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3D printable, excellent temperature adoptable and wearable supercapacitors from TPU/PPy/$MnCO_3$ matrix gel

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1. Experimental details

1.1. Materials and reagents

Thermoplastic polyurethane (TPU) purchased from Dongsung- Korea, pyrrole (Acros Organics) as a conductive polymer monomer, tetrahydrofuran (THF, Samchun chemical) was used as a solvent. potassium permanganate ($KMnO_4$), Manganese sulfate ($MnSO_4$), Urea (CH_4N_2O), Sodium sulfate (Na2SO4), and ionic liquid (IL) 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIMBF_4$) obtained from sigma- Aldrich.

1.2. Preparation of TPU/PPy/$MnCO_3$ composite gel

Initially 10 wt% of TPU was stirred and dissolved in THF for 4 h, followed by 3 wt% of PPy, $MnCO_3$ and IL stirred for 30 min., and the mixture setup kept in autoclave for hydrothermal process. The reaction setup was continued at 80 ^{0}C for 6 h. The collected gel was used for 3D printable gel.

1.3. Characterization

Morphological characteristics were measured by coating TPU/PPy/$MnCO_3$ composite film with Pt/Au and observing it at various magnifications under 10 kV voltage using Scanning electron microscopy (SEM, MIRA2, TESCAN). X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) (X-flash4010, Bruker) was used to confirm composite preparation. The tensile testing machine (UTM, Hounsfield, H10KS) was performed and the mechanical flexibility test machine (IPEN Co., Korea) to change durability. To check the performance as a supercapacitor using Workstarion (SP-150, biological) employed for cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge-discharge (CD).

1.4. Biocompatibility studies

All the $MnCO_3$, PPY, TPU, TPU/PPy, TPU/$MnCO_3$, TPU/PPy/$MnCO_3$ samples were treated to conduct biocompatibility experiments on skin computability wearable sensor combined supercapacitors, and the findings are graphed. Treatment with HT-29 cells and composite films resulted in changes in cell viability. The cell cultures (5 103) cells mL^{-1}) were grown in 24-well plates and preserved through IC50 (22.62 g mL^{-1}) in all the samples investigated using HT-29 cells in brief, the cell cultures (5 103) cells mL-1) were cultivated in 24-well plates and preserved through IC50 (22.62 g mL^{-1}). After 24 h of growth, the cell viability fluctuations were observed using an inverted light microscope (Nikon, Eclipse TS 100). The obtained MTT assay against HT-29 cell line performances and Cell viability changes of HT-29 cells observed results demonstrated the notable good biocompatibility of TPU/PPy/$MnCO_3$ gels influences on cell viability observed.

