

Cite this: *J. Mater. Chem. A*, 2022, 10, 24746

# Ultrahigh fluid sorption capacity of superhydrophobic and tough cryogels of cross-linked cellulose nanofibers, cellulose nanocrystals, and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets†

Golnoosh Akhlagi,<sup>ab</sup> Elaheh K. Goharshadi<sup>\*acd</sup> and Henrikki Liimatainen<sup>id</sup><sup>\*b</sup>

In this study, we present superhydrophobic, hierarchical, and nanostructured cryogels made from a nanocellulose (NC) skeleton comprising cellulose nanofibers (CNFs) and nanocrystals (CNCs), double cross-linked with  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene nanosheets and poly(vinyl alcohol) (PVA) in the presence of tetradecylamine. Compared to pure CNCs or CNFs, cryogels with a combination of CNCs and CNFs possessed significantly better mechanical performance. Unlike many green natural based nanoporous solids, the prepared mixed cryogels displayed rigid and durable structure, and possessed ultrahigh sorption capacity for several organic fluids, among the highest reported for aerogels/cryogels in the literature. By taking advantage of the synergistic effects of crosslinking between long-entangled CNFs with short-needle-like CNCs as well as the strong interaction between NCs, MXene nanosheets and PVA, highly porous (>92%), lightweight ( $\sim 20 \text{ mg cm}^{-3}$ ), and superhydrophobic cryogels with a water contact angle of  $\sim 150^\circ$  were designed. The hybrid cryogels possessed ultrahigh sorption capacity toward various oils/organic solvents ranging from approximately 110–320 times their weight. The cryogels were reused in more than ten cycles of sorption–squeezing without significantly reducing sorption capacity. Hence, these nanostructured porous solids have a high potential to be used in various purposes in environmental remediation, such as oil spill response and removal of water-insoluble organic solvents.

Received 15th August 2022  
Accepted 7th November 2022

DOI: 10.1039/d2ta06437e

rsc.li/materials-a

## 1. Introduction

With three dimensional (3D) interconnected network of nano- and micropores, aero- and cryogels, *i.e.*, lightweight porous solids constructed *via* supercritical or freeze-drying processes, are among the most promising designs for fluid sorbents because of their super-low density, large specific surface area, and porosity.<sup>1–4</sup> These materials have a high potential for use in environmental remediation, such as oil spill response and removal of water-insoluble organic solvent leakages and industrial oily wastewaters.<sup>5–7</sup> Generally, the materials used for oil or solvent removal possess superhydrophobicity and/or superoleophilicity to enable selective filtration or uptake of oil or solvent from aqueous mixtures,<sup>8,9</sup> or they promote water

removal,<sup>10</sup> or controllable separation of different phases.<sup>11</sup> Several types of aerogels based on inorganics,<sup>12,13</sup> and synthetic<sup>14–16</sup> and natural polymers<sup>17,18</sup> have been revealed as superabsorbents. However, due to the mechanical brittleness of inorganic aerogels (*e.g.*, silica aerogels), their use and recovery in fluid separation are limited. Despite several favorable properties of carbon-based aerogels, the shortcomings such as expensive precursors and complicated or time-consuming fabrication processes hamper their use in practical applications.<sup>6,19,20</sup> By contrast, aero- and cryogels based on biopolymers can be created from abundant and cheap renewable biomass sources such as wood chips and agricultural residues, being highly appealing, sustainable, and biodegradable structures for removal of oil and organic solvents from aqueous environments.<sup>10,21–24</sup>

Recently porous solids derived from cellulose nanomaterials, such as cellulose nanofibers (CNFs) and nanocrystals (CNCs), have attracted considerable research interest.<sup>25–27</sup> In most studies, CNCs or CNFs are used as a single component for the preparation of nanocellulose (NC)-based aerogels,<sup>28–30</sup> while very few reports focus on mixing different sizes of NC to prepare aerogels. Zhang *et al.*<sup>31</sup> combined CNFs and CNCs from eucalyptus wood pulp. The mixed aerogel of CNCs and CNFs showed a better performance compared to pure CNCs or CNFs aerogels.

<sup>a</sup>Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, 9177948974, Iran

<sup>b</sup>Fiber and Particle Engineering Research Unit, University of Oulu, PO Box 4300, FI-90014, Oulu, Finland

<sup>c</sup>Nano Research Center, Ferdowsi University of Mashhad, Mashhad, 9177948974, Iran

<sup>d</sup>Micro-Nano Technologies in Renewable Energies Center, Ferdowsi University of Mashhad, Mashhad, 9177948974, Iran. E-mail: Henrikki.Liimatainen@oulu.fi; gohari@um.ac.ir

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ta06437e>







planes.<sup>56</sup> The crystallite size of materials was calculated using the Debye–Scherrer formula:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2)$$

where  $\beta$  is the full width at half maximum (FWHM) of the dominating peak corresponding to the (002) plane.<sup>57</sup> Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups of the synthesized MXene powder at room temperature with a KBr pellet on a Thermo Nicolet-Avatar 370 FT-IR Spectrometer ranging from 400 to 4000  $\text{cm}^{-1}$  (Thermo Nicolet, USA). The morphology of MAX phase, MXene, and cryogels was investigated using a field emission scanning electron microscope (FE-SEM) on a Zeiss Sigma instrument (Germany) with a 5 kV accelerating voltage combined with energy dispersive X-ray (EDX) spectroscopy for elemental mapping. Samples were analyzed by placing them on a sample holder using a carbon pad and coating it with a thin layer of platinum. Transmission electron microscopy (TEM) images of samples were obtained using JEOL JEM-2200FS EFTEM/STEM (Japan). The composition and the electronic states of the delaminated MXene were investigated using X-ray photoelectron spectroscopy (XPS) with Al-K $\alpha$  using Thermo Fisher Scientific ESCALAB 250Xi XPS System (USA). CasaXPS and Origin software with a Shirley background type were used for the XPS peak fitting. The atomic force microscopy (AFM) images of prepared MXene nanosheets were obtained by Ara Research (model no. 0101/A, Iran) in a noncontact mode at room temperature. A Zetasizer (Nano-ZS) (Malvern, United Kingdom) was used to measure zeta potential. The surface wettability of cryogels was determined using the sessile drop technique using Krüss DSA 25 (Krüss GmbH, Hamburg, Germany) by placing a 4  $\mu\text{L}$  drop of DI water on the cryogel surface and capturing CCD images at the rate of 1 frame per s. The contact angle was determined based on the drop's shape analysis using the full Young–Laplace equation and assuming a spherical drop.

## 2.6. Density and porosity of cryogels

The mass and volume of the cryogels were used to calculate their density. The mass of the cryogels was measured by an analytical balance (readability 0.0001 g), and the volume was calculated by measuring diameters and heights with a digital caliper at three different positions.

The NC cryogels porosity ( $P\%$ ) was calculated according to the following equation:

$$P (\%) = \left( 1 - \frac{\rho_{\text{aerogel}}}{\rho_s} \right) \times 100\% \quad (3)$$

where  $\rho_{\text{cryogel}}$  and  $\rho_s$  are the density of the bulk cryogel samples and solid materials, respectively. The solid density,  $r_s$ , was calculated using the following equation:

$$\rho_s = \frac{1}{\frac{m_{\text{cellulose}}}{\rho_{\text{cellulose}}} + \frac{m_{\text{PVA}}}{\rho_{\text{PVA}}} + \frac{m_{\text{Ti}_3\text{C}_2\text{T}_x}}{\rho_{\text{Ti}_3\text{C}_2\text{T}_x}} + \frac{m_{\text{TDA}}}{\rho_{\text{TDA}}}} \quad (4)$$

where  $m_{\text{cellulose}}$ ,  $m_{\text{PVA}}$ ,  $m_{\text{Ti}_3\text{C}_2\text{T}_x}$ , and  $m_{\text{TDA}}$  are the mass fractions of cellulose, PVA,  $\text{Ti}_3\text{C}_2\text{T}_x$ , and TDA.  $\rho_{\text{cellulose}}$ ,  $\rho_{\text{PVA}}$ ,  $\rho_{\text{Ti}_3\text{C}_2\text{T}_x}$ , and  $\rho_{\text{TDA}}$  are the solid densities of cellulose (1.528  $\text{g cm}^{-3}$ ), PVA (1.29  $\text{g cm}^{-3}$ ),  $\text{Ti}_3\text{C}_2\text{T}_x$  (4.91  $\text{g cm}^{-3}$ ),<sup>58</sup> and TDA (0.993  $\text{g cm}^{-3}$ ), respectively.

