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Supporting Information

Mechanically strong and Highly Conductive MXene/Polyacrylamide–alginate Composite Hydrogel with Double-network Structure for Flexible Wearable Sensor

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1. Experimental Section

1.1 Chemicals and Materials

Titanium Aluminium carbide (Ti₃AlC₂) (400mes) was purchased from Jilin 11 Technology Co., Ltd. Sodium alginate (SA), acrylamide (AAM), amine persulfate (APS), N, N'-Methylenebisacrylamide (MBA), lithium fluoride (LiF), anhydrous calcium chloride, and other reagent drugs were purchased from Shanghai Titan Scientific Co., ltd. Hydrochloric acid (37%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All of the above medicines are used in their original packaging. The other reagents used were analytically pure and all the solutions were prepared with deionized (DI) water.

1.2 Methods

1.2.1 Preparation of MXene (Ti₃C₂T_x) nanosheets

MXene ($Ti_3C_2T_X$) was synthesized by selective etching the Al layer using LiF/HCl as an etching solution ¹. Specifically, the etching LiF/HCl solution was prepared by mixing LiF (1.0 g) and HCl solution (20 mL, 9 mol L⁻¹). Then, Ti_3AlC_2 (1.0 g) was slowly added to the LiF/HCl etching solution with gentle stirring to minimize the heat release from the exothermic reaction. Then, the mixture was sealed, and etched under magnetically stirring at 35 °C for 24 hours. Afterward, the etched Ti_3AlC_2 were collected by centrifugal separation washed with deionized water, and centrifuged repeatedly at 3500 rpm for 5 minutes until the pH value of the supernatant was neutral. Successively, the etched Ti_3AlC_2 was re-dispersed in water by 2 h of sonication under a nitrogen atmosphere and an ice bath. Then, after removing the un-etched impurities and unexfoliated MXenes by centrifugal separation at 3500 rpm for 1 hour, the obtained few-layered MXene nanosheets dispersion was finally obtained and the concentrations were quantitatively about 10 mg/mL.

1.2.2 Preparation of the MSP-Ca²⁺/Li⁺ composite hydrogel

The MSP-Ca²⁺/Li⁺ composite hydrogel is prepared through a simple thermal polymerization method using an initial solution consisting of monomers (MXene, SA, and AAm), a cross-linker (MBA), MXene (nanofillers), and an initiator (APS) followed with Ca²⁺ ions crosslinking and soaking in LiCl solution ². Specifically, the MXene is firstly dispersed in 13 ml of deionized water. Nitrogen gas is bubbled in order to remove oxygen. Then, desired amounts of SA and AM monomers are added into the MXene aqueous dispersion and stirred until completely dissolved in a nitrogen atmosphere. The temperature of the MXene/SA/AAM mixed dispersion is kept at 0 °C. Subsequently, a 2 ml mixture solution of APS and MBA (where the initiator and cross-linking agent are 1.0 wt% and 1.5 wt% of the mass of acrylamide, respectively) is added, and the mixture is stirred for 2 h under a 0 °C. After that, the evenly MXene/SA/AAM/APS/MBA mixed dispersion is transferred into a customized mold and placed in a vacuum oven for *in-situ* polymerization at 60 °C for 3 h to form MSP hydrogel. The obtained MSP hydrogel is first soaked in deionized water to remove homopolymers and unreacted monomers, and then sequentially transferred into a 2 wt% CaCl₂ solution for 2 h and a 5 wt% LiCl solution for 24 h to obtain MSP-Ca²⁺/Li⁺ hydrogels^{3,4}. The MSP-Ca²⁺/Li⁺ composite hydrogel is denoted as $M_tS_xP_y$ -Ca²⁺/Li⁺, where S, P, and M respectively represent hydrogels containing sodium alginate, polyacrylamide, and MXene, and x, y, and, t represents the feed amounts of SA, AAm and the relative weight ratio of MXene to the total amount of AAm. For example, M3S1P3-Ca²⁺/Li⁺ composite hydrogels indicate there are 0.3 g of SA, 1.0 g of AAm, and 30 mg of MXene (account for 3 wt% of AAm) in the feeding amounts of hydrogel preparation.

1.2.3 Instruments and characterizations

The morphology and structure of PAM, MSP, MSP-Ca²⁺/Li⁺ hydrogels, and MXene were observed by field emission scanning electron microscopy (SEM) (JEOL FEG-XL30S) and field emission transmission electron microscopy (TEM) (JEM-2010F). The crystal structure information of MXene was analyzed from X-ray diffraction (XRD) patterns which are collected on a Bruker D8 Advanced diffractometer. FT-IR spectra were recorded on a PerkinElmer Spectrum100 using KBr pellets. The X-ray photoelectron spectroscopy (XPS) characterization is performed on the Thermos SCIENTIFIC ESCALAB Xi + using monochromatic Al Kα radiation (1486.6 eV). The change rate of relative resistance was recorded by the TH2830 digital bridge test. The mechanical properties of the hydrogel are tested by an electronic universal testing machine controlled by the SongDun LDW-2 electronic testing machine.