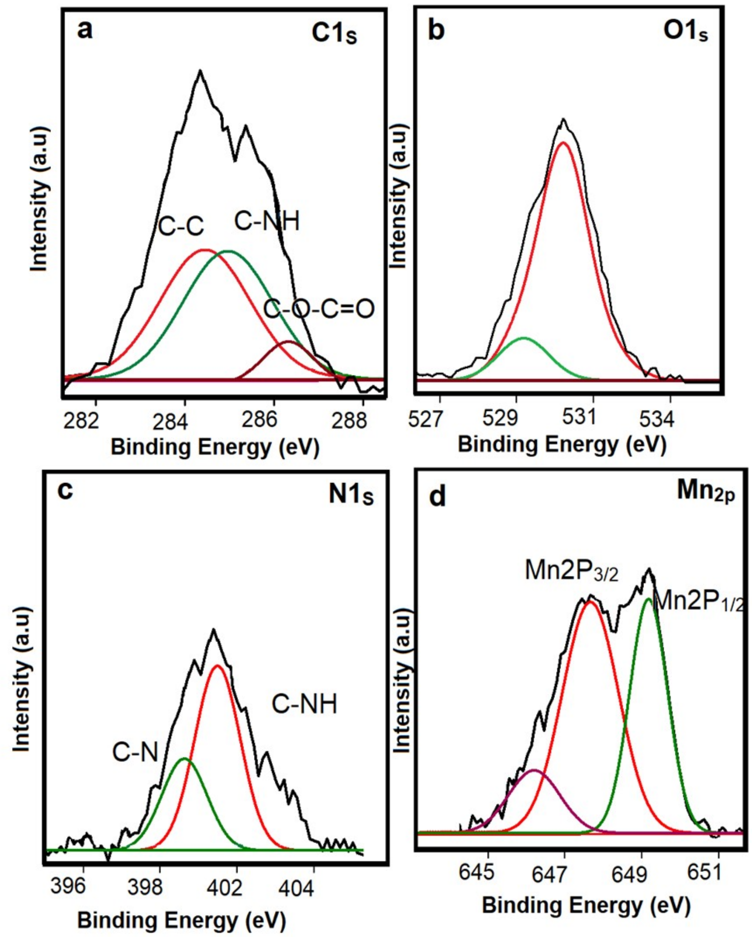

Fig. S1. XPS fitting graph for TPU/PPy/$MnCO_3$ composite

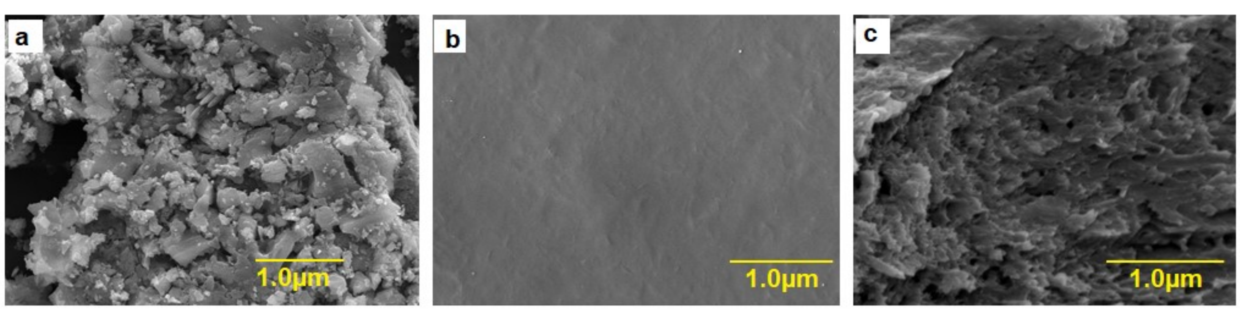

Fig. S2. SEM images of $MnCO_3$ (e), TPU (f) and TPU/PPy/$MnCO_3$ (g) respectively