## 2.7. Solvents sorption capacity and recyclability of cryogels

Five oils, including gasoline, motor oil, silicon oil, cooking oil, and linseed oil, and seven organic solvents, *i.e.*, chloroform, *n*-hexane, acetone, methanol, toluene, DMF, and THF, were used to measure the sorption capacity of cryogels. Prewighted cryogels were immersed in oil/organic solvents for 3 min to reach sorption equilibrium. The swollen cryogels were then removed and weighed. The sorption capacity ( $Q$ ,  $\text{g g}^{-1}$ ) was calculated according to eqn (5):

$$Q = \frac{m_1 - m_0}{m_0} \quad (5)$$

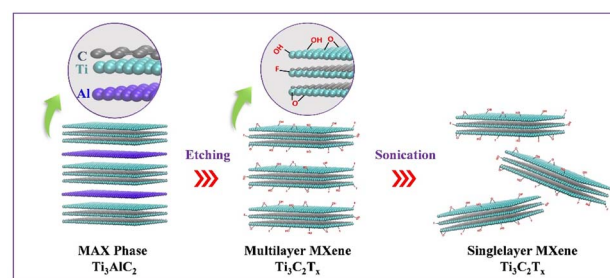
where  $m_0$  and  $m_1$  are the mass of the cryogel before and after oil/organic solvent sorption, respectively. All tests were repeated in triplicate and made at room temperature. A cyclic compression test was performed to evaluate the recyclability of cryogels by simply squeezing the cryogels manually. For this purpose, two parallel glass slides were used to compress the soaked cryogels to remove the adsorbed oils or organic solvents. The sorption and squeezing processes were performed in 10 cycles using edible oil, motor oil, chloroform, and methanol as the model oils/organic solvents.

# 3. Results and discussion

## 3.1. Exfoliation of mxene nanosheets

Scheme 1 shows the synthesis of delaminated MXene nanosheets by selectively etching Al layers of  $\text{Ti}_3\text{AlC}_2$  precursor *via* an *in situ*-produced HF (mixture of LiF/HCl). The extensive sonication led to the delamination of multilayered- $\text{Ti}_3\text{C}_2\text{T}_x$  terminated by fluorine, oxygen, and hydroxyl groups. A series of characterizations were conducted to verify the  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene nanosheets' successful preparation.

Fig. 1a shows the XRD patterns of the  $\text{Ti}_3\text{AlC}_2$  MAX phase and  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene nanosheets. The crystallinity and structural order of  $\text{Ti}_3\text{AlC}_2$  decrease after the etching treatment, confirming the removal of Al layers from  $\text{Ti}_3\text{AlC}_2$  and the presence of the  $\text{Ti}_3\text{C}_2\text{T}_x$  phase. The strong characteristic peaks



Scheme 1 Preparation of MXene nanosheets.



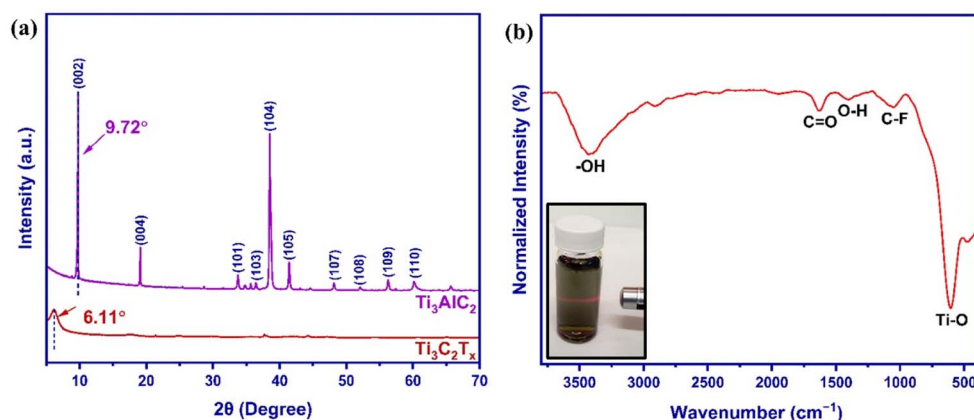


Fig. 1 (a) XRD patterns of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{C}_2\text{T}_x$ . (b) FTIR spectrum of  $\text{Ti}_3\text{C}_2\text{T}_x$ . Inset in (b) shows the Tyndall effect of  $\text{Ti}_3\text{C}_2\text{T}_x$  dispersion.

of  $\text{Ti}_3\text{AlC}_2$  at  $9.72^\circ$ ,  $19.10^\circ$ ,  $33.76^\circ$ ,  $36.44^\circ$ ,  $38.49^\circ$ , and  $41.42^\circ$  are assigned to the (002), (004), (101), (104), (104), and (105) crystal planes, respectively.<sup>46,47,59</sup> The most intense pyramidal plane peak (104) disappeared in the case of MXene compared with the  $\text{Ti}_3\text{AlC}_2$  MAX precursor, indicating the successful elimination of Al atomic layers from  $\text{Ti}_3\text{AlC}_2$  after the etching

process.<sup>46,60</sup> Moreover, the MXene powder (002) basal plane peak significantly shifted to the lower  $2\theta$  angle (from  $9.72^\circ$  to  $6.11^\circ$ ). It broadened, suggesting the increase of  $d$ -spacing from 10.56 to 16.79 Å due to the selective removal of Al atoms in  $\text{Ti}_3\text{AlC}_2$  according to Bragg's law (eqn (1)).<sup>47,56</sup> Furthermore, the average crystallite size of  $\text{Ti}_3\text{AlC}_2$  MAX phase and  $\text{Ti}_3\text{C}_2\text{T}_x$

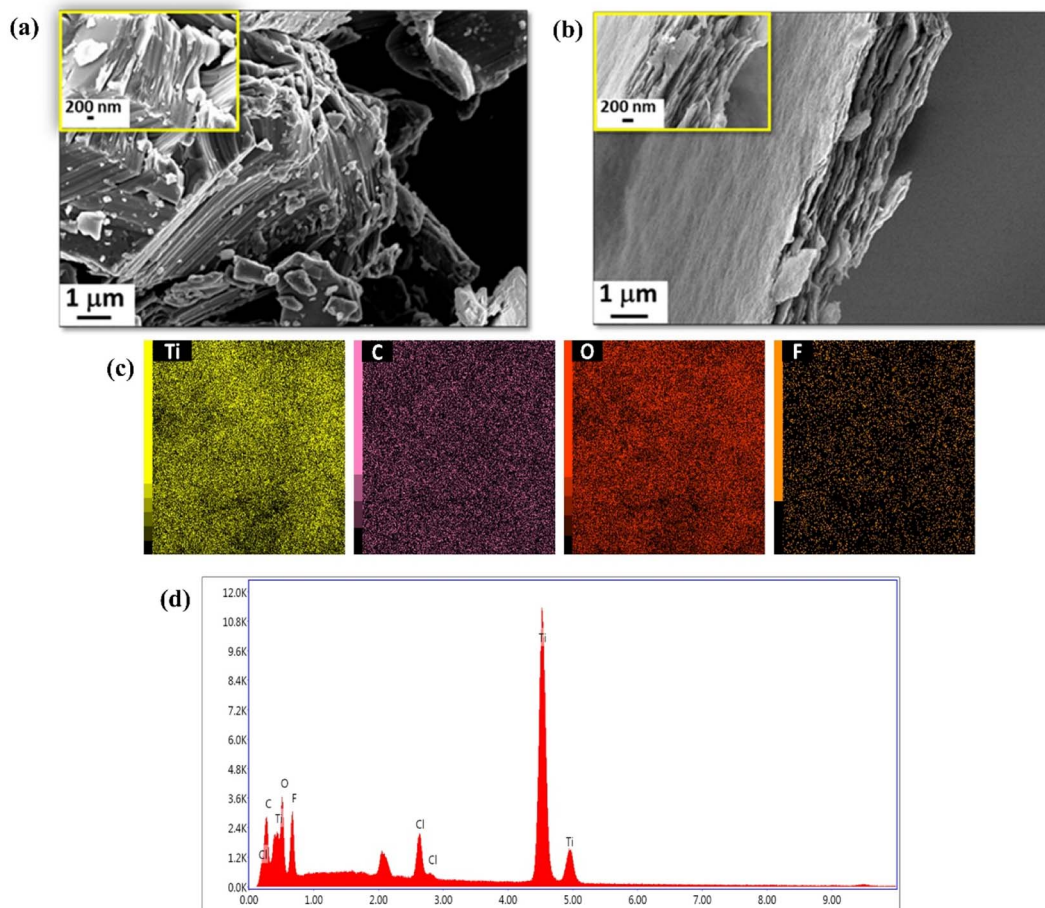


Fig. 2 Morphology structure of (a) MAX phase and (b) MXene. (c) Elemental mapping image and (d) EDX spectrum of MXene.



