Electronic Supplementary Material (ESI) for Soft Matter.

Realizing ultra-stable Ti_3C_2-MXene in aqueous solution via surface graft with ionomers

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1. Experimental section

1.1 Materials

Titanium aluminum carbide (Ti_3AlC_2) is received as a commercial product without any purification before use. Hydrochloric acid (HCl), 1,4-butanediol (BDO), dibutyltin dilaurate (DBTDL), ethylenediamine (EDA) and triethylamine (TEA) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Polyether diol (N210, Mn=1000) and 2, 2-dimethylol propionic acid (DMPA, Aladdin Reagents Co., LTD) was dried at 70 °C for 4 h in a vacuum oven before use. Isophorone diisocyanate (IPDI) was used as received. Acetone was purified by 4 Å molecular sieves.

1.2 Preparation of Ti_3C_2-MXene dispersion and Ti_3C_2-MXene powders

1g LiF was dissolved into 20mL HCl solution (9M), and then 1g Ti_3AlC_2 was added into the LiF/HCl solution. After stirring for 24h at 35°C, the mixture was rinsed with deionized water for several times until pH reached 6. Then, the mixture was top up with deionized water and votexed for another 24 h. Finally, the mixture was centrifuged at 3500 r/min for 1h, and the supernatant was either directly used as Ti_3C_2-MXene dispersion (1 mg/ml) or freeze-dried to form Ti_3C_2-MXene powders for SEM

and XRD characterization .

1.3 In-situ synthesis of anionic waterborne polyurethane (WPU)/MXene hydrid emulsions (IWPU)

Scheme S1. shows the synthesis diagram of polyurethane emulsion (WPU) and polyurethane emulsion with modified MXene (IWPU). First, N210 (10.37g), IPDI (11.1g) and DBTDL (0.1g) were added into a three-neck flask with a mechanical stirrer, thermometer and reflux condenser. The reaction was carried out in an oil bath at 85 °C for 2 h. Then, DMPA (1.46g) was added into the flask at 85 °C for 1h. Next, BDO (1.55g) was added in the flask for chain extension reactions at 80 °C for 2h. After cooling to 40 °C, TEA (1.1g) was added to neutralize the carboxylic groups from DMPA. At this point, an anionic polyurethane was achieved with a terminal of isocyanate (NCO) group. After 10 min, 26ml Ti_3C_2-MXene dispersion was added and stirred for 5min. Then 34.5 ml deionized water was added for emulsification and EDA was added for further chain extension. Finally, the acetone in the emulsion was removed by rotary evaporation and the solid content of the hybrid emulsion was about 30 wt%.

