Comb-type polymer-hybridized MXene nanosheets dispersible in arbitrary polar, nonpolar, and ionic solvents

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Solution-based processing of two-dimensional (2D) nanomaterials is highly desirable, especially for the low-temperature large-area fabrication of flexible multifunctional devices. MXenes, an emerging family of 2D materials composed of transition metal carbides, carbonitrides, or nitrides, provide excellent electrical and electrochemical properties through aqueous processing. Here, we further expand the horizon of MXene processing by introducing a polymeric superdispersant for MXene nanosheets. Segmented anchor-spacer structures of a comb-type polymer, polycarboxylate ether (PCE), provide polymer grafting–like steric spacings over the van der Waals range of MXene surfaces, thereby reducing the colloidal interactions by the order of 10^3, regardless of solvent. An unprecedented broad dispersibility window for Ti3C2T x MXene, covering polar, nonpolar, and even ionic solvents, was achieved. Furthermore, close PCE entanglements in MXene@PCE composite films resulted in highly robust properties upon prolonged mechanical and humidity stresses.

INTRODUCTION

The MXene, an emerging class of two-dimensional (2D) materials comprising transition metal carbides, carbonitrides, or nitrides with the general formula M<n>XY<T>x (n = 1 to 3), has attracted notable research attention owing to its unique water dispersibility (1) along with excellent electrical (2–4), electrochemical (5, 6), and mechanical (7, 8) properties, compared to those of the traditional 2D materials. In particular, the minimal perturbation of these properties upon hybridization with various organic and inorganic chemicals renders MXene a unique material platform to simultaneously achieve multifunctionality through solution-based processes, without compromising their geometric and electrical advantages (6). Moreover, their hydrophilic surface functional groups (i.e., –O, –OH, and –F) provide MXene a high solubility in polar solvents such as water, which constitutes another unique and outstanding characteristic of MXene in processing perspective. However, acquiring wider processing windows comprising various solvent conditions such as nonpolar and ionic solvents is also highly important for harnessing their full capability for broader applications, which potentially has inhospitality to polar and high-boiling point solvent processing. In particular, the most widely studied Ti3C2Tx MXene can be stably dispersed into high-purity water (HPW) with high concentrations of up to several tens of milligrams per milliliter (9, 10), while stable colloidal suspensions can hardly be achieved in common organic solvents, such as chlorobenzene, with surface tension below 40 mN/m (11).

In this sense, various methods for the covalent and noncovalent functionalization of MXene surfaces have been reported to achieve stable dispersions in nonaqueous and nonpolar solvents. Although various approaches for broadening the dispersion window for other low-dimensional materials (e.g., graphene and boron nitrides) have been intensively investigated, their largely different surface characteristics with MXene require a sophisticated design of the dispersion techniques for MXene. A general scheme for MXene functionalization can be described in two parts: (i) anchoring the functional groups onto the surface of MXene via either chemical reactions at the T-groups of MXene (12), electrostatic interactions (13), or hydrogen bonding (14) and (ii) the incorporation of nonanchoring functional groups such as long alkyl chains (15) or large aromatic rings (16), which can promote further electrostatic repulsion or steric stabilization among MXene nanosheets. These approaches have been successful in increasing the dispersion stability in water for up to several weeks and even enhance the solubility of MXene nanoparticles in nonpolar solvents such as normal hexane. The use of engineered solvent mixtures has also demonstrated the possibility of facile nonaqueous processing of MXenes. However, because the kinetics of the dispersion process relies on the balance of thermodynamic interactions, each surface modification can only provide a narrow stable dispersibility window; MXenes with polarity-reducing decorations quickly undergo a sedimentation process in polar or aqueous solvents, and vice versa (11, 17). Furthermore, the films deposited from MXene solutions sedimented by the polar or aqueous solvents exhibit a weak resistance to the vapors of casting solvents and thus have low oxidation stability in ambient environments. In harsh ionic environments such as seawater (SW), the decorated MXenes aggregate immediately because interactions among MXene nanosheets become dominated by attractive van der Waals (vdW) force rather than electrostatic double-layer repulsion (fig. S1A) (18–20). After aggregation, the 3D particles of MXene cannot be redispersed, even after being washed thoroughly to remove the ions. These properties further restrict the large-scale application of MXenes, such as building-integrated electromagnetic interference (EMI) shielding. In terms of large-scale printing processes, sophisticated control of MXene ink formulations, such as concentration, viscosity, and boiling points, is required, which can only be achieved using a broad range of solvents.
Therefore, it is imperative to develop a dispersion method that is generally applicable to a broad range of solvents, which can eventually provide the basis for the scaled-up production of environmentally and mechanically stable solid-state MXene films.

