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Article

Lignin as a bioderived modular surfactant and intercalant for $Ti_3C_2T_x$ MXene stabilization and tunable functions



Jiang et al. demonstrate inexpensive and bioderived lignin as an excellent surfactant/intercalant of $Ti_3C_2T_x$ for oxidation resistance and colloidal stability. The interlayer spacing can be altered at sub-nanometer precision owing to the dynamic interaction. The tunability of electrical conductivity, infrared emissivity, and electromagnetic interference shielding effectiveness is achieved.

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Highlights

A "dynamic" interaction between lignin and $Ti_3C_2T_x$ MXene is reported

Lignin largely improves colloidal and antioxidation stability of $Ti_3C_2T_x$ MXene

Lignin allows continuous and welldefined interlayer spacing tuning of $Ti_3C_2T_x$ MXene

Finely tuned electric and optic properties in MXene-lignin complex

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Article

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Lignin as a bioderived modular surfactant and intercalant for $Ti_3C_2T_x$ MXene stabilization and tunable functions

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SUMMARY

Controlled tailoring of atomically thin MXene interlayer spacings by surfactant/intercalants (e.g., polymers, ligands, small molecules) is important to maximize their potential for application. However, challenges persist in achieving precise spacing tunability in a welldefined stacking, combining long-term stability and dispersibility in various solvents. Here, we discovered that lignin can be used as surfactants/intercalants of Ti₃C₂T_x MXenes. The resulting MXene@lignin complexes exhibit superior colloidal stability and oxidation resistance in both water and different organic solvents. More important, we reveal a dynamic interaction between MXene and lignin that enables a wide-range fine interlayer distance tuning at a subnanometer scale. Such dynamic interaction is sparse in the reported organic surfactants/intercalants containing single types of functional groups. We also demonstrate the tunability of electrical conductivity, infrared emissivity, and electromagnetic interference shielding effectiveness. Our approach offers a starting point to explore the potential of MXene-biomacromolecule composites for electronics and photonics applications.

INTRODUCTION

The two-dimensional (2D) transition metal carbides or nitrides (MXenes), particularly the most studied Ti₃C₂T_x (where T_x represents various surface terminations), have an exceptionally high metallic electrical conductivity (up to 2 × 10⁴ S cm⁻¹).¹ The metallic conductivity, rich surface chemistry, and layered structure suggest that MXenes and their composites hold great promise for a wide range of applications, particularly in energy storage, electronics, and electromagnetic interference (EMI).^{2,3} For many of them, regulating the interlayer distance of MXenes (*d*-spacing) by metallic or organic ions^{4,5} or molecular intercalants^{6,7} is crucial to prevent restacking and to stabilize the conducting channel, thereby achieving desirable functions and physical properties.^{8,9} Among them, MXene-organic composites provide an important approach to regulate the *d*-spacing at molecular precision owing to the wide structure/function diversity of suitable organic molecules.^{9,10}

Polymers rich in hydroxyl or carboxyl groups (e.g., polyvinyl alcohol, polyacrylic acid, polysaccharides) or positive charges (e.g., poly(3,4-ethylenedioxythiophene), poly(diallyldimethylammonium chloride)) can strongly interact with the MXene surface via hydrogen bonding, electrostatic interaction, or even via covalent bond.¹¹ For example, the *d*-spacing of MXene can be altered by varying the OH-rich polymers, leading to an enhanced capacitance and mechanical properties.¹² However,

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the strong electrostatic interaction or covalent bond always leads to a fixed *d*-spacing regardless of the polymer content.^{7,13,14} However, the high polymer content can largely deteriorate the conductivity and randomize the lamellar structure when pursuing high *d*-spacing.¹⁵ Moreover, the strong interactions between MXene and polymers always lead to the crosslinking of MXene flakes, resulting in aggregates that can hardly be processed further.^{11,16}

To retain the superior solvent processibility of MXenes, comb-shaped or small-molecule surfactants/intercalants have been introduced, ^{17,18} where a well-defined asymmetric molecular structures where one end binds strongly to MXene surface and the other end provides dispersibility. The resulting MXene-organic composites have excellent dispersibility in various organic solvents, which is highly desirable for large-area fabrication of flexible multifunctional devices. The H₂O-free organic storage medium also largely enhances the shelf life of the dispersion.¹⁹ However, there is little room to tune the *d*-spacing with a fixed molecular structure; thus, the modulation of the properties needs to have a sophisticated molecular design of the surfactant/intercalant.

To realize well-controlled functions of MXene-organic composites for different applications, three key features need to be addressed: (1) continuously tunable *d*-spacing of MXene at sub-nanometer accuracy, (2) well-ordered lamellar structure in a large *d*-spacing range, and (3) good dispersibility in various solvents. Additionally, sophisticated procedures and costly and environmentally unfriendly chemicals need to be avoided. To the best of our knowledge, there is no reported approach to achieve all these features simultaneously. Thus, there is an urgent need for effective preparation strategies based on new surfactants/intercalants and a fundamental understanding of the interactions between MXene surface and functional groups.