MXene reduced from 2.78  $\mu\text{m}$  to 1.9 nm after etching (eqn (2)). These changes indicated that the Al layer was etched, and the MAX phase was converted successfully to delaminated MXene nanosheets.

FTIR spectroscopy (Fig. 1b) was used to determine the surface functional groups of MXene nanosheets. The bands at 3435 and 1400  $\text{cm}^{-1}$  confirm the presence of the terminal hydroxyl groups and possibly absorbed  $\text{H}_2\text{O}$  molecules or extremely strongly coordinated  $\text{H}_2\text{O}$ . The bands at 1631, 1052, and 610  $\text{cm}^{-1}$  are assigned to the stretching vibrations of  $\text{C}=\text{O}$ ,  $\text{C}-\text{F}$ , and the deformation vibration of  $\text{Ti}-\text{O}$  bonds, respectively, which is consistent with previous reports.<sup>60–62</sup> The terminated functional groups (O, OH, and F) endow the exfoliated MXene nanosheets to form a stable colloidal suspension in water. The dark green aqueous MXene nanosheet dispersion (with a  $\text{Cs}\% = 0.5$ ) exhibits a special “Tyndall effect,” indicating the excellent stability and nanosize of MXene nanosheets and evidence for fabricating high-quality MXene nanosheets (inset of Fig. 1b).<sup>55</sup> Furthermore, due to the hydrophilic functional groups on the surface of the prepared MXene nanosheets, the zeta potential was measured to be  $-32.27$  mV.

FE-SEM images of MAX phase and MXene nanosheets were obtained to evaluate the etching process and analyze the morphology of nanosheets. The commercially purchased MAX phase powder shows a lamellar and close-packed structure composed of metallic and strong covalent/ionic bonds (Fig. 2a). Clearly, after etching and the delamination process, a loosely stacked accordion-like layered structure and an opened interspace of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene nanosheets can be

observed (Fig. 2b), confirming the successful etching of  $\text{Ti}_3\text{AlC}_2$  and removal of Al layers. Also, the removal of aluminum was verified using EDX. The elemental mapping (Fig. 2c) and EDX spectrum (Fig. 2d) of MXene powder show that the exfoliated MXene mainly contains Ti (44.36 wt%), C (16.03 wt%), O (21.70 wt%), F (14.96 wt%), confirming the typical  $\text{Ti}_3\text{C}_2\text{T}_x$  composition.<sup>63–66</sup> Only a negligible Cl amount (2.94 wt%) was observed as an impurity due to the use of HCl in the etching process, suggesting the high purity of prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets.

As shown in TEM analysis (Fig. 3a), the MXene nanosheets possessed an ultralow thickness. The lateral diameter of MXene nanoflakes ranged from  $\sim 100$  to 500 nm, with the average thickness of around 1 nm, as validated by an AFM image (Fig. 3c), corresponding to the single or double-layer structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene.<sup>67</sup> The selected area electron diffraction (SAED) pattern in Fig. 3b shows the single-crystalline hexagonal structure of the nanosheets with a lattice spacing of 2.76 and 1.55  $\text{\AA}$  corresponding to the  $\text{Ti}_3\text{C}_2\text{T}_x$  (100) and  $(-2\ 1\ 0)$ . According to the MXene nanoflakes particle size distribution (PSD) (Fig. 3d), the mean volumetric diameter of nanosheets was about 23.75 nm.

XPS analysis was performed to investigate further the surface chemical composition and molecular structure of the as-prepared MXene (Fig. 4). The XPS survey spectra (Fig. 4a) show the typical peaks of Ti 2p, C1s, O1s, and F1s from 0 to 1300 eV, which suggest the presence of  $\text{Ti}_3\text{C}_2\text{T}_x$  together with  $=\text{O}$ ,  $-\text{OH}$ ,  $-\text{F}$  groups as a result of HCl and LiF aqueous solution. The peaks with binding energy values of 35, 284, 456, 477, 531,



Fig. 3 (a) TEM image, (b) its corresponding SAED pattern, (c) AFM image, and (d) PSD of MXene nanosheets.



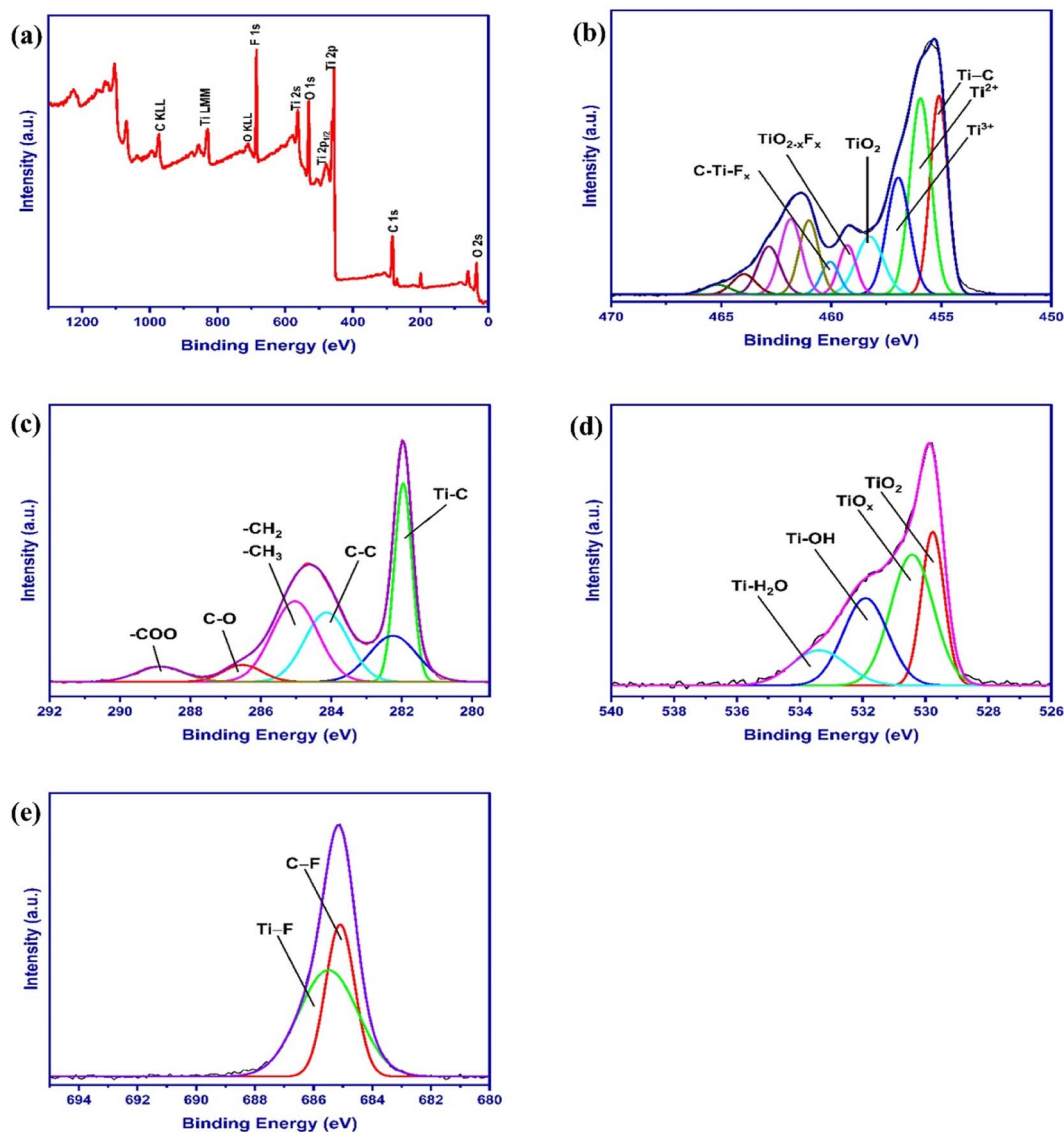


Fig. 4 (a) XPS survey spectrum of MXene and deconvolution of high-resolution XPS spectra for the elements in delaminated MXene nanosheets for (b) Ti 2p, (c) C 1s, (d) O 1s, and (e) F 1s.