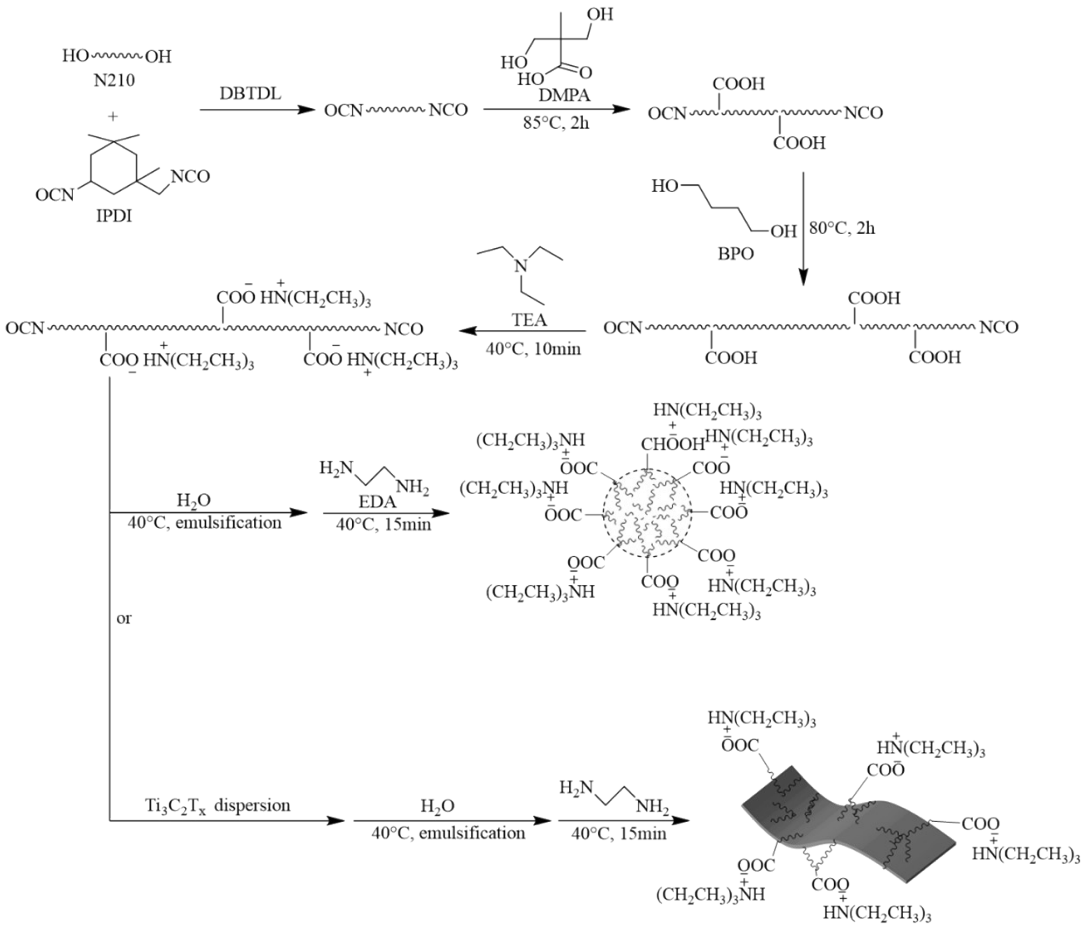
1.4 Preparation of composite emulsions and films

The same content of $Ti_3C_2T_x$ dispersion was directly blended with pre-synthesized PU emulsion without the involve of the reaction at room temperature, and the resulting $Ti_3C_2T_x$/WPU emulsions was labeled as BWPU. WPU, IWPU and BWPU was poured into polypropylene plate (3cm×6cm) and dried at 25 °C for 2 days. Finally, the films were placed in vacuum oven at 60 °C for further drying for 4 hours. The films were labeled as IWPU-x (0, 3, 10 and 33) and BWPU-x (0, 3, 10 and 33) for the observation at room temperature. The symbol of X represent the days of the storage.

1.5 Characterizations

X-ray diffraction (XRD) measurements were conducted from 5^o to 70^o at a scan rate of 10^o min^{-1} using a Rigaku X-ray diffractometer using Cu Ka radiation. The atomic force microscope (AFM; Bruker Dimension Icon) was used to determine the shapes

and thickness of Ti_3C_2-MXene flakes. The surface of Ti_3C_2-MXene was imaged by a scanning electron microscopy (SEM; JEM-6510). A transmission electron microscopy (TEM; JEM-2100) was applied to obtain the TEM images of samples. X-ray photoelectron spectroscopy (XPS) analysis was carried out by a Thermo ESCALAB 250XI spectrometer. The UV-Vis spectra of the films were measured on a Shimadzu UV2600 spectrophotometer. The morphologies and structures of I-Ti_3C_2, Ti_3C_2-MXene and the film of IWPU were illustrated by SEM. Fig. S1a and b show that chemical modification does not change the layered morphology of Ti_3C_2-MXene. The SEM image (Fig. S1c) of IWPU-33 film associated with Ti elemental mapping image in Fig. S1d confirms a good dispersion of Ti_3C_2-MXene in solid films.