To address the above challenges, we present a solvent-driven co-assembling method for complexing $Ti_3C_2T_x$ MXene and lignin, the common, inexpensive, and biodegradable industrial by-product, as a generic surfactant/intercalant. The resulting MXene@lignin complexes allow "on-demand" dispersion with high oxidation stability in multiple organic solvents and water. Compared to the current intercalants with a single type of functional group, which can only strongly affiliate to MXenes with a fixed *d*-spacing, lignin with diverse functional groups can provide mild binding in a wide interaction energy range. This new type of binding interaction between MXene and lignin is dynamically adjustable depending on the composition and solvent, which leads to well-defined hybrid Bragg stacks in thin films, where the *d*-spacing can be finely tuned at sub-nanometer scale. The mechanism is investigated using both experimental and theoretical approaches. We further demonstrate tunable physical properties of our MXene@lignin complexes, including wettability, electrical conductivity, infrared (IR) emissivity, and EMI shielding.

RESULTS AND DISCUSSION

Preparation and dispersibility of MXene@lignin complexes

Figure 1A illustrates the preparation process of MXene@lignin complexes. To ensure the maximum dispersibility in the target organic solvent, industrial raw lignin (L_{raw}) is first fractionated by DMSO, *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), and ethanol (EtOH), wherein the fractionated lignins are denoted as L_{DMSO} , L_{NMP} , L_{DMAc} , L_{DMF} , and L_{EtOH} , respectively. Tetrahydrofuran (THF) is used as a control solvent for L_{raw} due to its good dissolving capacity for lignin. Size-exclusion chromatography and ³¹P-NMR are employed to







Figure 1. Preparation, dispersibility, and morphology of MXene@lignin complexes

(A) Schematic illustration of MXene@lignin complex preparation.

(B) Schematic illustration of dynamic interaction between MXene and lignin, as well as the two different forms of the complexes used for the study, i.e., dispersion and film by filtration.





Figure 1. Continued

(C) Digital images of the dispersions of MXene and MXene@lignin complexes in different solvents. The photographs were taken 30 s after forming the dispersion by hand shaking. $MX@L_{DMAc}$ -W is used for demonstrating water dispersion (blue dashed box). $MX@L_{solvent}$ -O is dispersed in the same solvent for fractionation; $MX@L_{raw}$ -O is dispersed in THF (red dashed box). The numbers on the bottle represent the concentrations of the dispersions (mg mL⁻¹).

(D) TEM (left) and selected area enlargement TEM images (right) of MX-W, MX@L_{raw}-W, MX@L_{DMAc}-W, and MX@L_{DMAc}-O. Scale bars for the TEM image and magnified TEM image, 1 µm and 100 nm, respectively.

(E) The hydrodynamic size and zeta potential data of MX-W and MX@L_{solvent}-W complexes. The error bars represent the SD of 3 individual measurements.

quantitatively analyze the molecular weight and hydroxyl group content of L_{raw} and its fractions—OH from aliphatic chains, *p*-hydroxyphenyl unit (H), guaiacyl unit (G), syringyl unit (S), and carboxylic acid (Figures S1–S3; Tables S1 and S2). Thermal properties of lignin fractions are studied by thermal gravimetric analysis, which was further used for calculating lignin content within the MXene@lignin complexes (Figure S4; Table S3).

Few-layered $Ti_3C_2T_x$ (MXene) is synthesized by selectively etching the Al layer from the Ti₃AlC₂ MAX phase, followed by water intercalation and delamination, according to the previously reported method.²⁰ In a typical synthesis of the MXene@lignin complexes via co-assembly, the as-prepared MXene water dispersion (MX-W) is slowly added into the lignin organic solution using a peristaltic pump at room temperature with certain lignin to MXene mass feeding ratios (Figure 1A; also see supplemental information). The default lignin:MXene feeding ratio is 1:1 w:w, as specified. Then, the complexes are obtained by centrifugation, followed by redispersing the complexes into water or corresponding organic solvent used for lignin fractionation, denoted as $MX@L_{solvent}$ -W or $MX@L_{solvent}$ -O, respectively. The organic solvents are DMSO, NMP, DMAc, DMF, and EtOH. For MX@L_{raw}-O, the dispersant is THF. MX-W after solvent exchange can be dispersed in organic solvents, denoted as MX-O, including MX-DMSO, MX-NMP, MX-DMAc, MX-DMF, and MX-EtOH. The highly concentrated dispersions can be used as stock material or subsequently filtrated to form self-standing films (Figure 1B). The MX@L_{DMAc}-W films with a low lignin:MXene feeding ratio (1:1 w:w) are highly flexible and tailorable as pristine MX-W films, allowing bending or folding. However, a higher lignin:MXene feeding ratio (2:1 or 2.5:1 w:w) will lead to brittle films (Figure S5).

We have further compared the dispersibility of pristine MXene, MX@L_{solvent}-W, and MX@L_{solvent}-O. The high-concentration dispersions of MXene in most organic solvents have a homogeneous appearance, except in THF involving low polarity, where phase separation occurs (Figure 1C). Upon diluting the dispersions by 300 times, we found that pristine MXene could only form clear dispersion in water, and we observed severe aggregation in all the organic solvents, indicating its significant limitation in solvent processibility. In contrast, all MX@L_{solvent}-O are mostly well dispersed, as evidenced by the homogeneous concentrated dispersions and clear-greenish diluted dispersions. Even in THF, the MX@L_{raw}-O can be partially dispersed. We can prepare highly concentrated ink using MX@L_{solvent}-O (e.g., MX@L_{DMAc}-O, 82 mg mL⁻¹), indicating their superior dispersibility in organic solvents (Figure S6). Surprisingly, all the MX@L_{solvent}-W also exhibit remarkable solvent dispersibility (Figures 1C and S7). This result suggests that lignin is a versatile stabilizer for MXene, providing excellent dispersibility in both water and organic solvents.