562, 685, 830, and 978 eV are assigned to O 2s, C 1s, Ti 2p, Ti 2p<sub>1/2</sub>, O 1s, Ti 2s, F 1s, Ti LMM, and C KLL,<sup>68,69</sup> respectively, which is consistent with the EDX results shown in Fig. 2d. Notably, it can be seen that the Al 2p peak does not exist in the spectra, which proves the fact that Al atoms are successfully etched from the Ti<sub>3</sub>AlC<sub>2</sub> MAX phase. Fig. 4b–e show the deconvoluted spectra of Ti 2p, C 1s, O 1s, and F 1s within MXene powder. Table 1 summarizes the peak positions obtained from the fits. The Ti 2p core level peak can be fitted by a contribution of six doublets (Ti 2p<sub>3/2</sub>–Ti 2p<sub>1/2</sub>) corresponding to Ti atoms, Ti–O, TiO<sub>2</sub>–xF<sub>x</sub>, and C–Ti–F<sub>x</sub>. The C 1s region spectra of layered Ti<sub>3</sub>C<sub>2</sub> are fitted by six peaks assigned to Ti–C, 1, 2 hydrocarbons (–CH<sub>2</sub>– & CH<sub>3</sub>–), and carboxylates (–COO). The XPS spectra of O 1s are divided into O–Ti, C–Ti–O<sub>x</sub>, C–Ti–(OH)<sub>x</sub>, and H<sub>2</sub>O–Ti bonds. The F 1s peak is deconvoluted into Ti–F and C–F bonds. The calculated binding energy values of the components are consistent with those

obtained in previous XPS studies on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.<sup>70–75</sup> In summary, XPS analysis shows that MXenes nanosheets contain three types of surface functional groups: oxide (–O–), hydroxyl (–OH), and fluoride (–F), proving that etching treatment can introduce abundant hydrophilic surface termination O–H groups, which take part in covalent crosslinking and hydrogen bond interaction.

### 3.2. Characteristics of CNCs–CNFs@MXene cryogels

Fig. 5 shows a schematic representation of the general synthesis procedure and formation mechanism of the NC–MXene cryogels. In this work, cellulose nanomaterials, such as CNCs and CNFs, were produced using green DES-based pretreatments combined with microfluidization, and hybrid cryogels with different ratios and concentrations of CNCs



Table 1  $Ti_3C_2T_x$  XPS peak fitting results

Region	BE (eV)	FWHM (eV)	Assignment
Ti $2p_{3/2}$ ( $2p_{1/2}$ )	455.10 (461.01)	0.93 (1.03)	Ti (I, II or IV)
	455.94 (461.83)	1.12 (1.13)	$Ti^{2+}$ (I, II, or IV)
	456.95 (462.82)	1.22 (1.18)	$Ti^{3+}$ (I, II, or IV)
	458.25 (463.96)	1.43 (1.23)	$TiO_2$
	459.26 (465.15)	0.93 (1.33)	$TiO_{2-x}F_x$
	460.04 (465.99)	0.94 (1.03)	C-Ti-F <sub>x</sub> (III)
C 1s	281.95	0.58	C-Ti-T <sub>x</sub>
	282.24	1.57	C-Ti-T <sub>x</sub>
	284.12	1.47	C-C
	285.02	1.54	-CH <sub>2</sub> - and -CH <sub>3</sub>
	286.51	1.31	C-O
	288.85	1.54	-COO
O 1s	529.77	0.85	$TiO_2$
	530.42	1.59	C-T-O/ $TiO_2$ -F
	531.90	1.66	C-Ti-(OH) <sub>x</sub>
	533.38	2.03	Ti-H <sub>2</sub> O (adsorbed water)
F 1s	685.09	1.17	C-Ti-F <sub>x</sub> (III)
	685.49	2.36	$TiO_2$ -F

and CNFs were prepared. When the mixing ratio of CNCs and CNFs was 3 : 1 (solids content of 1 wt%), the Ref. cryogel presented good mechanical strength with no obvious cracks and high porosity of 99.61% compared to pure CNCs and CNFs aerogels. The excellent mechanical performance of Ref cryogel can be explained by a higher degree of crosslinking

between long-entangled fiber-like CNFs and short-needle-like CNCs. Nevertheless, the hydrophilic character of the cellulose skeleton led to the collapse of the NC cryogels porous structure in the presence of water, limiting their use in oil/water separation. Therefore, TDA was used as a hydrophobization agent to improve the wet strength of the mixed NC cryogels.

Table 2 shows the WCA of hydrophobized cryogels as a function of TDA dosage. By increasing the amount of TDA from 0.1 to 0.8 mg, the WCA of the cryogels increased from 56.00 to 91.30°, whereas it decreased at TDA contents greater than 0.8 mg. Moreover, the mixed cryogels with TDA content higher than 1 mg were very weak and disintegrated into powder after freeze-drying, and the WCA could not be measured. Also, the cryogels containing an optimized dosage of TDA (0.8 mg) suffered from poor mechanical performance, were easily collapsed or redispersed/disintegrated in water and had limited

Table 2 WCA of mixed CNCs–CNFs cryogels as a function of TDA dosage

CNCs–CNFs	TDA (mg)	WCA [°]
3 : 1, 1%	0.1	56.00
	0.5	62.40
	0.8	91.30
	1.0	84.09
	1.5	—

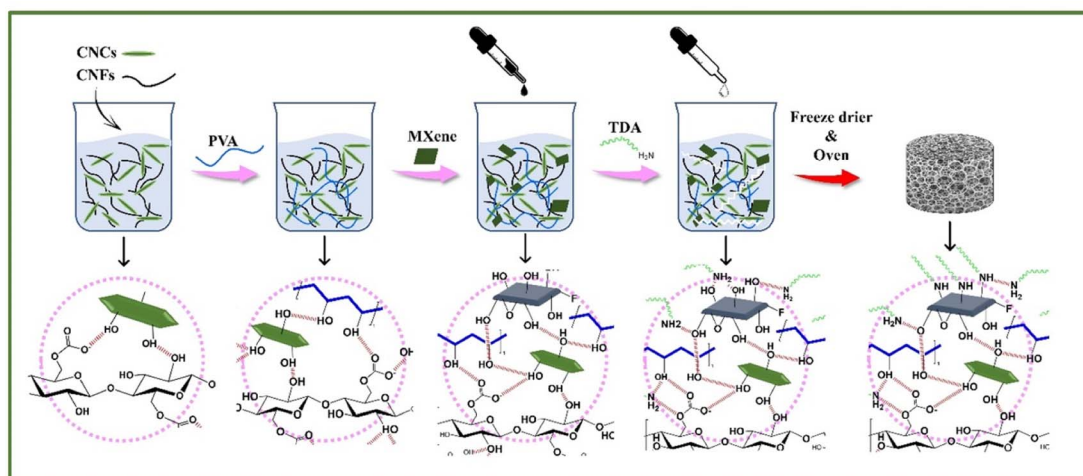


Fig. 5 Preparation of superhydrophobic and cross-linked CPMT cryogel containing MXenes.





shape recovery. Although they did not show any visible crack, the cryogels were very brittle when subjected to a slight compression.

The MXenes were incorporated into the cryogel structure to enhance the mechanical strength, hydrophobicity, and cross-linking of NC cryogels. As shown in Fig. 6a, the obtained NC cryogels containing MXenes and TDA (CMT) were strongly hydrophobic with a WCA of  $126.7^\circ$  and possessed a high porosity of 94.20%. Therefore, MXene nanoflakes acted as efficient cross-linkers in the CNCs/CNFs network and improved both the WCA and mechanical performance of cryogels. The presence of abundant hydroxyl groups on the surface of NC and MXene nanosheets promoted hydrogen bonding between the nano-constituents, while the amino groups of TDA reacted with surface hydroxyls during the heating process and reduced the surface free energy of cryogels.

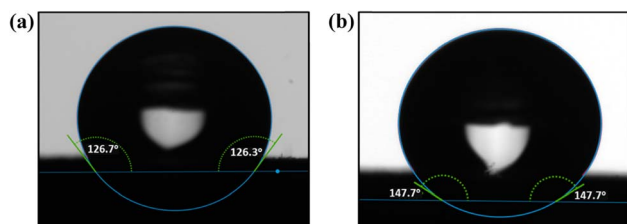


Fig. 6 WCA of (a) CMT and (b) CPMT cryogels.

