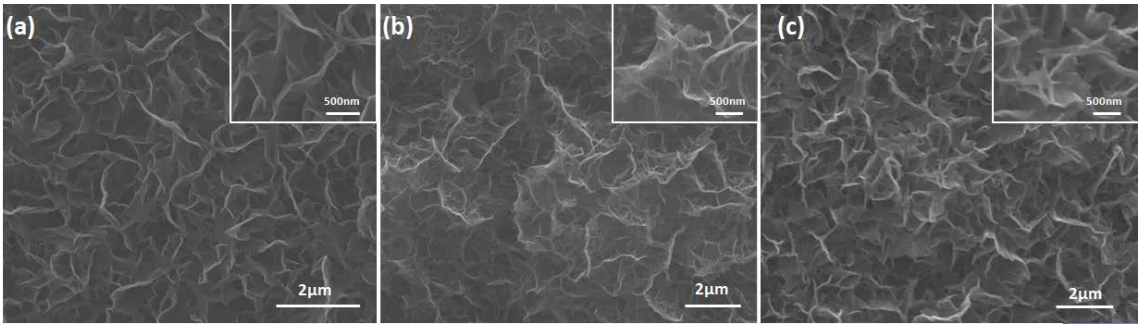

Fig. S3 SEM images of the as-prepared (a) MnO_2 electrodeposited on F doped SnO_2 (FTO) glass, (b) MnO_2 electrodeposited on flexible PET (polyethylene terephtalate)/ITO (indium tin oxide) substrates (PETI), (c) MnO_2 electrodeposited on Ti substrate.

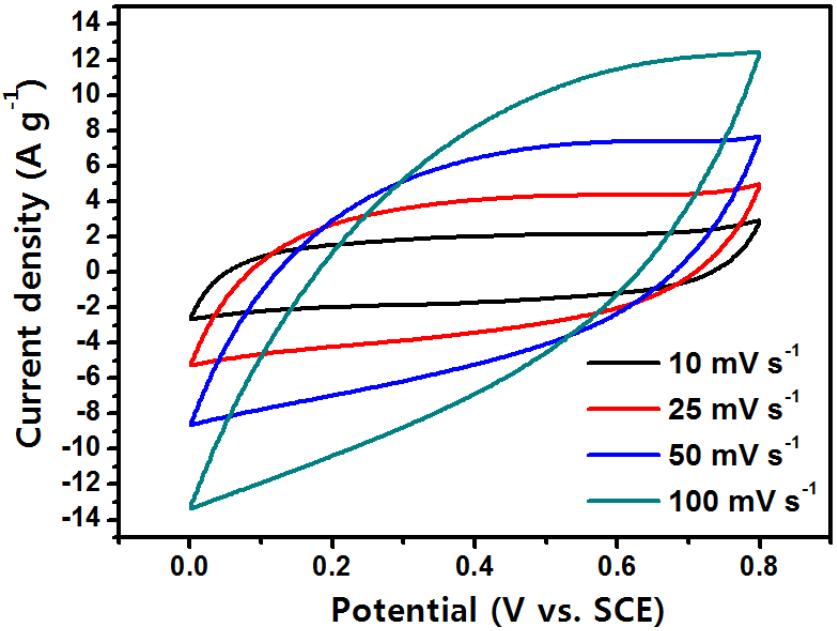

Fig. S4 Cyclic voltammetry curves of the $MnO_2/E_{49.5}B_{49.5}C_1$ composite at various scan rates with potential windows ranging from 0 to 0.8 V

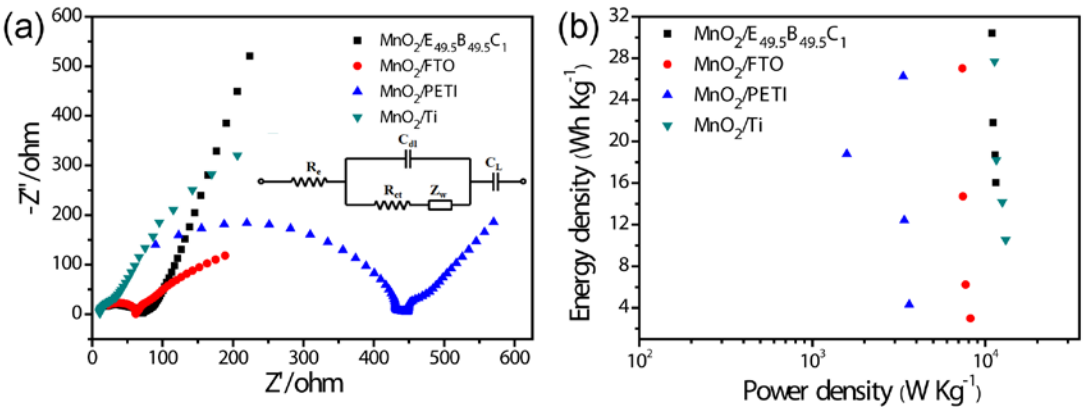

Fig. S5 (a) Nyquist plots and (b) Ragone plots of $MnO_2/E_{49.5}B_{49.5}C_1$, MnO_2/FTO and MnO_2/PETI composites electrodes measured in a frequency range of 0.1 Hz to 100000 Hz. Inset is the fitting model for the EIS.