Transmission electron microscopy (TEM) images revealed that $MX@L_{solvent}$ -W or $MX@L_{solvent}$ -O retained the few-layered flake morphology with sharp edges as MX-W (Figure 1D). No folding or aggregation of flakes in the complexes was









Figure 2. Chemical composition and stability of MXene@lignin complexes

(A and B) The yield and lignin content in (A) $MX@L_{solvent}$ -W and -O films and (B) $MX@L_{DMAc}$ -W and -O films with different lignin:MXene feeding ratios from 0.5:1 to 2.5:1 w:w. The error bars represent the SD of 3 individual measurements.

(C) Raman spectra of MX-W and MX@L_{solvent}-W films (excitation wavelength, 785 nm).

(D) Matrix results in color coding of the calculated binding energy between phenolic OH groups (left) and carboxylic OH groups (right) of lignin units (H, G, S) and MXene terminations (F, O, OH) in different solvents.

(E) XPS spectra of MX-W film, L_{DMAc} powder, and MX@L_{DMAc}-W and MX@L_{DMAc}-O films. From left to right, survey, Ti 2p, F 1s, and O 1s.

(F and G) The half-life $(t_{1/2})$ of (F) MXene and MXene@lignin complexes and (G) MXene@L_{DMAc}-W or -O (lignin:MXene feeding ratio from 1:0.5 to 1:2.5 w:w) dispersed in the aqueous phase and organic phases. Half-life is the time required for a quantity of the substance to reduce to half its initial value. The error bars represent the error of the fitting from the experimental data in Figure S16.

observed, proving their superior dispersibility. In MX@L_{raw}-W, where unfractionated lignin was used, we found negatively charged lignin colloidal spheres (LCSs) absorbed mainly on the positively charged edge of MXene through electrostatic interaction. Such LCSs were commonly obtained from the lignin intermolecular self-assembly driven by a synergistic effect of hydrogen bonding, van der Waals forces, electrostatic forces, and π - π interactions.²⁰ For example, micrometer-sized LCSs can be prepared by slowly adding water to a solution of L_{EtOH} in EtOH (Figure S8). However, complexes of lignin fractions, MX@L_{DMAc}-W and MX@L_{DMAc}-O, have clear edges without LCSs. From the scanning electron microscopy (SEM) of thin films of MX@L_{solvent}-W, we observed well-defined lamellar structures from the cross-sections, except in $MX@L_{raw}$ -W film, where a large amount of LCSs were found as in TEM (Figure S9). However, films deposited from the organic phases (MX@L_{solvent}-O) are mostly absent of LCS. In MX@L_{raw}-O, we can still find a few LCSs, but many fewer than in MX@L_{raw}-W due to the better solubility of lignin in THF (Figure S10). Dynamic light scattering confirmed a slight increase in the mean hydrodynamic radius from 543 nm of MX-W to 542-627 nm of MX@L_{solvent}-W (Figure 1E), which is attributed to the formation of lignin solvation layers on the MXene surface.²¹ Zeta potentials of MX@L_{solvent}-W also increased slightly compared to MX-W (ranged from -47 to -56 mV), except in MX@L_{raw}-W, where a major decrease was observed. These results implied that the solvation layers of lignin fractions provide both steric effects and strong repulsive potential to prevent the aggregation of MXene flakes.^{22,23}

Chemical composition and stability of MXene@lignin complexes

In Figure 2A, we calculated the yields and the lignin content within MX@L_{solvent}-W and MX@L_{solvent}-O films using (thermal) gravimetric methods (Figure S11; Table S4, and supplemental information for calculation methods). All the $\mathsf{MX}@\mathsf{L}_{\mathsf{solvent}}\text{-}\mathsf{W}$ have similar yields of 71-73 wt %, except MX@L_{raw}-W, which has a higher yield of 82 wt %. As the co-assembly medium of MX@L_{raw}-W, the mixture of water and THF has the lowest polarity, thus promoting depletion of MXene and increasing the yield. However, the lignin content in the $MX@L_{solvent}-W$ shows an increasing tendency upon the decreasing polarity of the organic solvent used for dispersing lignin (water > DMSO > NMP > DMAc > DMF > EtOH > THF), from 14 wt % MX@L_{DMSO}-W to 38 wt % in MX@L_{raw}-W. The results suggest that the gradually increased polarity is one of the driving forces for the co-assembly, promoted by the decreasing solubility of lignin.^{20,24} The yields of MX@L_{solvent}-O complexes are 52–58 wt %, roughly 20% lower than those of MX@L_{solvent}-W. The lignin contents in MX@L_{solvent}-O complexes (<15% for all samples) are also lower than in MX@L_{solvent}-W. The lower yield and lignin content from organic solvent deposited films are caused by the loss from re-dispersed MXene and the re-dissolved weakly interacted lignin from complexes.

We further use $MX@L_{DMAc}$ -W and $MX@L_{DMAc}$ -O as representative systems to study the yield and lignin contents with different lignin:MXene feeding ratios from 0.5:1



to 2.5:1 w:w (Figure 2B). We found that the yield is not affected much by the lignin:MXene feeding ratio in both MX@L_{DMAc}-W (70–76 wt %) and MX@L_{DMAc}-O (56–63 wt %). However, the lignin content increased linearly from 11 to 23 wt % upon an increasing lignin:MXene feeding ratio in MX@L_{DMAc}-W ($R^2 > 0.99$). The weakly interacted lignin will be dissolved by organic solvents in MX@L_{DMAc}-O, leaving only strongly interacted lignin with MXenes. Thus, the lignin content in MX@L_{DMAc}-O remained constant (~9.5 wt %) regardless of the lignin:MXene feeding ratio.