Scheme S1. Synthesis diagram of WPU and WPU/MXene hydrid emulsions

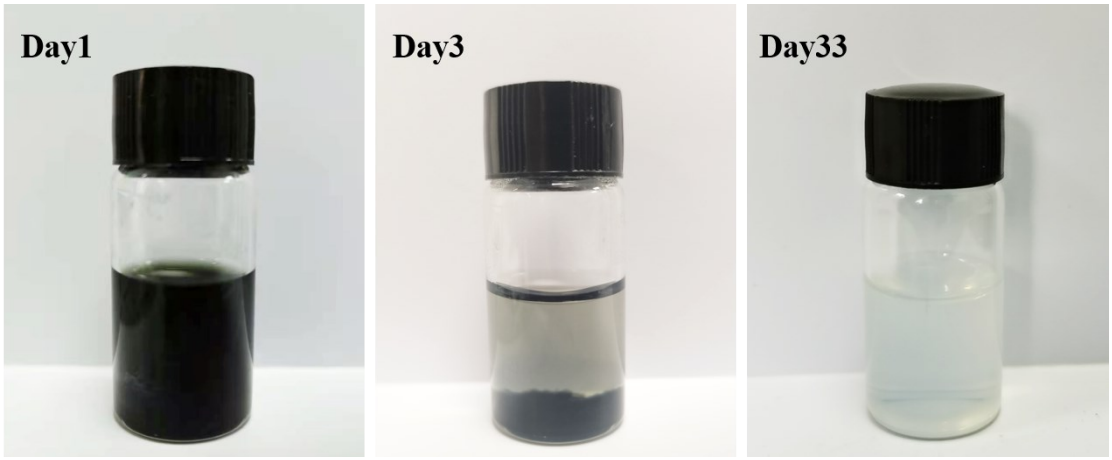


Fig. S1 The stability of MXene dispersion on the day1, 3 and 33.

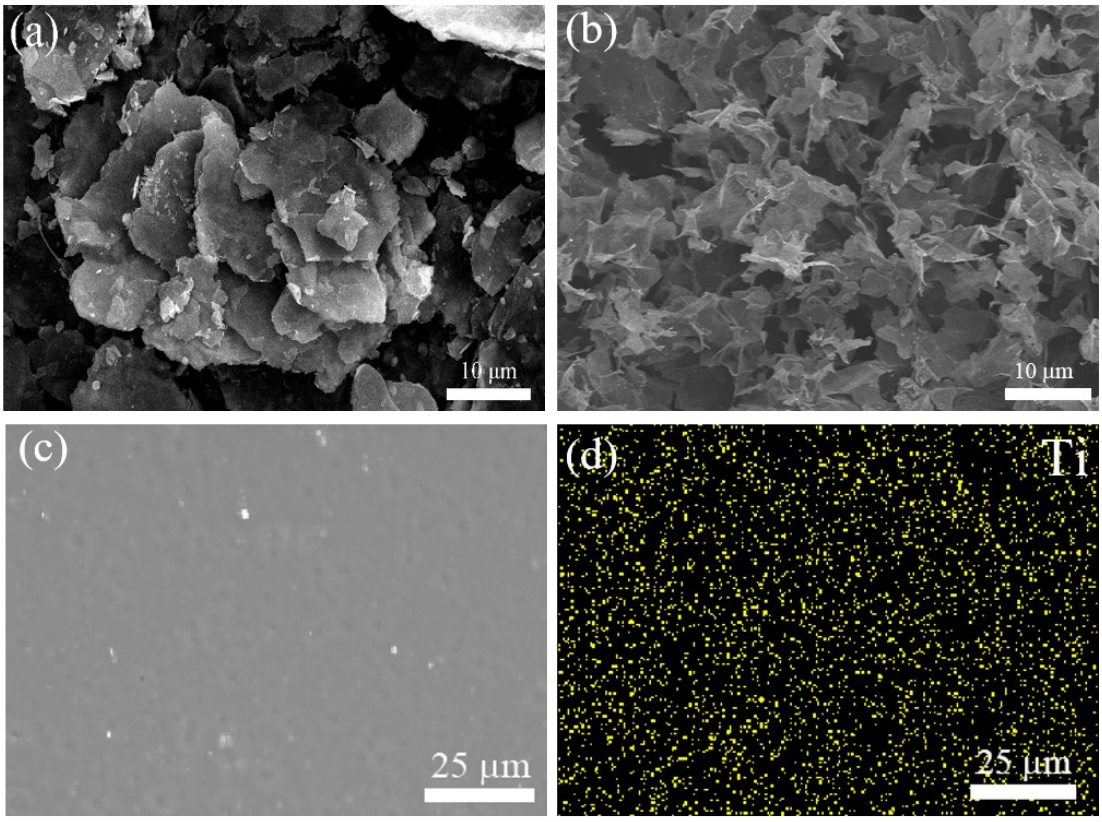


Fig. S2 SEM images of (a) I-Ti_3C_2, (b) Ti_3C_2-MXene and (c) IWPU-33; (d)elemental mapping of Ti for IWPU-33