Here, we present a covalently bonded “superdispersant” for Ti\(_3\)C\(_2\)T\(_x\) MXene nanosheets that can simultaneously provide largely enhanced sedimentation times in an unprecedented broad dispersibility window, ranging from polar to nonpolar and even ionic solvents, with which the inclusion of polymeric component further led to superior mechanical and moisture stabilities to the deposited composite films. A comb-type polycarboxylate ether (PCE) (Fig. 1A) was successfully introduced to form MXene@PCE hybrids, where the polyacrylic acid (PAA) segments anchor to the MXene surface with covalent Ti—O bonds, while flexible polyethylene glycol (PEG) segments provide a regulated steric spacing to shield against strong colloidal interactions. Figure 1B shows a schematic of the MXene@PCE surface in solvents and the characteristic interaction energy profiles of the MXene colloidal surfaces (details in fig. S1). The Flory radius \(R_F\) of PEG segments is approximately 2.5 nm in dispersed states (fig. S5) and 1.1 nm (poor solvent) to 6.8 nm (good solvent) as a grafted semidilute brush, which provides sufficient steric spacing to avoid colloidal interactions [i.e., compensation between the vdW and electronic double layer (EDL) interactions] among MXene nanosheets. The resulting MXene@PCE hybrids demonstrated a broad Hildebrand solubility window from 48 MPa\(^{0.5}\) (water) to 18.5 MPa\(^{0.5}\) (chloroform), which can simultaneously include various polar, nonpolar, and low-boiling point organic solvents. Owing to the shielding effect, the interaction parameter that governs the sedimentation of MXene nanosheets is reduced by more than 10\(^3\), compared to the bare MXene in nonpolar organic solvents. The hybrid demonstrated persistent dispersibility in various ionic aqueous solvents such as acid, base, and artificial SW. Furthermore, the incorporation of polymeric dispersant results in exceptionally robust EMI shielding capability of composite films deposited from the hybrid under both mechanical and humidity stresses.

RESULTS AND DISCUSSION

Ti\(_3\)C\(_2\)T\(_x\) MXene was synthesized by etching the Al layer from the Ti\(_3\)AlC\(_2\) MAX phase, following a previously reported method (22).

After the delamination, MXene was mixed and interacted with PCE [molecular weight (MW) of 50,000 with 92.6% PEG segmentation; see section S2, fig. S5, and table S5 in the Supplementary Materials for detailed characterizations] by vigorous agitation at set ratios. X-ray photoelectron spectroscopy (XPS) spectra of the MXene, PCE, and MXene@PCE composite films are shown in Fig. 1C. The Ti 2p peaks of pristine MXene at 454.4 eV (460.5 eV), 455.3 eV (460.9 eV), 456.9 eV (462.4 eV), 458.2 eV (464.8 eV), and 458.4 eV (466.1 eV) were assigned