Raman spectra (785 nm excitation) of MX-W, MX@L_{solvent}-W, and MX@L_{solvent}-O films were further performed (Figures 2C and S12). Sharp peaks at ~200 and ~720 cm⁻¹ correspond to the out-of-plane vibrations of Ti, C, and O (A_{1g} [Ti, C, O]) and the vibrations of C (A_{1g} (C)) in MXenes, respectively. The T_x region (230–470 cm⁻¹) denotes the vibrations of surface groups connected to Ti atoms, while the M–T_x region (~600 cm⁻¹) was attributed to vibrations of C.²⁵ We have noticed that lignin had a minor influence on the T_x region modes of MXene, implying mild interactions between lignin and MXene surface terminations. We also used Raman spectroscopy to study the lignin in the complexes (532 nm excitation). The remaining lignin in MX@L_{solvent}-O films was confirmed by its characteristic peaks at ~1,600 cm⁻¹ (Figure S12).²⁶

Density functional theory (DFT) calculations are employed to screen the favored interactions among various functional groups in different solvents (Table S5 and Figure 2D), using simplified models of lignin and $Ti_3C_2T_x$ MXene (Figure S13). In Figure 2D, the calculated binding energies (shown by green color codes) are in a wide range for typical hydrogen bonds, from a few kJ·mol⁻¹ to 40 kJ mol⁻¹, largely depending on the binding sites and selected solvents. For phenolic OH, only H-unit can bind efficiently to MXene terminations in all the solvents, especially in the high-polarity solvent DMSO. The carboxylic acid OH from lignin units mainly forms hydrogen bonds with –O terminations of MXenes in a favorable order of H > G > S. Overall, the carboxylic OH has a stronger interaction with MXene terminations than that of the phenolic OH, and the hydrogen bond energies among MXene terminations are in the order of -O > -OH > -F.

X-ray photoelectron spectroscopy (XPS) was employed to study the chemical composition of L_{DMAc}, MX-W, MX@L_{DMAc}-W, and MX@L_{DMAc}-O films (Figure 2E). The Ti 2p peaks at 454.8 eV (461.1 eV), 455.3 eV (462.1 eV), 456.2 eV, 457.5 eV, and 464.8 eV were assigned to the Ti-C, Ti^{2+} , Ti^{3+} , TiO_2 , and $TiO_{2-X}F_X$ components from MXene, respectively (the values in parentheses correspond to the 2p_{1/2} components).^{18,27,28} Compared to MX-W and MX@L_{DMAc}-O, we observed a more intense TiO₂ peak in MX@L_{DMAc}-W. We assume that the higher oxidation species in MX@L_{DMAc}-W can be attributed to the surface enrichment effect of TiO₂ by lignin via hydrogen bonding.²⁹ In the F 1s spectra of both MX@L_{DMAc}-W and MX@L_{DMAc}-O, we found extra satellite peaks of C-Ti-F_X at 686.2 eV. We assigned these peaks as the formation of hydrogen bonding and π -electron interactions between lignin OH groups and MXene terminations (F, –OH, –O), ¹⁸ because lignin is a complex aromatic compound with the ability to decrease the electron density leading to a high binding energy. In O 1s spectra, the intensity ratios of TiO_{2-X} -F_x peak (530.3 eV) to C-Ti-O (i) peak (529.6 eV) demonstrate a trend of MX- $W > MX@L_{DMAc}-W > MX@L_{DMAc}-O$, suggesting a better oxidation resistance of MXene films with the existing of lignin and organic solvents.

We also evaluated the oxidation stability of MXene@lignin complexes at ambient conditions, using the UV-visible absorption change of the MXene plasmonic peak



at \sim 785 nm (Figures S14 and S15).⁴ Pristine MXene in organic solvents was not included for comparison due to the poor dispersibility. To better quantify MXene oxidation processes, the normalized absorption curves (Figure S16) are fitted using the first-order reaction kinetic to obtain the experimental half-life of all the samples (see supplemental information and Table S6).³⁰ As expected, pristine MXene quickly degraded in water, with a half-life of only 2.4 days (Figure 2F). By complexation with lignin, the half-life of MX@L_{solvent}-W has increased to \sim 4 times, \sim 8–11 days. We assume that the existence of lignin can prevent the MXene flake interface from water molecule contact. 31 In the MX@L_{solvent}-O complexes, the half-life of degradation dramatically increased to ${\sim}50{-}300$ days, where MX@L_DMF-O and MX@L_DMAc-O show the best performance, and most of the lignin fractions work better than the L_{raw}. Among the MX@L_{DMAc}-W samples with different lignin:MXene feeding ratios, the half-life of degradation is positively correlated with the lignin content, where a maximum half-life of 22 days was found in MX@L_{DMAc}-W 2.5:1 w:w (Figure 2G). However, in the MX@L_{DMAc}-O, we did not observe a clear relationship between the halflife and lignin:MXene feeding ratio, as the lignin contents are similar among these samples (~9%). Our results suggest that as universally amphiphilic surfactants, lignin fractions are also good antioxidants for MXene in both water and organic solvents.

