

MXene/sPS nanocomposites: Rheological, electrical conductivity, polymorphism, mechanical, thermal, and flammability properties

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1. Experimental

1.1. Materials

Ti₃AlC₂ (MAX phases, ≥90%, ≤40 μm), lithium fluoride (LiF, 99%), and dodecyl triethoxysilane (DCTES, >93%) were bought from Aladdin. Hydrochloric acid (HCl, 37 wt%), aqueous ammonia (NH₃·H₂O, 25~28 wt% content of NH₃), and ethanol absolute (CH₃CH₂OH, ≥99.5%) were supplied by Guangzhou Chemical Reagent Factory. All experimental water was deionized (DI) water, and all drugs in the experiment need no secondary treatment.

1.2. Synthesis of Ti₃C₂T_x MXene nanosheets

To prepare the Ti₃C₂T_x MXene Nanosheets, the Al atomic layers of the Ti₃AlC₂ MAX powder were etched by LiF/HCl solution. In a typical procedure, 3.2 g of LiF was dissolved in 40 mL of an aqueous solution of 9M HCl in a Teflon vessel under slow stirring, and 2 g of Ti₃AlC₂ powder was then added into the LiF/HCl solution slowly and carefully to avoid overheating and gas evolution too fast. After reacting for 48 h with continuous stirring in a water bath at 35°C, the resultant black suspension was centrifuged at 3500 rpm and washed with ultrapure water repeatedly until the pH value of the supernatant was close to 6.

Finally, the precipitant was redispersed in deionized water and ultrasonicated for 1 h under the protection of nitrogen atmosphere in an ice bath. Finally, the dispersion was centrifuged at 3500 rpm for 30 min, and the homogeneous monolayer MXene dispersion (the supernatant liquid) was collected (The concentration of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersion was $15 \text{ mg}\cdot\text{mL}^{-1}$).

1.3. Synthesis of DCTES-modified $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets

The resulting exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets dispersion (50 mL , $15 \text{ mg}\cdot\text{mL}^{-1}$) was added into the mixture of ethanol absolute (200 mL) and aqueous ammonia (10 mL) and stirred at room temperature for 24 h . Afterwards, DCTES (0.4 mL) was introduced into the above solution and stirred vigorously for another 24 h . After the reaction was finished, DI water and ethanol absolute were used for centrifugal cleaning in turn and followed by drying in a vacuum oven at 80°C for 24 h to obtain DCTES-modified $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.

1.4. Characterization

Atomic force microscopy (AFM) was conducted using a Bruker Dimension Icon AFM (USA). Conventional X-ray diffraction (XRD) measurements were conducted on a Rigaku D/Max 2200 VPC X-ray diffractometer (Japan) at a scanning rate of $10^\circ\cdot\text{min}^{-1}$ under Ni-filtered $\text{Cu-K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation with a 2θ range of $5\text{-}60^\circ$. Fourier Transform Infrared (FT-IR) spectra were collected on a Thermo Scientific Nicolet iS 50 (USA) spectrometer in the range of $4000\text{-}1000 \text{ cm}^{-1}$. High-temperature gel permeation chromatography analysis of the weight-average molecular weight (M_w) and molecular weight distribution (PDI) of sPS at 150°C were performed on a PL-GPC 220 high-temperature chromatograph equipped with two GPC columns (USA PLgel $10 \mu\text{m}$ MIXED-B) and a differential refractive-index detector. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$. The molecular weight data were analyzed using narrow polystyrene standards (Polymer Laboratories) and were corrected for polymer samples by universal calibration. ^{13}C NMR spectra of the sPS was obtained with a Bruker Avance III 500

MHz NMR instrument at 130°C. The sample was dissolved in a 5 wt % solution of a mixed solvent of deuterated *o*-dichlorobenzene/*o*-dichlorobenzene with a volume ratio of 1:1 in the 10 mm high temperature NMR tubes.