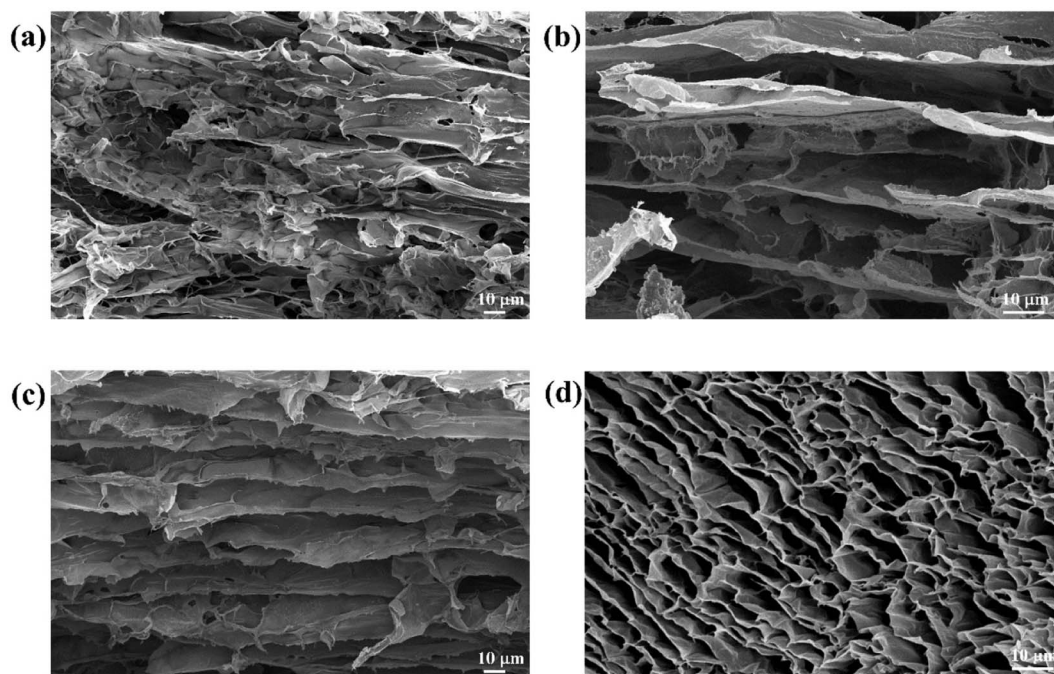


Fig. 7 FE-SEM of longitudinal structure of (a) Ref., (b) CMT, (c) CPMT cryogels; (d) cross-section of CPMT cryogel, and (e) average pore diameter of the CPMT cryogel.





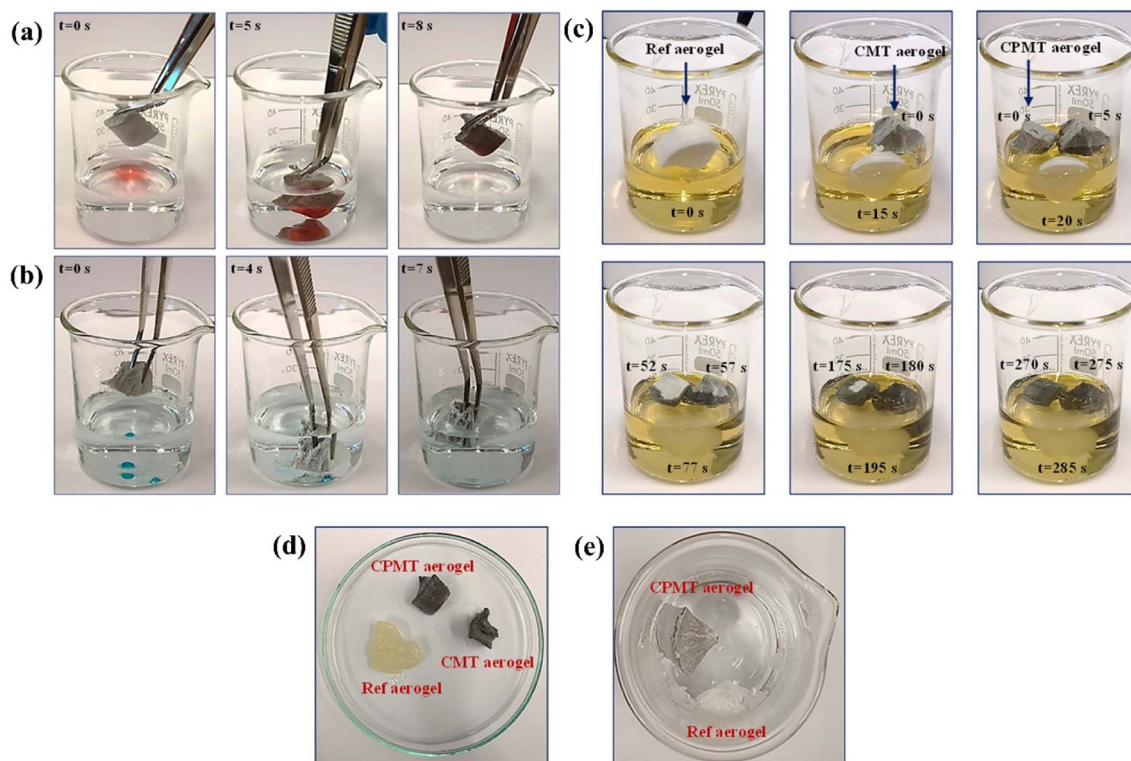


Fig. 9 Removal of (a) motor oil (dyed with oil red O) and (b) chloroform (dyed with methylene blue) from the surface and bottom of the water with CPMT cryogel, (c) the sorption performance of Ref., CMT, and CPMT cryogels as a function of time, (d) Ref., CMT, and CPMT cryogels after 1, 4, and 10 cycles of the edible oil sorption, and (e) Ref. and CPMT cryogels on the surface of the water.

structure was elucidated with several oils and organic solvents from water. When the cryogel was placed into the motor oil (stained with oil red O)/water mixture, it absorbed the floating oil on the water surface completely and quickly (<8 s), leaving the clean water, as shown in Fig. 9a (and Video S1†). Furthermore, the CPMT cryogel could selectively and quickly (<6 s) absorb organic solvents with a density greater than water, such as chloroform (dyed with methylene blue) underwater and was easily removed without any solvent release within 6 s (Fig. 9b, Video S2†). After sorption, the cryogel retained its shape and floated on the water surface without oil/solvent release, enabling easy sorbent collection in practical applications. Hence, the prepared cryogel is an ideal sorbent for treating oil spills and oily wastewater remediation.

Fig. 9c shows the sorption performance of Ref., CMT, and CPMT cryogels in edible oil. The Ref. cryogel was sinking in oil after approximately 1 min. By contrast, the modified CMT and CPMT cryogels were saturated with oil after approximately 3 and 5 min, respectively, but were still partly floating. The structure of Ref. cryogel collapsed when exposed to oil, and it was not possible to use it for the recycling test (Fig. 9d). The CMT and CPMT cryogels maintained their porous appearance and after four cycles of sorption–desorption of edible oil, the CMT cryogel structure failed to maintain its original shape. In comparison, the CPMT cryogel maintained its shape still after ten cycles

without any obvious failure in its structure with super high oil sorption efficiency, as shown in Fig. 9d. The CPMT cryogel also had good wet strength, as shown when exposed to pure water, whereas Ref. cryogel lost its structural integrity after contact with water (Fig. 9e).

Seven organic solvents (chloroform, *n*-hexane, methanol, toluene, acetone, DMF, and THF) and five oils (gasoline, motor oil, silicon oil, edible oil, and linseed oil) were investigated to quantify the sorption efficiency of Ref., CMT, and CPMT cryogels (Fig. 10a). These substances are contaminants commonly existing in our daily lives and industries. The pristine NC cryogel (Ref.) had a sorption capacity ranging from 10 to 72 g g<sup>-1</sup>, at a similar level to previously reported NC aerogels.<sup>21</sup> The introduction of MXene into the cryogel structure resulted in outstanding increase in sorption efficiency, with the sorption capacities of 107–278 g g<sup>-1</sup>. Although this improvement was achieved without PVA, the shape recovery and recyclability of CMT cryogels were insufficient. Thus, PVA was incorporated in the mixture of CNCs/CNFs and MXenes, resulting in mechanically robust designs with a greater sorption capacity of 110–320 g g<sup>-1</sup>. This excellent oil/organic solvent sorption performance was presumably assigned to superhydrophobicity and the channeled and hierarchical microporous structure of CPMT, which promoted the capillary uptake of nonpolar fluids.



