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Supporting Material

Dynamic interfacial cross-linking and chain entanglement enabling robust mechanical

and conductive TPU composite fiber for knitted wearable strain sensors

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1.Experimental Section

The construction of the dispersing model

The primitive chemical structure of two dispersing models were performed by using the PACKMOL software packages from Accelrys Inc. To providing a wonderful selection of the number of repeat units on a single chain, the solubility parameter of the TPU was chosen as the criterion indicator. the solubility parameter. The first model was 5 SWCNT (6,6) with a length of 120.52 Å incorporating in the 100 TPU chains, and the second one was the same polymer matrix containing 5 SWCNT-DMPA with a length of 120.52 Å, 2 Ti₃C₂T_x MXene, 10 GAHD, 10 PEDOT: PSS, and 100 AgNPs. The interatomic interactions between TPU conductive materials in the Forcite Module are described by applying the opls-aa forcefield.

To get an equilibrium interfacial structure, the energy of SWCNT@TPU and GAHD@SWCNT-DMPA@ TPU@ $Ti_3C_2T_x$ MXene @PEDOT: PSS @AgNPs (GCTMP-Ag) composite system was minimized employ a conjugate gradient algorithm to eliminate the unreasonable structure preliminarily respectively. The canonical (NVT) ensemble at 500K and 101.325 Kpa for 800ps with time step of 1 fs and isothermal-isobaric ensemble (NPT) simulations at 500 K and 101.325 Kpa for 800ps were then performed. Afterward, the system is cooled to 298 K in each 50 K decrements for 800 ps with a 1 fs timestep. it was immediately relaxed under an NVT ensemble at 298 K for 800 ps for getting the final global energy minimum configurations. Meanwhile, during the NVT simulation process, the upper wall moves to the negative direction of x-axis, while the lower wall moves to the positive direction of x-axis. The sliding speed was chosen as 0.001Å/fs. Finally, conductive materials of two dispersing models were homogeneously dispersed in the TPU matrix to obtain the equilibrium dispersing model, as depicted in Fig. In the MD simulation systems, the motion of the atom was performed via the classical Newton equations, and all molecular dynamics simulations were conducted using the LAMMPS software package.

The construction of pull-out model

To studied the improved electromechanical performances via the incorporation of conductive materials as reinforcements, two pull-out models were performed by using the PACKMOL software packages from Accelrys Inc. To provide a wonderful selection of the number of repeat units on a single chain, the solubility parameter of the TPU was chosen as the criterion indicator. the solubility parameter, δ , was defined as follows:

$$\delta = \sqrt{\boldsymbol{E}_{\text{CED}}} \tag{1}$$

where E_{CED} represents the cohesive energy density.

The first model was 5 SWCNT (6,6) with a length of 120.52 Å incorporating in the 300 TPU chains, and the second one was the same polymer matrix containing 5 SWCNT-DMPA with a length of 120.52 Å, 1 Mxene, 4 GAHD, 10 PEDOT: PSS, and 100 AgNPs.

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was applied to conducted MD simulations. The intra- and intermolecular interactions were described by applying the opls-aa forcefield, which could measure the electromechanical performances of GAHD@SWCNT-DMPA@ Ti₃C₂T_x MXene @PEDOT: PSS @AgNPs@TPU (GCMP-Ag) composite nanomaterials. In the opls-aa forcefield, the total potential energy, E, was summered as follows:

$$E_{\text{total}} = E_{\text{bonded}} + E_{\text{non - bonded}}$$
(2)

 $E_{\rm total} = E_{\rm bond} + E_{\rm angle} + E_{\rm torsion} + E_{\rm outp} + E_{\rm elec} + E_{\rm vdW} + E_{\rm other}$

$$E_{total} = \sum_{bonds} \frac{1}{2} k_b (b - b_0)^2 + \sum_{angles} \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

$$+ \sum_{\text{outp}} \frac{1}{2} k_{\varphi} [1 + \cos(n\varphi - \delta)]^2 + \sum_{\text{torsions}} \frac{1}{2} k_{\xi} (\xi - \xi_0)^2 + \sum_{i < j} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} + \sum_{i < j} \left[\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right] + E_{\text{other}}$$

where E_{total} was the total potential energy, the total potential energy was composed of both bonded E_{bonded} , and non-bonded $E_{\text{non-bonded}}$ interaction terms; The non-bonded interaction energy was included with van der Waals (vdW) interaction energy E_{vdW} and electrostatic interaction energy (E_{elec}). The bonded interaction energy was consisted of bond angle energy (E_{angle}), bond extension energy (E_{bond}), torsion angle energy (E_{torsion}), and non-planar energy (E_{outp}). the constants k_{b} , k_{θ} , k_{φ} , and k_{ξ} were the bond, angle, torsional and improper stiffness, respectively. b_0 , θ_0 , ξ_0 were the bond lengths, bond angles, and the out of plane angles between particles respectively. $^{\Gamma_{ij}}$ was the euclidean distance between two interacting particles. q was the electrostatic charge. ε was the electrical permittivity. σ was the average distance between two atoms. We computed long-range Coulomb interactions and set the cut-off distance both the van der Waals (vdW) and Coulomb interactions at 12 Å via. the particle-particle particle-mesh (PPPM) approach.