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**Fig. 1. Morphology and structural characterizations.** (A) Chemical structure of the comb-type PCE. (B) Schematic of MXene@PCE hybrid surfaces and the corresponding interaction potential profiles. (C) Ti 2p (left), O 1s (middle), and F 1s (right) XPS spectra of pristine MXene, 30 weight % (wt %) MXene@PCE, and PCE from top to bottom. (D) High-resolution TEM image of 30 wt % PCE-MXene. (E) XRD patterns of 30 wt % MXene@PCE, pristine MXene, and PCE from top to bottom. a.u., arbitrary units.
The ratio of Ti\(^{2+}\) to Ti\(^{3+}\) increased from 4.4 (pristine MXene) to 2.5 nm, and the radius of gyration, \(R\), tercalation spacing (~0.5 nm) than the height of semidilute brush MXene in the dispersed state. Furthermore, smaller changes in in- ordered structure of PCE@MXene composite, and the reason for the formation of MXene-polymer interfacial bonding (either through covalent/ionic bonding or hydrogen bonding) and the MW of polymer \(G\), tetragonal Ti–O–O bonds with increased ionic charac- ter. The O 1s peak at 533.6 eV for COO\(^-\) decreased in the case of the PCE@MXene composite compared with the PCE polymer, indicating the formation of a Ti–O–bond (24, 25). The peak splitting observed in the F 1s spectra was attributed to the hydrogen bonding effects between remnant F groups on the MXene surface and partially hydrolyzed COO\(^-\) of PCE (i.e., COOH) (26). The cross- sectional transmission electron microscopy (TEM) images of the pristine MXene and PCE@MXene composite are presented in fig. S1B and Fig. 1D, respectively. The dark-colored MXene sheets were uniformly intercalated by the bright PCE polymer, and the layer distance of MXene increased from 1.30 to 1.81 nm. The increasing distance of MXene increased from 1.30 to 1.81 nm. The increasing layer distance was confirmed by the x-ray diffraction (XRD) patterns. As demonstrated in Fig. 1E, the (002) peak of MXene shifted from 6.98° to 4.70°, revealing that the interlayer spacings changed from 1.27 to 1.81 nm. Note that both the regular distance in the TEM image and the sharp (002) peak in the XRD pattern confirmed the self-assembly structure of PCE@MXene composite, and the reason for the formation of this structure was strong bonding between PCE and MXene in the dispersed state. Furthermore, smaller changes in intercalation spacing (~0.5 nm) than the height of semidilute brush \(h_B\) for PEG anchored on MXene in good (6.8 nm) and poor (1.1 nm) solvents, \(R_g\) (2.5 nm), and the radius of gyration, \(R_G\), (1.1 nm) of PEG also indicated that PEG molecules (fig. S4) can undergo amorphous entanglement with each other in solid-state films, which constitutes a basis for the excellent mechanical and solvent-vapor stability in solid states.

The stability of colloidal suspensions of MXene nanosheets can be described by a modified Derjaguin, Landau, Vervey, and Over- beek theory of colloidal interactions (27). For nonionic solutions, the vdW interaction, \(W_{\text{vdW}}\), for 2D nanosheets can be described by \(W_{\text{vdW}} = -H/12\pi d^2\), where \(H\) and \(d\) stand for Hamaker’s constant and the interlayer spacing, respectively (19). Given that the \(H\) for Ti\(_3\)C\(_2\)T\(_x\) is approximately 3.9 \times 10^{-20} \text{ J} \) (in chloroform) and 4.8 \times 10^{-20} \text{ J} \) (in water), the strong vdW interaction among MXene surfaces quickly dissipates after 1 nm (details in fig. S1, tables S1 to S4, and section S1). In ionic solutions, EDL built on the charged surfaces of MXene nanosheets forms a repulsive energetic barrier that retards the sedimentation process, the height of which is dependent on the density of the surface charges and the ionic strengths. As the ionic concentra- tion increases, the interaction becomes governed by attractive vdW forces; thus, the sedimentation process accelerates, as observed in other 2D materials such as graphene oxides (28–30). In particular, the relatively lower surface charge density of MXenes makes them more susceptible to ion-induced rapid aggregation. In this sense, the observation of the dispersion behavior of MXenes in ionic solutions can facilitate the understanding of the inherent interactions among MXene nanosheets and thus can verify the effectiveness of the dispersant introduced in the system.