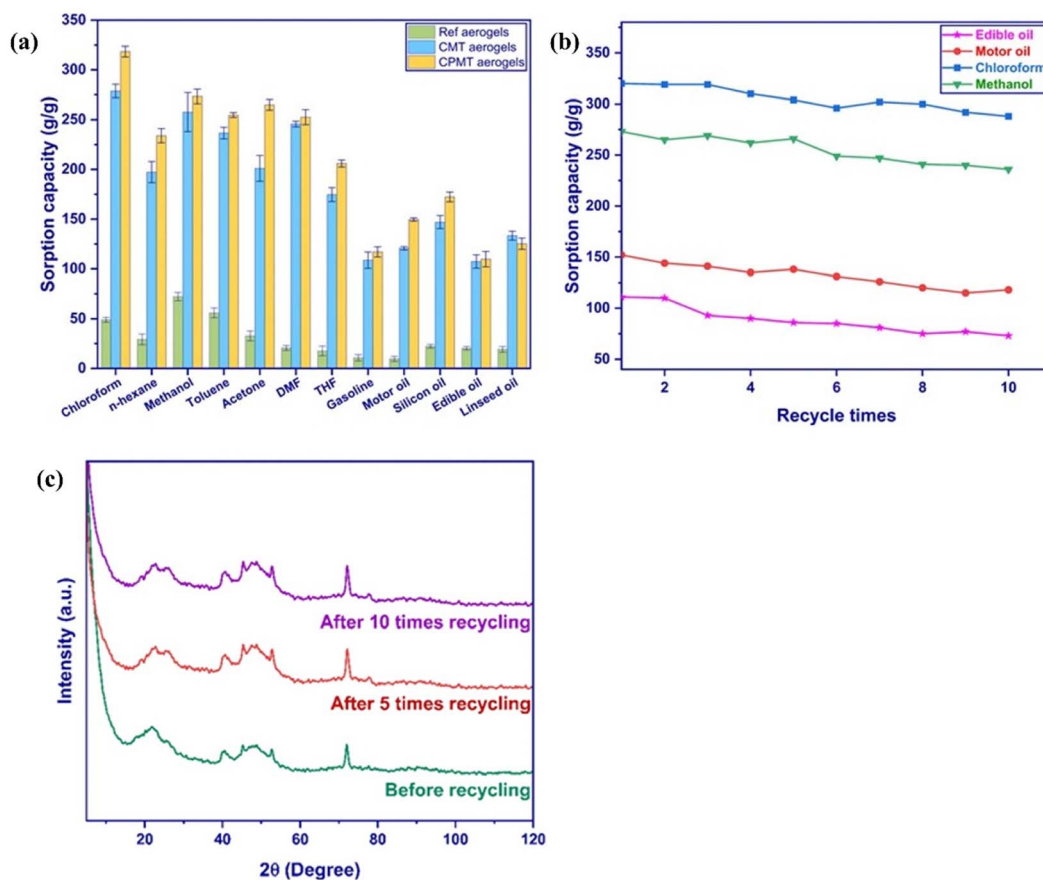


Fig. 10 (a) Sorption capacity of Ref., CMT, and CPMT cryogels for various oils and organic solvents, (b) recyclability of the CPMT cryogel after ten cycles of squeezing, and (c) XRD patterns of CPMT cryogel before and after 5 and 10 times recycling.

Reusability, recyclability, and chemical stability of cryogels is critical for their practical applications as sorbents for oils and organic solvents. Although the fluids can be recovered from saturated sorbents *via* distillation, solvent extraction, or combustion, these methods are often complicated, time-consuming, inefficient, and energy-intensive.<sup>34</sup> In this study, oils/organic solvents were recovered using a simple mechanical squeezing that can be considered the simplest and most sustainable recycling approach regarding energy, material, and chemical use. Fig. 10b shows the sorption capacity of recovered CPMT cryogels for motor oil, edible oil, chloroform, and methanol. The CPMT cryogel retained the high sorption capacity with all tested oils and organic solvents even after 10 cycles of squeezing–sorption, showing only a slight decrease in removal efficiency and indicating the good cryogels recyclability.

Furthermore, to confirm the reusability of the CPMT cryogels, the XRD patterns of the cryogels prior to exposure to chloroform (the highest sorption capacity) and after five and ten cycles of squeezing were measured. As shown in Fig. 10c, there is no significant difference in the patterns of the cryogels before and after dipping into chloroform, which indicates their excellent recyclability and chemical stability.

The chemical stability of the CPMT cryogels was also confirmed by exposing them to motor oil, silicon oil, chloroform, and methanol for 10 min and 24 hours. Video S3 and S4† show that after removing the cryogels from the oil/organic solvents, they were still solid and rigid even after 24 h. The color of the oil/solvent remained unchanged, indicating that the CPMT cryogels are chemically stable and have a good structural integrity.

The as-prepared CPMT cryogel possessed ultrahigh sorption capacity, being one of the highest reported in the literature fabricated by only pure CNCs or CNFs cryogels or complicated and high-cost approaches (Table 3), including aerogels and sponges of chemically cross-linked cellulose aero- and cryogels (12–168 g g<sup>-1</sup>),<sup>21,34,39,77–80</sup> MXene based aerogels and sponges,<sup>40,46–48,81–83</sup> carbon aerogels,<sup>12,84–86</sup> and graphene-based aerogels.<sup>87,88</sup> The sorption capacity of CPMT, especially, outperforms that of previously studied porous MXene materials. Thus, the straightforward fabrication process and abundant green resources of cellulose nanomaterials make CPMT cryogel a highly appealing, cost-effective, and sustainable alternative for water remediation.



Table 3 Comparison of the oil and organic solvent sorption capacity of different sorbents with our prepared CPMT cryogel

Sorbents	Absorbed substances	Sorption capacity (g g <sup>-1</sup> )	Ref.
Modified cellulose aerogel	Crude oil, engine oil, pump oil, paraffin liquid, silicon oil. DMSO, cyclohexane, isopropyl alcohol, CH <sub>2</sub> Cl <sub>2</sub>	9–48	21
Silane modified cellulose/PVA aerogel	Trichloromethane, dichloromethane, chlorobenzene, hexane, cyclohexane, toluene, peanut oil	28–65	78
CNCs/PVA aerogel	Gasoline, motor oil, crude oil, sesame oil, cooking oil, and olive oil, chloroform, acetone, ethanol, DMF, 2-propanol, ethyl acetate, toluene, hexane	69–168	39
Copper nanoparticles-coated cellulose aerogel	<i>n</i> -Hexane, trichloromethane, soybean oil, pump oil	67.8–164.5	80
Polyimide/MXene aerogel	Pump oil, chloroform, tetrahydrofuran, soybean oil, acetone, toluene, <i>n</i> -hexane, waste pump oil	18–58	40
MXene functionalized melamine sponge	<i>n</i> -Hexane, soybean oil, diesel oil, silicone oil, lubricating oil, toluene, petroleum ether and cyclohexane	60–112	81
Polyimide nanofiber/MXene aerogel	<i>n</i> -hexane, ethanol, isopropanol, soybean oil, acetone, ethyl acetate, ethanediol, CCl <sub>4</sub>	55.85–135.29	46
Polyurethane sponge wrapped with MXene	Hexane, toluene, pump oil, vegetable oil, silicone oil, ethylene glycol	20–42	82
MXene-based melamine sponge	Petroleum ether, ethyl acetate, toluene, DCM, chloroform	80–176	47
CNCs/MXene aerogel	DMSO, DMF, olive, pump oil, soybean oil, diesel oil, acetone	45–63	48
MXene/RGO/carbon hybrid aerogel	<i>n</i> -Hexane, toluene, <i>N,N</i> -DMF, DMSO	50–90	83
Carbon aerogel	<i>n</i> -Hexane, toluene, pump oil, soybean oil, chloroform, dichloromethane	80–161	84
Carbon aerogel	Acetone, toluene, chloroform, pump oil, soybean oil, nitrobenzene, gasoline, dichloromethane	105–276	12
Carbon nanofiber aerogel	Gasoline, diesel oil, 2-propanol, diethyl ether, methanol, toluene, palm oil, soy oil, sunflower oil, coconut oil, cyclohexane	37–87	86
Carbon nanofiber aerogels	Toluene, cyclohexane, acetone, methanol, diethyl ether, gasoline, pump oil, palm oil, soy oil, sunflower oil, coconut oil	35–85	85
Graphene aerogel	<i>n</i> -Hexane, octane, hexadecane, toluene, chloroform, diesel oil, crude oil, engine oil, peanut oil, gasoline	109–236	87
Cysteamine/L-ascorbic acid graphene aerogel	<i>n</i> -Hexane, ethanol, petroleum ether, methylbenzene, gasoline, light crude oil	Up to 310	88
CPMT cryogel-this work		110–320	

## 4. Conclusion

In summary, a mechanically robust hybrid, double cross-linked cryogel of NC (combination of CNCs and CNFs), PVA, TDA, and