2. Additional Results

The TEM image of MXene exhibited the ultrathin layered structure (Figure S1a). The AFM mapping and height profile showed that the average thickness of single layer was determined to be about 0.6 nm (Figure S1b and c), which confirmed the exfoliated MXene nanosheets were few layers. The XRD patterns indicated a thorough etching of the Al layers from the Ti_3AlC_2 MAX phase and exfoliation of multiple layers. As shown in Figure S1d, the disappearance of main peak (104) at 39° of Ti_3AlC_2 after HF etching suggested the complete etching of Al layer, and the left shift of the peak (002) indicated enlarged interlayer spacing [1]. The characteristic diffraction peak (002) at $2\theta = 9.54^\circ$ belonging to the original Ti_3AlC_2 MAX phase, which was broadened and shifted to lower angle (6.48°) after exfoliation. The interlayer distance (d) of MXene was calculated to be 13.62 Å. In comparison, the peak (002) of D-MXene shifted to a lower position (5.74°) corresponding to a d value of 15.38 Å as compared to MXene, clearly indicating an increase in the distance between nanosheets and suggesting successful surface modification. Chemical structures of MXene and D-MXene were further characterized by FT-IR (Figure S1e). MXene show peaks of $\nu(\text{O-H})$ and $\delta(\text{C=O})$ at around 3450 and 1640 cm^{-1} , respectively. For D-MXene, it showed several addition characteristic absorption peaks at 2960 ($\nu(\text{CH}_3)$), 2925, 2860 ($\nu(\text{CH}_2)$), 1460 ($\delta(\text{CH}_2)$), 1380 ($\delta(\text{CH}_3)$), 1118 ($\nu(\text{Si-O-C})$), and 1025 ($\nu(\text{Si-O-Si})$) cm^{-1} . The C-H vibrations were ascribed to the existence of the long alkyl chains from DCTES. The hydroxyl groups in MXene reacted with the DCTES, leading to the formation of Si-O-C bond in D-MXene. The Si-O-Si stretching bands after the DCTES modification indicated the hydrolysis condensation reaction of the unreacted silanol groups on the surface of MXene [2].

Figure S1f shows the TGA curves of MXene and D-MXene. The first weight loss stage (50-150°C) was

mainly attributed to the physical adsorption of water on the MXene surface. A higher mass loss in MXene (4.1 wt%) was owing to its hydrophilicity that can easily absorb water molecules. In the second stage (150-800°C), the slight weight loss of MXene (3.5 wt%) was ascribed to the thermal degradation of the terminating groups (=O and -OH) on the surface. The D-MXene sample (16.8 wt%) shows significant mass decline in comparing with MXene in the second stage, which was mainly due to the degradation of the long alkyl chains introduced by condensation reaction in addition to the thermal degradation of the original terminating groups. By comparing the weight losses of MXene and D-MXene before and after DCTES modification in the temperature range from 150 to 800 °C, the weight percentage of -C₁₂H₂₅ grafted on the D-MXene surface was calculated to be 13.3 wt%. Figure S1g shows the dispersibility of MXene and D-MXene in DI water and chloroform for 0 and 24 h, respectively. MXene dispersed well in water even after 24 h but the dispersion was poor in chloroform. D-MXene could hardly disperse in water and float on the surface of water while the dispersion of D-MXene in chloroform was still homogenous and stable after 24 h. The surface treatment made MXene surface coated by a layer of long alkyl chain, thus the surface of D-MXene became hydrophobic and exhibited good suspension in CHCl₃ after ultrasonic treatment.