The effectiveness of polymeric dispersant on the retardation of the colloidal interactions was investigated among five types of common water-soluble polymers, i.e., polyethylene oxide (PEO), sodium alginate (SA), PAA, polyvinyl alcohol (PVA), and PCE in ionic solvents (fig. S3). Some of these polymers have already been used in the MXene systems that exhibit remarkable performance. For example, SA with carboxylate functional groups (—COONa) and hydroxyl groups (—OH) have been added to MXene to form composite films, and the MXene composite showed excellent EMI shielding ability because of the formation of nacre-like MXene structures (4). The electrically neutral PVA polymer with only —OH notably improved the mechanical strength and thermal stability of the Ti\(_3\)C\(_2\)T\(_x\) films, which was attributed to the interfacial interaction between —OH of PVA and the MXene surface (7, 31). In addition, PAA polymers with carboxyl groups (—COOH) and PEO polymers with ether groups (C—O—C) have been shown to have a strong interaction with the hydrophilic MXene sheets (32). Figure 2A shows the ultraviolet–visible–near-infrared (UV-Vis-NIR) absorbance spectra of the MXene@polymer hybrids dispersed in a harsh ionic solution of artificial SW. The pristine MXene dispersed in HPW has strong absorption across the entire spectrum, with two major peaks at approximately 750 nm in the visible spectrum and 300 nm in the UV region (fig. S11). With the protection of PCE and PVA, the absorbance of polymer-MXene composite dispersed in the ionic solution increased by varying degrees, compared to that of the bare MXene and its hybrids with PAA, PEO, and SA. As shown in fig. S8, the aggregated MXene still occurred when PEO, SA, and PAA were used as dispersants, making the cuvette partially trans- parent and resulting in low light absorption. The same trend persisted regardless of the type of ionic solution, including hydrochloric acid (HCl; 1 M), sodium hydroxide base (NaOH; 1 M), sodium chloride (NaCl; 1 M), calcium chloride (CaCl\(_2\); 1 M), and SW [NaOH (1 M);NaCl (1 M);CaCl\(_2\) (10 mM)], as summarized in Fig. 2B. It is clear that the degree of dispersion for the MXene polymer composite qualitatively follows the order PCE > PVA > PAA > SA > PEO. In ionic solutions, the double-layer repulsion strengthens as the surface charge density increases; thus, ionic functional groups such as —COO\(^-\) on PCE, PAA, and SA could be advantageous for the dispersion. However, as the concentration of ions increases, vdW interaction dominates the aggregation process where the surface coverage of MXene and the adsorbed polymer layer thickness be- come important. In this sense, the dispersion behavior of MXene@polymer hybrids dispersed in the XPS spectra shows that the \(R_g\) (2.5 nm) or the grafted semidilute brush height (1.1 to 6.8 nm) of PEG segment is sufficient to screen the abovementioned strong vdW interaction (<1 nm), thus providing effective shielding from precipitation. These results are consistent with the action mecha- nism of PCE and other substances, such as graphene oxides, silica, and cement (33–35).

Figure 2C shows the particle-size distribution in colloidal solutions of bare MXene and MXene@PCE hybrids in SW, estimated by dynamic light scattering (DLS). Without PCE, a large number of particles with size of up to 6 \(\mu\)m were observed, which is the upper limit of DLS detection. With the protection of 30 weight % (wt %) PCE, particles larger than 5 \(\mu\)m were not detected, and the average size of the PCE-encapsulated MXene was estimated to be 445 nm. The difference in the size distribution can be understood from the changes in the growth rates, which depend on the surface conditions of the MXenes. The growth rate of the particles was estimated using
the modified Avrami equation for particle precipitation. When particles collide with each other in the Avrami process, they form an agglomerate, the size of which increases geometrically until the decrease in dispersed particle density slows down the entire precipitation process. Thus, the degree of agglomeration, $Y$, for dispersed particles can be described as follows (36):