MXene with superhydrophobicity (WCA ~150°), low density (~20 mg cm<sup>-3</sup>), high porosity (≥92%), and ultrahigh sorption capacity (>300 g g<sup>-1</sup>) was fabricated using a simple freeze-drying process. CNCs and CNFs were prepared *via* a green DESs-



based technique, whereas MXene nanosheets  $\text{Ti}_3\text{C}_2\text{T}_x$ , were synthesized *via* the etching of Al layers of MAX phase ( $\text{Ti}_3\text{AlC}_2$ ) and ultrasonic exfoliation. In ref. cryogels with a combination of CNCs and CNFs, the mechanical performance of the cryogels were significantly higher than those of pure CNCs or CNFs. Due to the strong interaction between NC, PVA chains, and MXene nanosheets, the CNCs–CNFs/PVA/TDA@MXene cryogels displayed mechanical durability and superior fluid sorption capacity ( $110\text{--}320\text{ g g}^{-1}$ ) toward various oils and organic solvents. The sorption capacity was one of the highest reported in the literature for bio-based porous solids. The hybrid cryogels could not only selectively absorb oils and organic solvents from polluted water but also exhibited a very good recyclability rate (at least 10 cycles), suggesting their great potential in oil/water separation. Thus, the CPMT cryogel is a highly appealing, cost-effective, and sustainable material for water remediation because of its simple fabrication process and abundant green resources of cellulose nanomaterials.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The authors acknowledge the support from the Academy of Finland project “ACNF” (325276). The SEM part of the work was carried out with the support of the Centre for Material Analysis, University of Oulu, Finland. Also, the authors would like to express their gratitude to Ferdowsi University of Mashhad for supporting this project (Grant no. 3/52259).

## References

- 1 E. S. Ferreira, C. A. Rezende and E. D. Cranston, *Green Chem.*, 2021, **23**, 3542–3568.
- 2 S. ben Hammouda, Z. Chen, C. An and K. Lee, *J. Clean. Prod.*, 2021, **311**, 127630.
- 3 L. Yi, Y. Xia, Z. Tan, X. Fang, L. Zhao, H. Wu and S. Guo, *J. Clean. Prod.*, 2020, **264**, 121558.
- 4 W. Ma, Z. Jiang, T. Lu, R. Xiong and C. Huang, *Chem. Eng. J.*, 2022, **430**, 132989.
- 5 E. K. Sam, J. Liu and X. Lv, *Ind. Eng. Chem. Res.*, 2021, **60**, 2353–2364.
- 6 Y. Lv, X. Xi, L. Dai, S. Tong and Z. Chen, *Adv. Mater. Interfac.*, 2021, **8**, 2002030.
- 7 R. Ganesamoorthy, V. K. Vadivel, R. Kumar, O. S. Kushwaha and H. Mamane, *J. Clean. Prod.*, 2021, **329**, 129713.
- 8 Z. Xue, Y. Cao, N. Liu, L. Feng and L. Jiang, *J. Mater. Chem. A*, 2014, **2**, 2445–2460.
- 9 W. Li, K. Liu, Y. Zhang, S. Guo, Z. Li and S. C. Tan, *Chem. Eng. J.*, 2022, **446**, 137195.
- 10 H. Li, P. Mu, J. Li and Q. Wang, *J. Mater. Chem. A*, 2021, **9**, 4167–4175.
- 11 M. Wu, G. Shi, W. Liu, Y. Long, P. Mu and J. Li, *ACS Appl. Mater. Interfaces*, 2021, **13**, 14759–14767.
- 12 J. Dong, J. Zeng, B. Wang, Z. Cheng, J. Xu, W. Gao and K. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 15910–15924.
- 13 P. K. Renjith, C. Sarathchandran, V. Sivanandan Achary, N. Chandramohanakumar and V. Sekkar, *J. Hazard. Mater.*, 2021, **415**, 125548.
- 14 Y. Fang, L. Yan and H. Liu, *ACS Appl. Polym. Mater.*, 2020, **2**, 3781–3788.
- 15 A. Jamsaz and E. K. Goharshadi, *J. Mol. Liq.*, 2020, **307**, 112979.
- 16 A. Jamsaz, E. K. Goharshadi, A. Barras, M. Ifires, S. Szunerits and R. Boukherroub, *Sep. Purif. Technol.*, 2021, **274**, 118931.
- 17 Z. Tajmoradi, H. Roghani-Mamaqani and M. Salami-Kalajahi, *Chem. Eng. J.*, 2021, **417**, 128005.
- 18 F. Wahid, X.-J. Zhao, Y.-X. Duan, X.-Q. Zhao, S.-R. Jia and C. Zhong, *Carbohydr. Polym.*, 2021, **257**, 117611.
- 19 R. K. Gupta, G. J. Dunderdale, M. W. England and A. Hozumi, *J. Mater. Chem. A*, 2017, **5**, 16025–16058.
- 20 N. Zhang, Y. Qi, Y. Zhang, J. Luo, P. Cui and W. Jiang, *Ind. Eng. Chem. Res.*, 2020, **59**, 14546–14568.
- 21 X. Xu, F. Dong, X. Yang, H. Liu, L. Guo, Y. Qian, A. Wang, S. Wang and J. Luo, *J. Agric. Food Chem.*, 2019, **67**, 637–643.
- 22 M. Rajinipriya, M. Nagalakshmaiah, M. Robert and S. Elkoun, *ACS Sustain. Chem. Eng.*, 2018, **6**, 2807–2828.
- 23 X. Yue, T. Zhang, D. Yang, F. Qiu and Z. Li, *J. Clean. Prod.*, 2018, **199**, 411–419.
- 24 G. Kumar, D. T. K. Dora, D. Jadav, A. Naudiyal, A. Singh and T. Roy, *J. Clean. Prod.*, 2021, **298**, 126744.
- 25 G. Akhlamadi, E. K. Goharshadi and S. V. Saghir, *Ceram. Int.*, 2021, **19**, 27042–27049.
- 26 Y. Ji, Y. Wen, Z. Wang, S. Zhang and M. Guo, *J. Clean. Prod.*, 2020, **255**, 120276.
- 27 Y. Fu and Z. Guo, *J. Mater. Chem. A*, 2022, **10**, 8129–8158.
- 28 Y.-D. Dong, H. Zhang, G.-J. Zhong, G. Yao and B. Lai, *Chem. Eng. J.*, 2021, **405**, 126980.
- 29 H. Maleki, *Chem. Eng. J.*, 2016, **300**, 98–118.
- 30 H. Liu, B. Geng, Y. Chen and H. Wang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 49–66.
- 31 T. Zhang, Y. Zhang, X. Wang, S. Liu and Y. Yao, *Mater. Lett.*, 2018, **229**, 103–106.
- 32 R. Lin, A. Li, T. Zheng, L. Lu and Y. Cao, *RSC Adv.*, 2015, **5**, 82027–82033.
- 33 G. Akhlamadi and E. K. Goharshadi, *Process Saf. Environ. Prot.*, 2021, **154**, 155–167.
- 34 O. Laitinen, T. Suopajarvi, M. Osterberg and H. Liimatainen, *ACS Appl. Mater. Interfaces*, 2017, **9**, 25029–25037.
- 35 M. Mu, Y. Li, H.-Y. Yu, Z. Li, Y. Cao and X. Chen, *ACS Sustain. Chem. Eng.*, 2021, **9**, 9951–9960.
- 36 L. Guo, Z. Chen, S. Lyu, F. Fu and S. Wang, *Carbohydr. Polym.*, 2018, **179**, 333–340.
- 37 D. Wang, H. Yu, X. Fan, J. Gu, S. Ye, J. Yao and Q. Ni, *ACS Appl. Mater. Interfaces*, 2018, **10**, 20755–20766.
- 38 L. Liang, S. Bhagia, M. Li, C. Huang and A. J. Ragauskas, *ChemSusChem*, 2020, **13**, 78–87.
- 39 G. Akhlamadi and E. K. Goharshadi, *Process Saf. Environ. Prot.*, 2021, **154**, 155–167.