To get an equilibrium interfacial structure, the energy of SWCNT@TPU and GCTMP-Ag composite system was minimized employ a conjugate gradient algorithm to eliminate the unreasonable structure preliminarily respectively. The canonical (NVT) ensemble at 500K and 101.325 Kpa for 1000ps with time step of 1 fs and isothermal-isobaric ensemble (NPT) simulations at 500 K and 101.325 Kpa for 1000ps were then performed. Afterward, the system is cooled to 298 K in each 50 K decrements for 1000 ps with a 1 fs timestep. it was immediately relaxed under an NVT ensemble at 298 K for 1000 ps for getting the final global energy minimum configurations. Finally, conductive materials of the TPU matrix were pulled out in the *z* direction to obtain the equilibrium pull-out model. The pull-out speed

was chosen as 0.001Å/fs. In the MD simulation systems, the motion of the atom was performed via the classical Newton equations, and all molecular dynamics simulations were conducted using the LAMMPS software package.

Preparation of Ti₃C₂T_x MXene

 $Ti_3C_2T_x$ MXene was prepared by selectively etching the Al layer from the MAX phase (Ti_3AlC_2) using LiF/HCl aqueous solution. Lithium fluoride (2.5g) was firstly dissolved in 50 mL hydrochloric acid solution (12 mol/L) under stirring. Then MAX (Ti_3AlC_2) (2.5g) was slowly added into the mixture solution. Subsequently, they were conducted under magnetic stirring and filtering for 48 h at 40 °C. Then the obtained simple immediately was diluted and centrifuged with deionized water. Finally, the centrifuged sample was freeze-dried for 12 hours to obtain MXene nanosheet layers.

To obtain $Ti_3C_2T_x$ MXene nanosheets with few or single layers, $Ti_3C_2T_x$ MXene nanosheet layers were put into the DMF solution under the ice bath condition for 1 h via the ultrasonic treatment. Subsequently, they were centrifuged at 9000 rpm for 20 minutes and washed with deionized water to remove the excessive DMF. Then the sediment was freeze-dried for 12 hours to obtain $Ti_3C_2T_x$ MXene nanosheet with few or single layers.

The fabrication of AgNPs

AgNO₃ (2g/L) was dissolved in deionized water to prepare 100 mL of silver nitrate solution A.

Ascorbic acid (1.5 g/L) and polyethylene glycol (0.5 g/L) were dissolved in deionized water to prepare 100 mL of silver nitrate solution B. Adjust the pH of solution B to an appropriate value using concentrated ammonia and concentrated nitric acid. Pour solution B into a 250 mL beaker and place it in a constant temperature water bath, with the stirring speed controlled at 500 rpm. Add solution A to the beaker at a rate of 3 mL/min. After solution A is completely added, continue

stirring at a constant temperature for another 10 minutes to ensure complete reaction. After precipitation and filtration, wash the obtained precipitate several times with deionized water, and then clean it with anhydrous ethanol in an ultrasonic cleaner for 30 minutes. Finally, place the cleaned precipitate in a vacuum drying oven and dry it at a constant temperature of 60°C for 5 hours to obtain silver powder.

The fabrication of SWCNT-DMPA

SWCNT powders (2 g) were dissolved in a 500 mL three-necked flask including 80 mL mixture solution with sulfuric acid and nitric acid (volume ratio 3:1). After ultrasonic treatment for 40 min, the process was carried out under magnetic stirring and filtering for 15 h at 60 °C. Finally, carboxylated SWCNT powders were thoroughly washed with deionized water and dried at 80 °C vacuum.

Carboxylated SWCNT powders (1.5 g) were dissolved in a 250 mL four-necked flask with N, Ndimethylformamide (30 mL) under ultrasonic treatment for 15 minutes. Then SOCl₂ (90 mL) was slowly put into the mixture solution. After magnetic stirring for 14 h, these samples thoroughly filtered and washed with DMF to remove unreacted SOCl₂. Subsequently, they were dissolved in a 200 mL conical flask containing DMPA (60 g) and TEA (15 mL) at 50 °C. After magnetic stirring for 24 h, SWCNT-DMPA powders were filtered and washed with deionized water and dried at 60 °C vacuum.

2. Results and discussion



Fig. S1 (a, b) Conductive nanochannels intertwined with cross-linked polymeric framework between

TPU and GCMP-Ag nanomaterials.



Fig. S2 The interactions between TPU and GCMP-Ag nanomaterials.



Fig. S3 EDS mapping of GCTMP-Ag composite fibers.



Fig. S4 FTIR spectra of TPU fibers, SWCNT@TPU composite fibers and GCTMP-Ag composite

fibers



Fig. S5 The Raman spectra of GCTMP-Ag composite fibers and Ti₃C₂T_xMXene



Fig. S6 High-resolution C 1s XPS spectra of SWCNT@TPU composite fibers; (b) High-resolution S 1s XPS spectra of GCTMP-Ag composite fibers. (c) High-resolution Ag 1s XPS spectra of GCTMP-Ag composite fibers. (d) High-resolution Ti 1s XPS spectra of GCTMP-Ag composite fibers. (e) High-resolution F 1s XPS spectra of GCTMP-Ag composite fibers. (f) High-resolution N 1s XPS spectra of TPU fibers. (g) High-resolution N 1s XPS spectra of GCTMP-Ag composite fibers. (h) The effective

phase separation between PEDOT and PSS.



Fig. S7 (a-d) The pull-out process of SWCNT and (e-h) GCMP-Ag nanomaterials from the TPU

substrate



Fig. S8 (a) Structural model diagram of CMP-Ag nanocomposites. (b) The formation energy and (c)

band gap of CMP-Ag nanocomposites under tensile (40 %, 80 %) and compressive (-40 %, -80 %) strain conditions.



Fig. S9 (a) and (b) Demonstration of the resistance model of the GCTMP-Ag fabric; (c) Resistance

model under the applied strain.