Moreover, the films of MX@lignin complexes showed excellent resistance against water and dilute NaCl solutions under long-term storage or short-term sonication (Figure S17). We also studied the film resistance against organic solvents using MX@L_{DMAc}-W and -O. The MX@L_{DMAc}-W films can be gradually redispersed in DMAc under short-term sonication, especially for those with a high lignin:MXene feeding ratio (Figure S18). However, for MX@L_{DMAc}-O films with lower lignin content, the films cannot be easily redispersed in DMAc under sonication (Figure S18). These results indicate that the weakly bound lignin in MX@L_{solvent}-W plays an important role in weakening the interlayer interactions of MXenes. The good water resistance and superior organic solvent re-dispersibility of MX@L_{solvent}-W films are also critical features for their practical application and material reuse.

Structures of MXene@lignin complexes

The X-ray diffraction (XRD) measurements of MX-W, and MXene@lignin complexes provide the structural information at sub-nanometer scale (Table S7). In the XRD of MX-W, we found a narrow (002) peak with a full width at half-maximum (FWHM) of 0.86 and visible high index peaks (Figure 3A), implying a well-ordered lamellar structure with d-spacing of 1.20 nm. The (002) peaks in complexes with lignin fractions have larger d-spacings of 1.97-2.23 nm and their FWHM only slightly increased to 1–1.37. A weak satellite peak at \sim 7° can be assigned to the secondary layered structure of lignin.¹⁴ In contrast, the MX@L_{raw}-W with the highest lignin content (38.2 wt %), the d-spacing is only 1.87 nm, and a weak and very broad (002) peak (FWHM 3.50) was observed. However, the XRD patterns of MX@L_{NMP}-O, MX@L_{DMAc}-O, and MX@L_{DMF}-O films resemble the corresponding MX-O films (Figure S19), in which the *d*-spacing and FWHM are only slightly increased, and the high index peaks were also visible (Figure 3B). However, in MX@L_{DMSO}-O and MX@L_{FtOH}-O, the *d*-spacing and FWHM are larger than the corresponding MX-O. For MX@L_{raw}-O, although there is no MX-THF for comparison, we can still conclude that the most intercalated lignin was removed by THF, due to the small d-spacing (1.44 nm), FWHM (1.22), and low lignin content (9.8%).

We plotted the lignin content versus *d*-spacing to better visualize the relationship between the composition and the sub-nanometer structure. Among MX-W and MX@L_{solvent}-W of high-polarity solvents, a strong correlation between the lignin







Figure 3. Structures of MXene@lignin complexes

(A and B) XRD patterns of (A) MX-W and MX@L_{solvent}-W films and (B) MX@L_{solvent}-O films. The *d*-spacing and FWHM calculated from (002) peaks are also given.

(C) Scatterplot of lignin content versus *d*-spacing in MX@ $L_{solvent}$ -W and MX@ $L_{solvent}$ -O. The error bar of MX-O indicates the SD among different solvents. The colored dashed lines indicate the major trend of the datasets.

(D and E) XRD patterns of (D) MXene@L_{DMAc}-W films (lignin:MXene feeding ratio from 1:0.5 to 2.5:1 w:w) and (E) MXene@L_{DMAc}-O films (lignin:MXene feeding ratio from 0.5:1 to 2.5:1 w:w). The *d*-spacing and FWHM calculated from (002) peaks are also given.

(F) Scatterplot of lignin content versus *d*-spacing in MX@L_{DMAc}-W and MX@L_{DMAc}-O (lignin:MXene feeding ratio 0.5:1 to 2.5:1 w:w). The green line is the linear fitting of the MX@L_{DMAc}-W dataset.

(G) Azimuthal plot for (002) peaks marked in the azimuth range of -90° to 90°. The Herman's orientation factor franging from 0 to 1 implies random flake orientation to complete alignment, respectively.

(H and I) Schematic illustrations of the structures of (H) MX@L_{solvent}-W and (I) MX@L_{solvent}-O films.

content and the *d*-spacing can be observed (red line, Figure 3C). However, in $MX@L_{EtOH}$ -W and $MX@L_{raw}$ -W, the *d*-spacings are much lower than the expected values, indicating that a large portion of lignin was phase separated without intercalation, which is consistent with the observation of LSCs from SEM (Figure S9). These results indicate that selecting proper lignin fractions is crucial to achieving efficient intercalation in the MXene layers and forming highly ordered hybrid Bragg stacks. The *d*-spacings are mostly recovered in MX@L_NMP-O, MX@L_DMAc-O, MX@L_DMF-O,



and MX@L_{raw}-O (blue horizontal line, Figure 3C), which is strong evidence that the intercalated lignin in MX@L_{solvent}-W is weakly bound and can be removed by their good solvents. We assume that the remaining strongly bound lignin (6.5–12 wt %) with negative charges is mainly adsorbed on the positively charged edges of MXenes, which does not increase the *d*-spacing. However, in MX@L_{DMSO}-O and MX@L_{EtOH}-O, there is a small portion (those exceeding 10 wt %) of strongly intercalated lignin contributing to the *d*-spacing expansion. Interestingly, we found a similar slope of the red and blue lines, implying that *d*-spacing expansion is a linear function of intercalated lignin amount, regardless of the solvent system used.