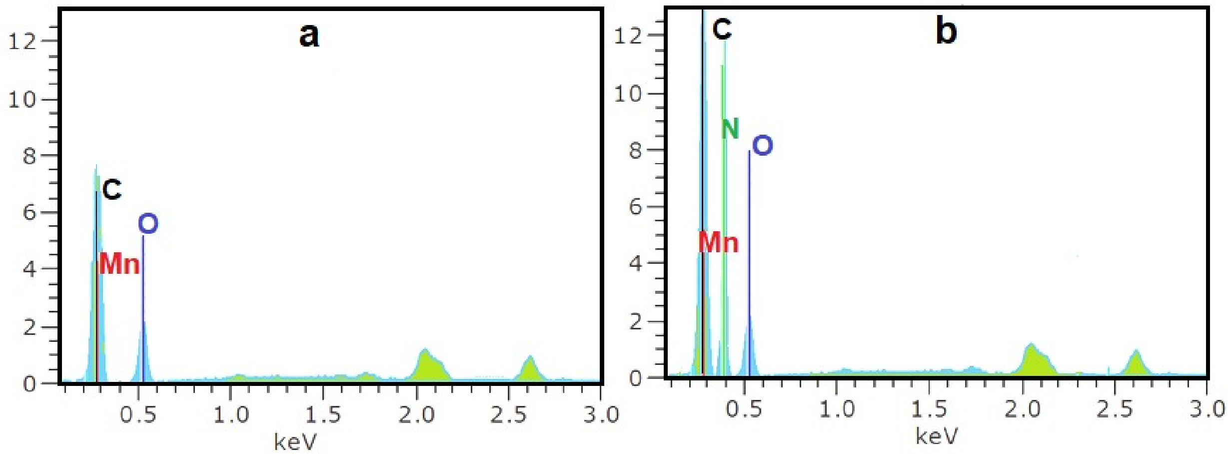

Fig. S3. EDS spectrum of $MnCO_3$ and TPU/PPy/$MnCO_3$ gel matrix

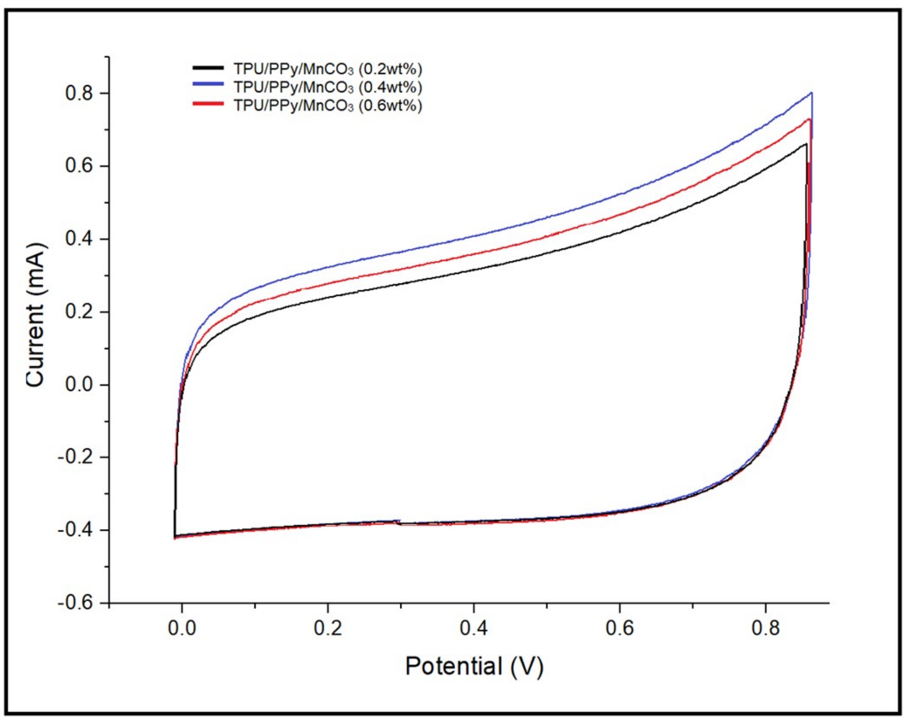

Fig.S4. CV profile of various $MnCO_3$ wt% of TPU/PPy/$MnCO_3$ composites

Table. S1. EIS fit parameters of TPU/PPy/$MnCO_3$ composite supercapacitors at different temperature environments.

Temperature conditions	R_s Ω cm^2	R_{sl} Ω cm^2	R_{ct} Ω cm^2	W_1 Ω cm^2	W_2 Ω cm^2
-10 ^{0}C	31.2	4.91	20.5	161.4	187.5
-5 ^{0}C	30.2	4.46	21.4	159.7	174.2
-0 ^{0}C	29.7	4.79	20.7	154.6	169.7
25 ^{0}C	29.9	4.51	19.8	153.7	157.4
50 ^{0}C	30.1	3.98	20.1	149.7	155.2
75 ^{0}C	28.7	3.96	19.7	151.2	157.1
100 ^{0}C	29.4	4.01	19.6	150.4	158.3

R_s is the total resistance of the electrolyte, the current collector, and the composite interface; R_{sl} is the resistance created in the surface layer of the composite electrode; R_{ct} is the charge transfer resistance through the electrode/electrolyte. W_1 and W_2 of the Warburg impedance are used to organize the semi-infinite diffusion transport resistance of electrolyte ions;

Calculations

Capacitance could also be calculated from the galvanostatic discharge curves, using the following equation S1.