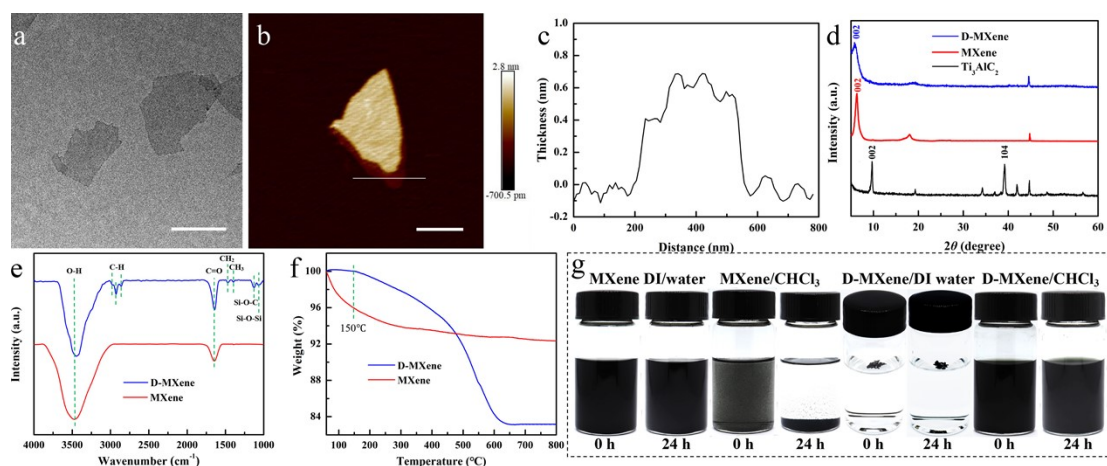


Figure S1. (a) TEM image of MXene, (b, c) AFM image and height profile of MXene, (d) XRD patterns, (e) FTIR spectra, (f) TGA curves. (g) Dispersion of MXene and D-MXene in DI water and CHCl₃ for 0 h and 24 h. The scale bars in a and b are 500 nm.

The ^{13}C NMR solution spectrum of our homemade sPS sample recorded in o-dichlorobenzene at 130°C is presented in Figure S2b. That region of the spectrum containing the protonated phenyl ring carbon resonances (C_{4-6} in Figure S1b) is not shown because of extensive overlap with the more abundant solvent o-dichlorobenzene resonances (127.7, 130.5, 132.6 ppm). However, it is apparent from the remaining spectral regions, particularly the methylene carbon region known to be highly sensitive to the PS stereosequence, that only single resonances are observed for the CH_2 (C_1 , 45.0 ppm), CH (C_2 , 45.0 ppm), and C_3 (145.7 ppm) carbons, which correspond to the syndiotactic stereosequence [3].

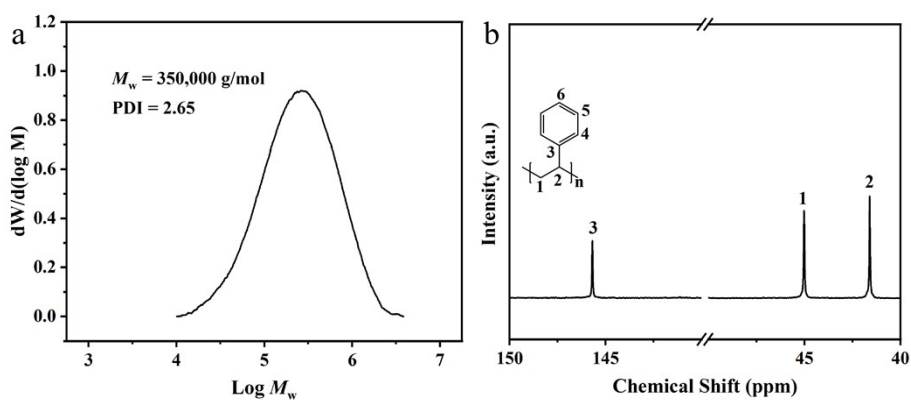


Figure S2. (a) High-temperature GPC trace, and (b) ^{13}C NMR spectrum of sPS.

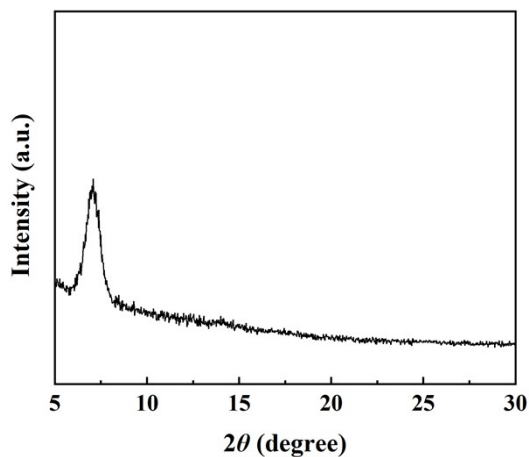


Figure S3. HT-XRD pattern of the sample of blank.

References

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