We further investigated the interactions of lignin and MXenes by studying the correlation between the intercalated lignin amount indicated by *d*-spacing expansion and the intrinsic lignin characteristics (i.e., number average molecular weight, weight average molecular weight, polydispersity index, and OH content of different functional groups). Among MX@L_{solvent}-W samples (Figure S20), the correlation between intrinsic lignin characteristics and *d*-spacing expansion is very weak ($R^2 = 0.0009-0.445$), again proving the weak interaction of the intercalated lignin. However, in MX@L_{solvent}-O samples (Figure S21), number average molecular weight, weight average molecular weight, and polydispersity index exhibit a strong negative correlation with *d*-spacing expansion among all quantifiable parameters ($R^2 > 0.8$), implying that monodispersed lignin molecules with smaller molecular weights are advantageous for intercalation. The carboxylic OH content also shows strong positive correlation, which aligns well with our DFT calculations, where carboxylic OH has high binding energy with MXene O-termination.

MX@L_{DMAc}-W and -O with different lignin:MXene feeding ratios are used to study the relationship between lignin content and structure. In the XRD of MX@L_{DMAc}-W, we observed a gradually increasing d-spacing from 1.79 to 2.77 nm upon a higher lignin:MXene feeding ratio (Figure 3D). The intensity of the shoulder peak also increased with higher lignin content, indicating its origin from intercalated lignin. The FWHM has increased from 0.86 in MX-W to 0.95-1.14, meaning that the lamellar stacking order only slightly deteriorated by the lignin intercalation. As discussed previously, all the XRD patterns of MX@L_{DMAc}-O are similar to MX-DMAc, demonstrating the removal of weakly bound intercalated lignin by DMAc (Figure 3E). In the lignin content and d-spacing plot (Figure 3F), a perfect linear relationship ($R^2 > 0.99$) was observed for MX@L_{DMAc}-W films, suggesting that a fine d-spacing modulation at sub-nanometer scale is achieved. In MX@L_{DMAc}-O, no clear trend was found due to the lignin removal. Wide-angle X-ray scattering experiments of MX@L_{DMAc}-W reveal the effect of intercalated lignin on the orientation of MXene (Figure S22). The calculated Herman's orientation factor (f) from the azimuthal profile of (002) peaks indicate that a higher lignin: MXene feeding ratio gradually decreased the packing orientation of MXene flakes in MX@L_{DMAc}-W films as a slow drop in f value was observed (Figure 3G). The SEM images of the cross-section cut by a focused ion beam under cryo-mode (cryo-FIB) for MX-W, MX@L_{DMAc}-W, and -O films were used to study the packing order at microscopic scale (Figure S23). The MX-W has dense packing with minor porous defects hundreds of nanometers in size. As the lignin:MXene feeding ratio increased in MX@L_{DMAc}-W films, more defects with larger sizes were observed. In contrast, all MX@L_{DMAc}-O films maintain a consistently low defect level, primarily due to the removal of intercalated lignin.

According to the structural analysis, we could draw comprehensive schemes of $MX@L_{solvent}$ -W and -O in both dispersions and films. After co-assembly, $MX@L_{solvent}$ -W complex is well dispersed in water, in which both weakly and strongly





Figure 4. Tunable functions of MXene@lignin complexes

(A) WCA measurements of MX-W, MX@L_{solvent}-W (bottom), and MX@L_{solvent}-O (top) films. The error bars represent the measurement error from the experimental data in Figure S24.

(B and C) Scatterplot of *d*-spacing versus conductivity in the films of (B) MX@L_{solvent}-W, MX@L_{solvent}-O, and MX-O and (C) MX@L_{DMAc}-W and MX@L_{DMAc}-O. The error bars represent the SD of 3 individual measurements. The gray line in (B) is the linear fitting of all datasets, and the green line in (C) is the exponential fitting of the MX@L_{DMAc}-W dataset.

(D) IR emissivity of MX-W and MX@L_{DMAc}-W films with different lignin:MXene feeding ratios.

(E) EMI SE of MX-W and MX@L_{DMAc}-W films with different lignin:MXene feeding ratios.

(F) Benchmarking SSEt of this work (green scatters, average of 5.3–8.7 GHz) with previous works (gray scatters, average of 8.2–12.4 GHz).

bound lignin molecules are coated on the MXene surface due to the limited solubi-

lity of lignin in water (Figure 3H). While forming film via filtration, most of the lignin molecules are retained in the lamellar structure (d_{002}). The strongly bound ones are on the positive MXene edges, and the weakly bound ones are intercalated between MXene layers, where their secondary structure (d_{lignin}) may contribute to the satellite peak in XRD. This weak binding of lignin also allows the "dynamic" intercalation where the d_{002} can be gradually altered. When using L_{raw} , there are also LCSs forming from lignin self-assembly. The d_{lignin} can be gradually tuned from 6 to 16 Å, smaller than the diameter of lignin cylinder aggregates in the organic phases (16-28 Å).³² It is reasonable to assume that the intercalated lignin molecules undergo amorphous packings leading to a decreased dimension. A similar phenomenon was reported in the polyethylene glycol intercalated MXenes.¹⁸ In MX@L_{solvent}-O, the weakly bound lignin are mostly detached from MXene and dissolved in organic solvents (Figure 3I). Filtration will remove most of the dissolved lignin, thus leading to an intercalation-free stacking. The strongly bound lignin still exists on the MXene edges and thus did not lead to larger d-spacing (except in MX@L_{DMSO}-O and MX@L_{EtOH}-O).