$$C_A = \frac{I\Delta t}{A\Delta V} \qquad (S1)$$

The energy density (E) evaluated by equation (S2)

$$E = \frac{C(\Delta V)^2}{2} \qquad (S2)$$

Where C is the specific capacitance of the active materials, and ΔV is the potential window of discharge [1]. Where I (A) is charge or discharge current, Δt (s) is the time for a full charge or discharge, m (g) indicates the mass of the active material, and ΔV represents the voltage change after a full charge or discharge. Where C is the specific capacitance of the active materials, and ΔV is the potential window of discharge.[1]

Table S2. Areal capacitance and energy density results at various temperature environments

Temperature conditions	Areal Capacitance (mF cm^{-2})	Energy density (mW h cm^{-2})
-10 ^{0}C	140	19.4
-5 ^{0}C	240	33.3
-0 ^{0}C	248	34.4
25 ^{0}C	266	36.9
50 ^{0}C	230	31.9
75 ^{0}C	220	30.6
100 ^{0}C	182	25.3

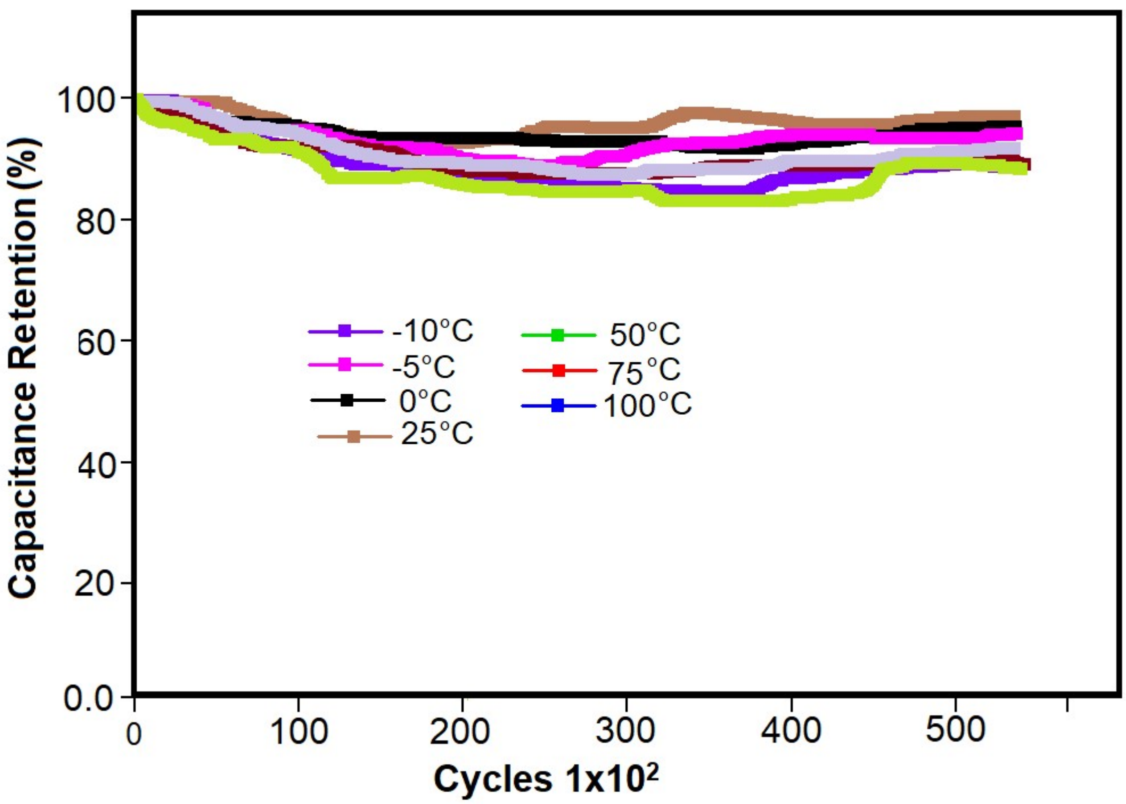

Fig. S5. Cyclic stability performance of TPU/PPy/$MnCO_3$ composite supercapacitor at various temperature conditions.