- 40 N.-N. Wang, H. Wang, Y.-Y. Wang, Y.-H. Wei, J.-Y. Si, A. C. Y. Yuen, J.-S. Xie, B. Yu, S.-E. Zhu, H.-D. Lu, W. Yang, Q. N. Chan and G.-H. Yeoh, *ACS Appl. Mater. Interfaces*, 2019, **11**, 40512–40523.
- 41 W. Tian, A. VahidMohammadi, M. S. Reid, Z. Wang, L. Ouyang, J. Erlandsson, T. Pettersson, L. Wågberg, M. Beidaghi and M. M. Hamed, *Adv. Mater.*, 2019, **31**, 1902977.
- 42 C. E. Shuck, A. Sarycheva, M. Anayee, A. Levitt, Y. Zhu, S. Uzun, V. Balitskiy, V. Zahorodna, O. Gogotsi and Y. Gogotsi, *Adv. Eng. Mater.*, 2020, **22**, 1901241.
- 43 K. Rasool, R. P. Pandey, P. A. Rasheed, S. Buczek, Y. Gogotsi and K. A. Mahmoud, *Mater. Today*, 2019, **30**, 80–102.
- 44 S. Mallakpour, V. Behranvand and C. M. Hussain, *Ceram. Int.*, 2021, **47**, 26585–26597.
- 45 R. Bian, G. He, W. Zhi, S. Xiang, T. Wang and D. Cai, *J. Mater. Chem. C*, 2019, **7**, 474–478.
- 46 H. Liu, X. Chen, Y. Zheng, D. Zhang, Y. Zhao, C. Wang, C. Pan, C. Liu and C. Shen, *Adv. Funct. Mater.*, 2021, **31**, 2008006.
- 47 M. Wang, J. Zhu, Y. Zi and W. Huang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 47302–47312.
- 48 C. Cai, Z. Wei, Y. Huang and Y. Fu, *Chem. Eng. J.*, 2021, **421**, 127772.
- 49 X. Gong, Y. Wang, H. Zeng, M. Betti and L. Chen, *ACS Sustain. Chem. Eng.*, 2019, **7**, 11118–11128.
- 50 X. Zhang, H. Wang, Z. Cai, N. Yan, M. Liu and Y. Yu, *ACS Sustain. Chem. Eng.*, 2018, **7**, 332–340.
- 51 L. Zhou and Z. Xu, *J. Hazard. Mater.*, 2020, **388**, 121804.
- 52 J. A. Sirviö, M. Visanko and H. Liimatainen, *Biomacromolecules*, 2016, **17**, 3025–3032.
- 53 O. Laitinen, J. Ojala, J. A. Sirviö and H. Liimatainen, *Cellulose*, 2017, **24**, 1679–1689.
- 54 J. A. Sirviö, M. Visanko and H. Liimatainen, *Green Chem.*, 2015, **17**, 3401–3406.
- 55 M. Alhabeab, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 7633–7644.
- 56 L. Ding, Y. Wei, L. Li, T. Zhang, H. Wang, J. Xue, L.-X. Ding, S. Wang, J. Caro and Y. Gogotsi, *Nat. Commun.*, 2018, **9**, 155.
- 57 W. Peng, R. Hu, W. Jiang, J. Kang, J. Li, Y. Cao and M. Xiang, *ACS Omega*, 2021, **6**, 19973–19982.
- 58 T. Zhang, W. Zhang, H. Xi, Q. Li, M. Shen, G. Ying and J. Zhang, *Cellulose*, 2021, **28**, 4281–4293.
- 59 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4248–4253.
- 60 J. Hu, Y. Zhan, G. Zhang, Q. Feng, W. Yang, Y.-H. Chiao, S. Zhang and A. Sun, *J. Membr. Sci.*, 2021, **637**, 119627.
- 61 J. Luo, X. Tao, J. Zhang, Y. Xia, H. Huang, L. Zhang, Y. Gan, C. Liang and W. Zhang, *ACS Nano*, 2016, **10**, 2491–2499.
- 62 B. Rashid, A. Anwar, S. Shahabuddin, G. Mohan, R. Saidur, N. Aslfattahi and N. Sridewi, *Materials*, 2021, **14**, 4370.
- 63 L. Wang, H. Liu, X. Lv, G. Cui and G. Gu, *J. Alloys Compd.*, 2020, **828**, 154251.
- 64 W. Feng, H. Luo, Y. Wang, S. Zeng, L. Deng, X. Zhou, H. Zhang and S. Peng, *RSC Adv.*, 2018, **8**, 2398–2403.
- 65 A. Pazniak, P. Bazhin, N. Shplis, E. Kolesnikov, I. Shchetinin, A. Komissarov, J. Polcak, A. Stolin and D. Kuznetsov, *Mater. Des.*, 2019, **183**, 108143.
- 66 A. Feng, Y. Yu, Y. Wang, F. Jiang, Y. Yu, L. Mi and L. Song, *Mater. Des.*, 2017, **114**, 161–166.
- 67 F. Shi, J. Sun, J. Wang, M. Liu, Z. Yan, B. Zhu, Y. Li and X. Cao, *J. Membr. Sci.*, 2021, **620**, 118850.
- 68 Y. Cao, Q. Deng, Z. Liu, D. Shen, T. Wang, Q. Huang, S. Du, N. Jiang, C.-T. Lin and J. Yu, *RSC Adv.*, 2017, **7**, 20494–20501.
- 69 Y. Guo, X. Zhou, D. Wang, X. Xu and Q. Xu, *Langmuir*, 2019, **35**, 14481–14485.
- 70 M. Ghidiu, J. Halim, S. Kota, D. Bish, Y. Gogotsi and M. W. Barsoum, *Chem. Mater.*, 2016, **28**, 3507–3514.
- 71 J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen and M. W. Barsoum, *Appl. Surf. Sci.*, 2016, **362**, 406–417.
- 72 J. Halim, M. R. Lukatskaya, K. M. Cook, J. Lu, C. R. Smith, L.-Å. Näslund, S. J. May, L. Hultman, Y. Gogotsi, P. Eklund and M. W. Barsoum, *Chem. Mater.*, 2014, **26**, 2374–2381.
- 73 J. Wang, Z. Cai, D. Lin, K. Chen, L. Zhao, F. Xie, R. Su, W. Xie, P. Liu and R. Zhu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 32495–32502.
- 74 S. A. Shah, T. Habib, H. Gao, P. Gao, W. Sun, M. J. Green and M. Radovic, *Chem. Commun.*, 2017, **53**, 400–403.
- 75 Y. Lu, D. Li and F. Liu, *Materials*, 2022, **15**, 307.
- 76 G. G. de Lima, B. D. Ferreira, M. Matos, B. L. Pereira, M. J. D. Nugent, F. A. Hansel and W. L. E. Magalhães, *Carbohydr. Polym.*, 2020, **245**, 116612.
- 77 C. Shi, Y. Chen, Z. Yu, S. Li, H. Chan, S. Sun, G. Chen, M. He and J. Tian, *Sustainable Mater. Technol.*, 2021, **28**, e00277.
- 78 Y. Yu, X. Shi, L. Liu and J. Yao, *J. Mater. Sci.*, 2021, **56**, 2763–2776.
- 79 Z. Wu, H. Sun, Z. Xu, H. Chi, X. Li, S. Wang, T. Zhang and Y. Zhao, *ACS Appl. Nano Mater.*, 2021, **4**, 8979–8989.
- 80 Z. Li, L. Zhong, T. Zhang, F. Qiu, X. Yue and D. Yang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 9984–9994.
- 81 J. Xue, L. Zhu, X. Zhu, H. Li, C. Ma, S. Yu, D. Sun, F. Xia and Q. Xue, *Sep. Purif. Technol.*, 2021, **259**, 118106.
- 82 C. Gong, J. Lao, B. Wang, X. Li, G. Li, J. Gao, Y. Wan, X. Sun, R. Guo and J. Luo, *J. Mater. Chem. A*, 2020, **8**, 20162–20167.
- 83 D. Jiang, J. Zhang, S. Qin, D. Hegh, K. A. S. Usman, J. Wang, W. Lei, J. Liu and J. M. Razal, *ACS Appl. Mater. Interfaces*, 2021, **13**, 51333–51342.
- 84 L. Li, T. Hu, H. Sun, J. Zhang and A. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 18001–18007.
- 85 P. Ieamviteevanich, W. Mongkolthananaruk, K. Faungnawakij, E. Daneshvar, A. Bhatnagar and S. Pinitsoontorn, *ACS Appl. Nano Mater.*, 2022, **5**, 2885–2896.
- 86 P. Ieamviteevanich, D. Palaporn, N. Chanlek, Y. Poo-arporn, W. Mongkolthananaruk, S. J. Eichhorn and S. Pinitsoontorn, *ACS Appl. Nano Mater.*, 2020, **3**, 3939–3950.
- 87 S. Yang, C. Shen, L. Chen, C. Wang, M. Rana and P. Lv, *ACS Appl. Nano Mater.*, 2018, **1**, 531–540.
- 88 C. Dai, W. Sun, Z. Xu, J. Liu, J. Chen, Z. Zhu, L. Li and H. Zeng, *Langmuir*, 2020, **36**, 13698–13707.