Tunable functions of MXene@lignin complexes

Water contact angle (WCA) measurement was used to determine the surface wettability of MX-W, MX@L_{solvent}-W, and MX@L_{solvent}-O films (Figures 4A and S24). MX-W film is hydrophilic, with a WCA of 53.3° \pm 0.1°. The WCA of MX@L_{solvent}-W films is in the range of 65°–69°, which is slightly higher than that of MX-W. The MX@L_{solvent}-O films are more hydrophobic, and the WCA values further raised to 76°–89°,





suggesting a more hydrophobic surface of MX@L_{solvent}-O films compared to MX@L_{solvent}-W films. In MX@L_{DMAc}-W and MX@L_{DMAc}-O, there is a weak positive correlation between the lignin:MXene feeding ratio and the WCA. The incorporation of lignin does make the MXene films more hydrophobic—nevertheless, still accessible to water, with WCA values always less than 97°. The result also demonstrates a simple approach to modulate the surface wettability of MXene films, due to the amphiphilic nature of lignin.

We also measured the electrical conductivities (*o*) of MX@L_{solvent}-W, MX@L_{solvent}-O, and MX-O films from the sheet resistance using a four-point probe system and plotted them against d-spacing (Figure 4B). There is a weak negative correlation $(R^2 = 0.49)$ between σ and d-spacing, indicating that the existence of intercalated non-conductive lignin hinders the electron transfer among MXene flakes. The σ values are quite close among MX@L_{solvent}-O films and MX-O films with similar d-spacing, again proving that remaining lignin in MX@L_{solvent}-O are located on the edges rather than intercalation, which has minor effects on conductivity. It is worth noting that the choice of solvents also has a large impact on σ , which may be caused by the various structure order of the MXene stacking from solvents with different physical properties.³³ For instance, films deposited from DMSO or containing L_{DMSO} have the highest σ among MX@L_{solvent}-W, MX@L_{solvent}-O, and MX-O films. We then studied the relationship of *d*-spacing and σ of MX@L_{DMAc}-W and MX@L_{DMAc}-O with different lignin:MXene feeding ratios (Figure 4C). The σ of MX@L_{DMAc}-W can be well described as an exponential function of their *d*-spacing, d ($R^2 = 0.93$), as $\sigma \sim e^{-\beta d}$, with $\beta = 2.7$ nm⁻¹. This confirmed that the electron transport is dominated by hopping mechanism among the well-separated MXene flakes by intercalated lignin.³⁴ In MX@L_{DMAc}-O, the conductivity values are quite similar due to the removal of the intercalated lignin. The conductivity is smaller than MX-W owing to the DMAc solvent intercalation and the structure disorder from organic solvent.³³ The results indicate that the conductivity of MX@L_{solvent}-W can be finely tuned in a large range by using different lignin fractions with various lignin:MXene feeding ratios.

MX@L_{DMAc}-W films with various lignin:MXene feeding ratios ($\approx 2-4 \,\mu$ m thick) exhibit a tunable IR emissivity in the mid-IR region $(3-14 \mu m)$ (Figure 4D). High conductivity (or low sheet resistance) is believed to be the key factor of low emissivity for MXenes.³⁵ Surprisingly, the emissivities of MX@L_{DMAc}-W films with low lignin:MXene feeding ratios (0.5:1 and 1:1 w:w) are 1%-2% lower than pristine MXene, even though they have smaller conductivities than MX-W. The emissivity then rises by increasing the lignin:MXene feeding ratio, but it remains below 20%. We assume the gradual sub-nanometer structure tuning by lignin intercalation is the major reason for achieving the emissivity modulation. Furthermore, we observed a tunable EMI shielding effectiveness (SE) between the frequency range of 5-8.5 GHz in MX@L_{solvent}-W films by varying the lignin:MXene feeding ratio (Figure 4E). Again, the low lignin:MXene feeding ratio samples (0.5:1 and 1:1 w:w) exhibit higher EMI SE than pristine MXene. Specifically, the MX@L_{DMAc}-W 0.5:1 w:w has a surprisingly high EMI SE value of approximately 49 dB in the range between 6 and 7 GHz. For higher lignin:MXene feeding ratios, the EMI SE value gradually decreases. We attribute the EMI SE tuning ability to the fine structure evolution of MX@L_{DMAc}-W at subnanometer scale. We further calculated the specific SE (SSE/t) by dividing the EMI SE by sample density per unit area and comparing the values of the reported works with various types of materials (Figure 4F; Table S8). It is evident that our MX@L_{DMAc}-W films show exceptional higher SSE/t with much smaller thickness, with the highest value of 57,844 dB cm² g⁻¹.