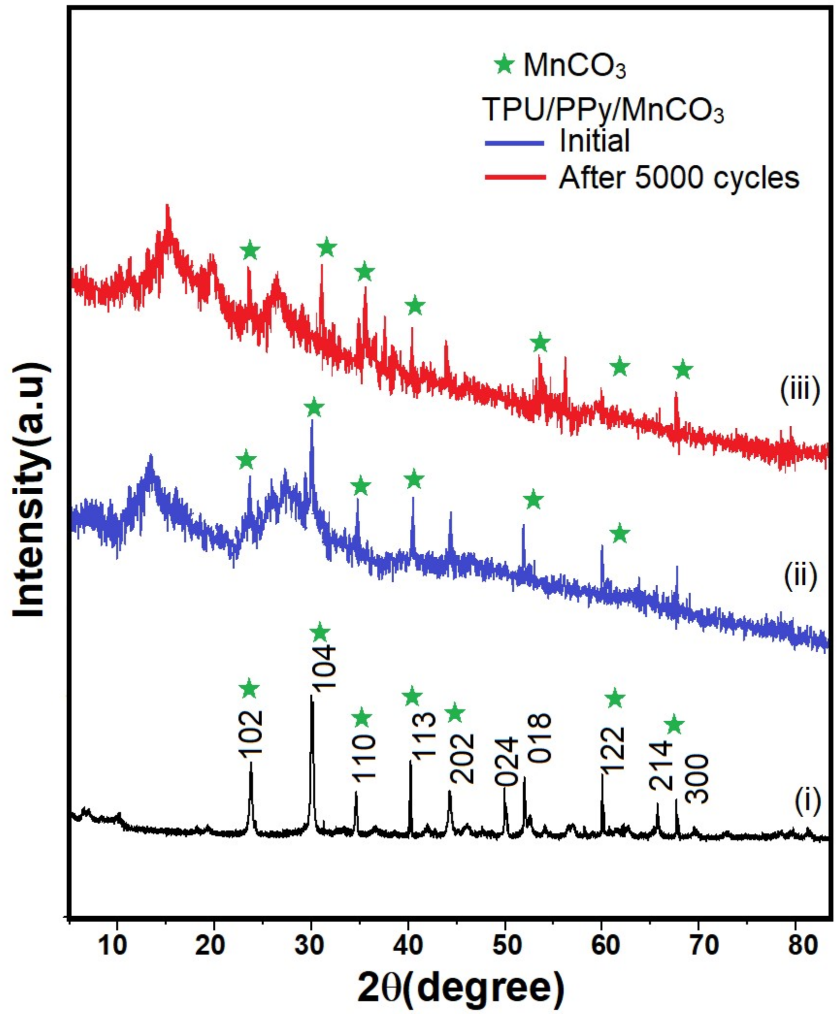

Fig. S6. XRD pattern of TPU/PPy/$MnCO_3$ composite after cyclic stability performance (i) $MnCO_3$, (ii) initial and (iii) after 5000 cycles.