1.2.3.1 Mechanical properties

For the compression test, the composite hydrogels were prepared in plastic test tubes with round bottom diameters of 25 mm and height of 50 mm. The compression test of the composite hydrogel was performed using the SongDun LDW-2 electronic testing machine, and the cylindrical hydrogel with a bottom diameter of 25 mm and a height of 30 mm was tested under equilibrium swelling conditions. The compression test conditions are as follows: crosshead speed 50 mm min⁻¹, force sensor 2 kN, temperature 25 °C, initial distance 30 mm, final distance 9 mm. Similar to the compression test, the tensile test of the hydrogel is also carried out in the equilibrium swelling state. However, the hydrogel film specimens are formed inside of customized mold with a size of 50 mm (length) \times 10 mm (width) \times 3 mm (depth). Tensile testing is also carried out on the SongDun LDW-2 electronic testing machine. The conditions of the tensile test are as follows: crosshead speed 25 °C, initial distance 50 mm min⁻¹, force sensor 2 kN, temperature 25 °C, initial distance sensor 2 kN, tensile test are as follows: crosshead speed mole with a size of 50 mm (length) \times 10 mm (width) \times 3 mm (depth). Tensile testing is also carried out on the SongDun LDW-2 electronic testing machine. The conditions of the tensile test are as follows: crosshead speed 25 °C, initial distance 50 mm.

1.2.3.2 Sensing performance testing

The test employs rectangular splines with a length of 50 mm, a width of 10 mm, and a thickness of 3 mm. The resistance values of different tensile states are recorded by using an LCR bridge (TH2830) under an applied voltage of 3 V and a scanning frequency of 1 kHz. In this study, the strain factor corresponding to sensitivity is defined as $GF=(\Delta R/R_0)/\epsilon$, and the relative resistance change is defined as $\Delta R/R_0=(R-R_0)/R_0$, where R_0 and R are the original resistance of the hydrogel and the resistance in the tensile state, and ϵ is the strain in the current tensile state.



Fig. S1. Photographs of as-prepared MXene aqueous dispersions and after 24 hours of standing.



Fig. S2. TEM image for exfoliated MXene nanosheets.



Fig. S3. XRD patterns of Ti_3AlC_2 MAX phase and MXene nanosheets.



Fig. S4. Photographs of MSP-Ca²⁺/Li⁺ composite hydrogels with different shapes.



Fig. S5. Compressive stress-strain curves of hydrogels with different loading contents of MXene before cross-linking with Ca²⁺ ions.



Fig. S6 Compressive stress-strain curves between M3S1P3-Ca²⁺ and M3S1P3-Ca²⁺/Li⁺ composite hydrogels



Fig. S7. The sensing response and recovery time of hydrogels without Li⁺ ions under 150% tensile strain.



Fig. S8 Relative resistance changes of hydrogel sensors at 5-25% strain. Stable sensing characteristics even in small strain ranges.



Fig. S9. The radar chart of GF, maximum elongation at break, GF, cyclic stability of sensing, response and recovery times for M3S1P3-Ca²⁺/Li⁺ and previously reported some similar hydrogels.

Table S1 Initial resistance data before and after immersion in LiCl solution. By testing the initial resistance (R₀) of each group of gels, the introduction of MXene and Li⁺ significantly affects the hydrogel resistance, and the data show that M3S1P3-Ca²⁺/Li⁺ has the smallest resistance, so M3S1P3-Ca²⁺/Li⁺ was selected for the electrical performance test.

| Sample name | 1 time / R ₀ | 2 time / R ₀ | 3 time / R ₀ |
|--|-------------------------|-------------------------|-------------------------|
| (NO-Li ⁺ /Li ⁺) | (Ω) | (Ω) | (Ω) |
| M0S1P3-Ca ²⁺ | 1157.08 | 1213.69 | 1264.35 |
| M0S1P3-Ca ²⁺ /Li ⁺ | 416.55 | 416.55 | 385.19 |
| M1S1P3-Ca ²⁺ | 500.42 | 519.33 | 507.49 |
| M1S1P3-Ca ²⁺ /Li ⁺ | 187.23 | 191.28 | 197.33 |
| M2S1P3-Ca ²⁺ | 482.54 | 487.67 | 490.22 |
| M2S1P3-Ca ²⁺ /Li ⁺ | 188.53 | 193.44 | 190.31 |
| M3S1P3-Ca ²⁺ | 418.78 | 420.32 | 412.61 |
| M3S1P3-Ca ²⁺ /Li ⁺ | 167.96 | 176.58 | 170.29 |

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