In summary, we demonstrated that industrial lignin is a modular surfactant and intercalant of Ti₃C₂T_x MXene. The fractionated lignin enables Ti₃C₂T_x MXene on-demand dispersion with superior colloidal stability in water and various organic solvents. The existence of lignin also largely enhances the oxidation resistance of MXene, as evidenced by an \sim 4- to 9-fold increase in degradation half-life in water and a maximum degradation half-life of 300 days in DMF. We also systematically studied the chemical composition and structural information of the resulting MXene@lignin complexes. Different from the previously reported surfactant/intercalant designed with strong interactions, the binding between functional groups of lignin and MXenes surface is "dynamic." As a result, the amount of intercalated lignin, which was weakly bound to the MXene surface, can be finely tuned or can be easily removed by good solvents. Thanks to such weak interaction, the *d*-spacing in MXene@lignin complexes can be altered linearly to the lignin content from 1.2to 2.8 nm. The increasing *d*-spacing only slightly deteriorated the lamellar structure, where a hybrid Bragg stack is achieved. Owing to the finely tunable d-spacing and well-ordered 2D stacking, we also successfully demonstrated the tunable physical properties of the MXene@lignin complexes, including surface wettability, electrical conductivity, IR emissivity, and electromagnetic shielding. Remarkably, the emissivity of MXene@lignin complexes films with proper lignin content is even lower than pristine MXene. These ultrathin films also show uncommonly high specific EMI SE, up to 57,844 dB cm² g⁻¹, superior to the pristine MXene of 47,563 dB cm² g^{-1} .

For clearly highlighting the advancement of using lignin as a surfactant and an intercalant for MXenes, we made a comparison of the key parameters with previously reported materials (Table S9).^{4,17,18,36–43} While antioxidation is commonly achieved with most of the surfactant/intercalant, lignin provides MXene a wider solvent spectrum owing to its amphiphilic nature and rich functional groups. The fractionation process of lignin also offers a possibility of on-demand dispersity, which is lacking for other dispersants with fixed chemical composition. Most important, our work demonstrates for the first time that the *d*-spacing of MXene can be finely tuned, which is extremely important for many applications. The replacement of synthetic surfactant/intercalant to bioderived lignin, which is a highly underused biomaterial, not only prolongs the shelf life of MXenes in various solvent systems and allows tunable structure at sub-nanometer scale with excellent physical properties but it also substantially decreases the carbon footprint in scalable production. We believe our work will inspire interdisciplinary research on low-dimensional lignin and 2D materials and encourage a fresh perspective on lignin valorization, particularly toward high-end applications (e.g., electronics, photonics). Further efforts are needed to maximize the capacity of MXene-lignin complexes systems toward real-world applications such as fundamental research on the structure-performance relationship, exploration of more MXene phases or lignin species, the development of reliable fabrication processes, new fractionation or structural design methods of lignin, and more.

EXPERIMENTAL PROCEDURES

Synthesis and delamination of Ti₃C₂T_x MXene

 $Ti_3C_2T_x$ MXene was synthesized by selectively etching the Al phase from the Ti_3AlC_2 MAX phase, followed by delamination.¹⁴ First, 2 g MAX phase (Ti_3AlC_2 powder, 325 mesh, Carbon-Ukraine) was fully dispersed in 10 mL deionized water and gradually added into a mixture of 30 mL 12 M HCl and 2 g LiF at 35°C under magnetic stirring (500 rpm). Second, after 24 h, the mixture was centrifuged (3,500 rpm, 30 min) to





collect the sediment and washed with deionized water until the pH was >6. Vortexing 40 mL deionized water with the sediment for 30 min, the mixture was then transferred to centrifugation (3,500 rpm, 30 min) to collect the supernatant, which was the few and multilayered $Ti_3C_2T_x$ MXene. The concentration of the prepared MXene was measured by weighing a vacuum-dried freestanding film of a certain volume dispersion. The method of solvent exchange into organic solvents was based on our previous report.³³

Fractionation of industrial lignin

Kraft lignin (UPM BioPiva 100, ash content <2%) was mixed with organic solvents (0.2 mg mL⁻¹) under magnetic stirring for 5 h to promote dissolving. The lignin solution was then filtered (3,000 rpm, 10 min) to collect the supernatant. Lignin fraction powder was obtained by rotary evaporation of the supernatant. Here, DMSO, NMP, DMAc, DMF, and EtOH were employed to fractionate lignin.

Preparation of MXene@lignin complexes

Lignin fraction (5, 10, 15, 20, and 25 mg) was dissolved in 4 mL corresponding fractionation solvent (e.g., L_{NMP} was dissolved in NMP). We pumped the $Ti_3C_2T_x$ MXene dispersion (10 mg in 16 mL water) into the lignin solution at a speed of 3 mL min⁻¹ under magnetic stirring at 500 rpm. After 10 min of stirring, the mixture was centrifuged (3,500 rpm, 30 min) to collect the sediment. Then, we redispersed and washed the sediment with water until the supernatant became clear. The final MXene@lignin product was redispersed in water/organic solvent for storage or filtered to obtain a freestanding film.

Characterizations and DFT calculation

Details regarding the materials characterizations and DFT calculation can be found in the supplemental experimental procedures.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Zhong-Peng Lv (zhongpeng.lyu@aalto.fi).

Materials availability

This study did not generate new unique reagents.

Data and code availability

This study did not generate any code. The data are available in the main text and supplemental information. Any additional information required is available from the lead contact upon reasonable request.

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AUTHOR CONTRIBUTIONS

Z.-P.L. conceived the idea for the study. P.J. performed the experiments, with help from X.H., J.Z. and Z.-P.L. B.P. conducted the theoretical calculations. P.J. and Z.-P.L. analyzed the data and wrote the original manuscript, with help from J.S., J.K., X.H., B.P., and Y.H. Z.-P.L. and F.C. supervised the work. All the authors discussed and revised the manuscript.

DECLARATION OF INTERESTS

Aalto University has filed provisional patent FI20237049 and is working on a Patent Cooperation Treaty (PCT) application involving the fabrication of MXene@lignin complexes in this work.

SUPPLEMENTAL INFORMATION

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