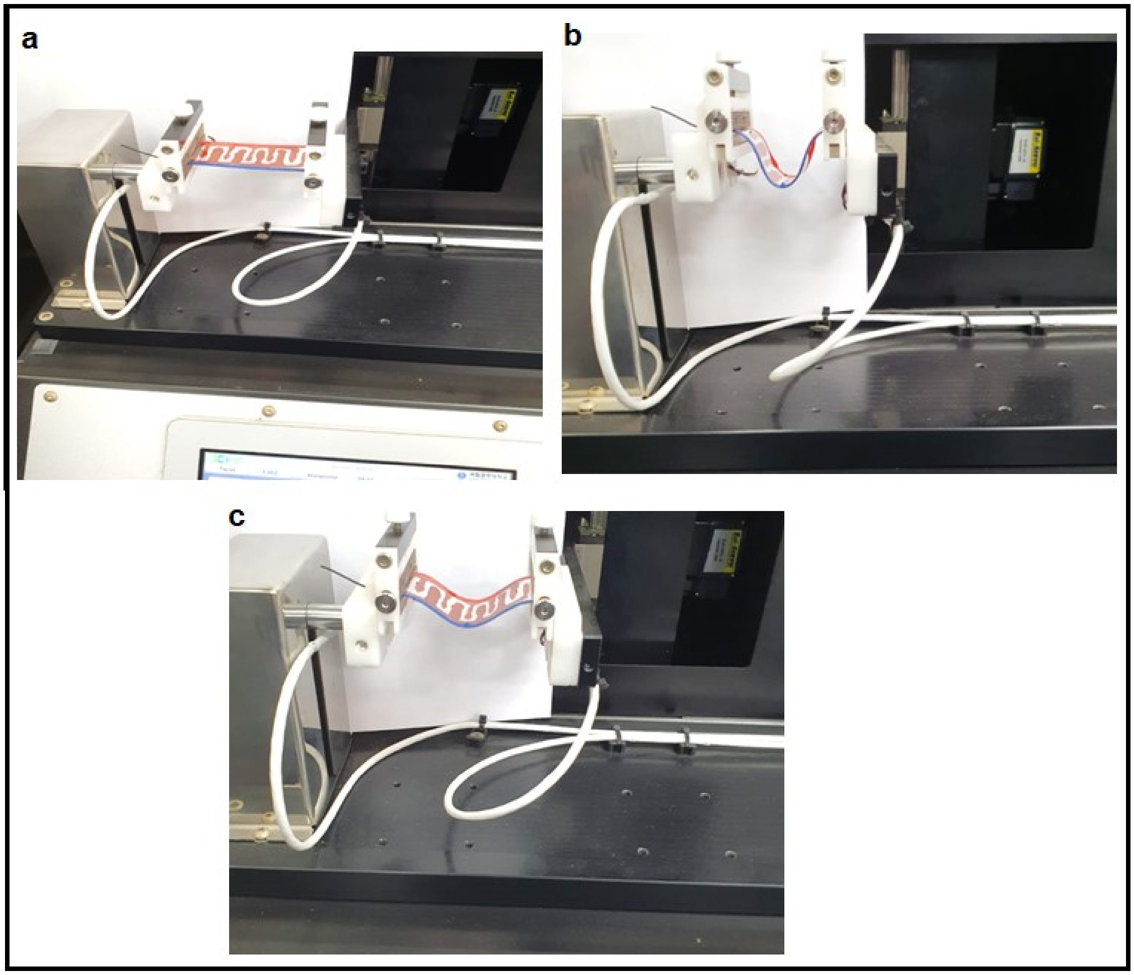

Fig. S7. Mechanical flexibility test of 3D printable supercapacitors at various bending conditions (a) horizontal, (b) 3.4mm (c) 7.0 mm radius.

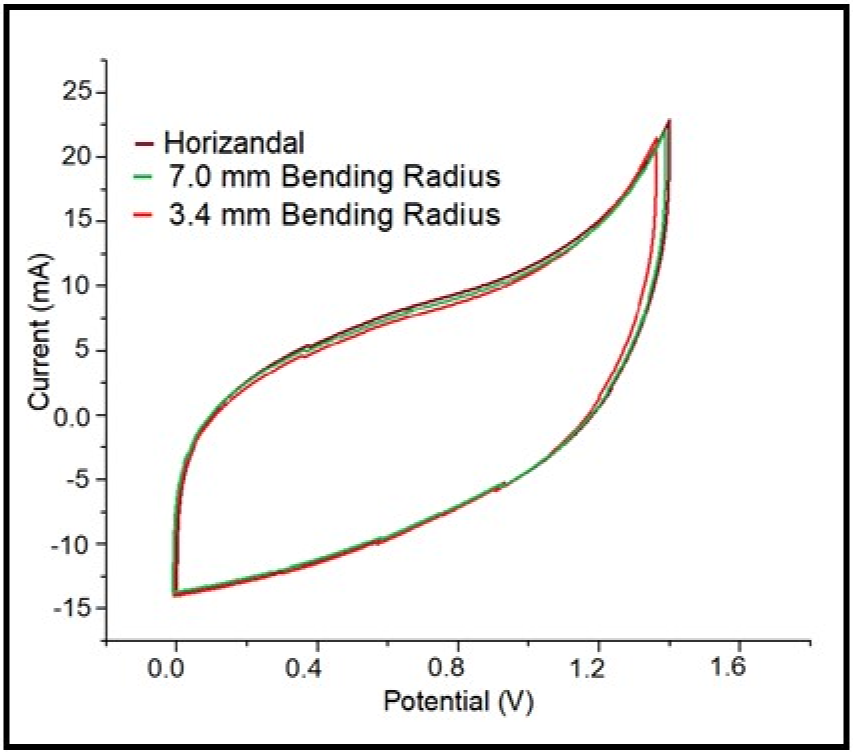

Fig. S8. CV profile of 3D printable supercapacitors at various bending conditions (a) horizontal, (b) 3.4mm (c) 7.0 mm radius.

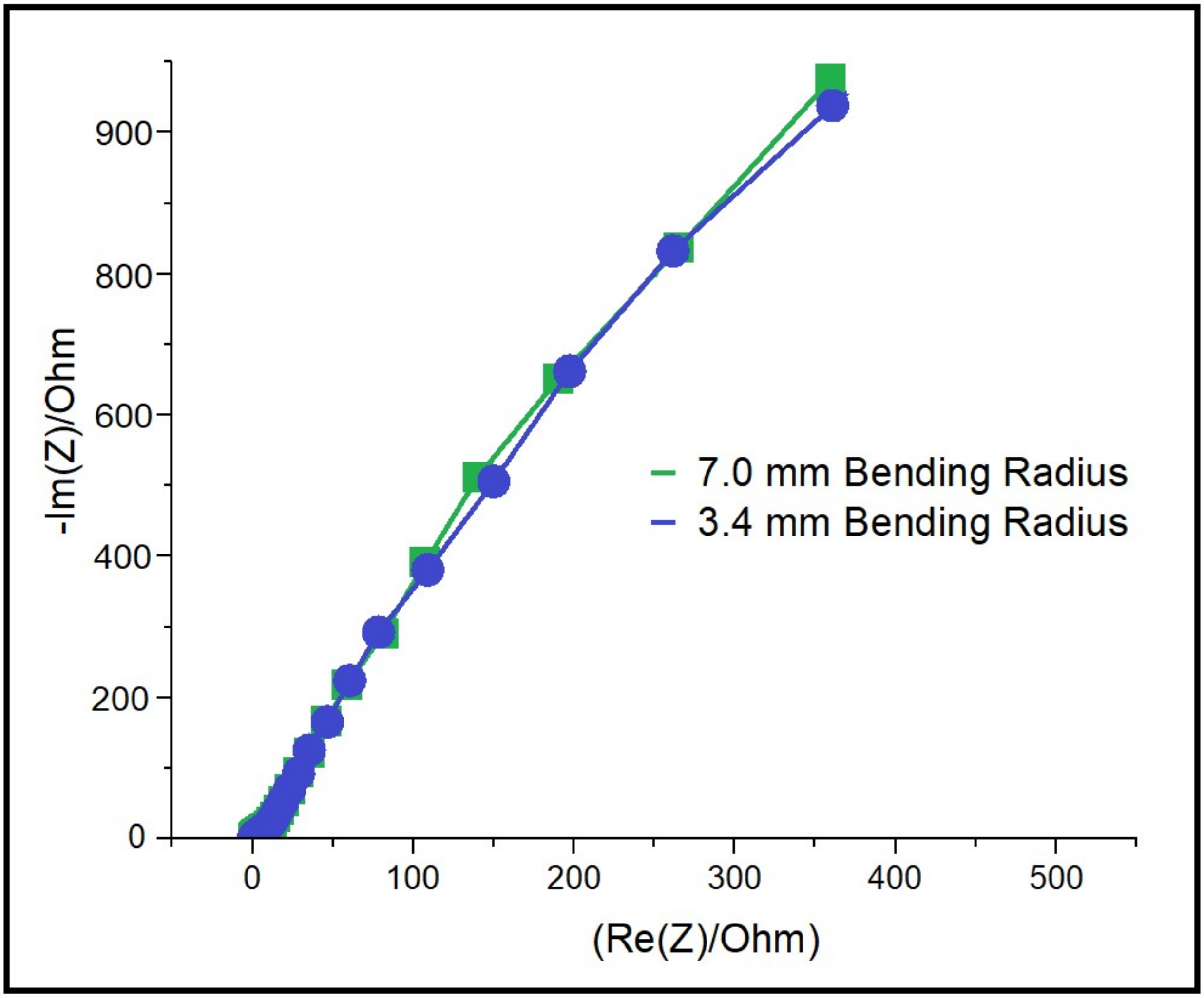

Fig. S9. Mechanical stability EIS at various bending radius

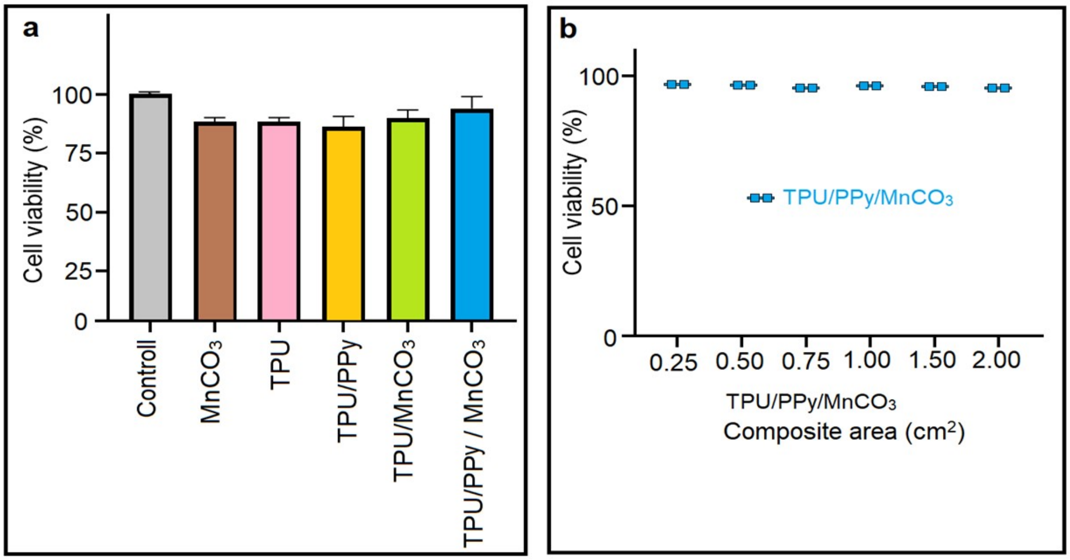

Fig. S9. (a) Biocompatibility test of $MnCO_3$. TPU, TPU/PPy, TPU/$MnCO_3$, TPU/PPy/$MnCO_3$ composite and (b) biocompatibility performance at various area of TPU/PPy/$MnCO_3$ composite.

Table S3: Comparison of TPU/PPy/$MnCO_3$ composites from literature based on PPy and 3D printed composites

PPy based composites	Electrolyte	Specific capacitance (mF cm^{-2})	Cyclic stability	Ref.
TPU/PPy/$MnCO_3$	BMIMBF4	266	50000	This work
PPy/MXene)@Cotton	H_2SO_4	455.9	2000	2
Ti_6Al_4V/PPy	PVA-H_3PO_4	75	1000	3
PPy@Ag	PVA-H_2SO_4 gel	90 mF cm^{-2}	10000	4
PPy	H_3po_4/PVA gel	170 F g^{-1}	10000	5
Ag@PPy NCs	PVA /H_3PO_4	47.5mF cm^{-2}	10000	6
Ti_3C2T_x//PPy/MnO_2	PVA/H_2SO_4	61.5 mF cm^{-2}	5000	7
3D Printed Composites				
MoS_3−x@nanocarbon// Ti3C2Tx	PVA/H_2SO_4	55.60 mF cm^{-2}	25000	8
graphene/PEDOT: PSS	PVA/H_2SO_4	13.8 mF cm^{-2}	2000	9
graphene/CNT/Ag	H_3PO_4/PVA	21.6 mF cm^{-2}	2000	10
PEDOT:PSS/GQD/EEG	PSS/H_3PO_4	2 mF cm^{-2}	10000	11
SWCNT/V_2O_5// SWCNT/VN	PVA/KOH	116.2 mF cm^{-2}	8000	12

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