$$Y(t) = 1 - e^{-kt^n}$$

where $k$, $t$, and $n$ correspond to the conversion rate, time, and order of transformation, respectively, and $n$ is dependent on the dimensionality of the conversion, such that a value of 3 can be adopted for the uniform nucleation of 2D agglomerates. Assuming homogeneous particle-size growth, the volumetric share of particles with diameters smaller than $a_i$ at time $t_i$ can be estimated using the relation: $a_i = g_i \times t_i$, where $g_i$ indicates the growth rate. Considering that particles with diameters larger than a specific size preferentially sediment, the kinetic trace of the solution absorbance at time $t$, $A_0$, can provide the delayed trace of $Y$ and thus the conversion rate of dispersed particles to agglomerates: $Y(t + t_c) = 1 - A_t / A_0$, where $t_c$ is the critical time at which a particle with a specific growth rate starts to sediment. On the basis of this, the growth rates in the system can be estimated from DLS (details in fig. S12). Figure 2D summarizes the size distribution and growth rate depending on the PCE proportions. As the PCE proportion increased, the rates of slow ($g_1$), intermediate ($g_2$), and fast ($g_3$) growth were effectively inhibited. Although $g_1$ only gradually decreased with increasing PCE proportion, the abrupt decrease in $g_2$ and $g_3$ indicates that the average crystal size and thus the sedimentation rate can be substantially reduced at approximately 30% PCE.

The effective lowering of surface-inherent colloidal interaction can further improve the dispersion of MXene hybrids in solvents with a broad range of polarity, boiling points, and solubility parameters. Figure 3A shows the optical images of MXene@polymer dispersions in various organic solvents after dispersion for 30 min. As indicated by the Flory-Huggins (F-H) interaction parameters derived from the Hildebrand solubility parameters of the polymers and solvents (tables S1 and S2 and fig. S4), PEO with less polarity, among other candidate polymers, is adequate for the dispersion of MXene in less polar solvents such as chlorobenzene. In contrast, PVA and PAA showed a gradual increase in the affinity for more polar solvents. The theoretical estimation agrees with the experimental results summarized in the bottom panel of Fig. 3A. Although the steric spacing groups of PCE mainly comprised PEG segments, the MXene@PCE hybrids exhibited far superior dispersibility in almost-nonpolar organic solvents, down to 18 MPa$^{0.5}$ (toluene, polar contribution of <7%), compared to PEG itself.

The effectiveness of PCE was more obvious in the kinetic traces of the solution absorbance ($A_t / A_0$) (Fig. 3B). As observed in the ionic solvent dispersions, PCE is also highly effective in the suppression of sedimentation in non- or less polar solvents. The kinetic traces of the dispersion can be further fitted to the modified Avrami equations for quantitatively extracting the conversion rate. Figure 3C shows the Avrami rate depending on the F-H parameters in chloroform. As the enthalpy of mixing decreased, the rate decreased accordingly. However, the MXene@PCE hybrid completely deviates from the trend and exhibits a rate of sedimentation that is at least three orders of magnitude lower than the expected trend of MXene@PEO. This behavior can be understood in the framework of a reduced Avrami process. The Avrami process dictates that the collision of particles in the system leads to agglomeration, which increases in size with repeated collisions. However, it can be speculated that in the MXene@PCE hybrid system, the collision does not necessarily result.
in agglomeration, but rather, a portion, $\gamma$, of the initial agglomerate splits back into the dispersed particles, thus leading to a reduced Avrami process with a conversion rate of $k_r = (1 - \gamma)k$. Therefore, it can be concluded that PCE boosts the reduction process by $10^3$ times compared to the next best candidate with the same chemical moiety, PEG. As observed previously, the density and strength of the surface anchoring can be considered as key parameters, by which the PCE demonstrates superior results owing to the comb-type anchor-spacer segmented structures.

With the superior dispersion capability of PCE, it is also important to demonstrate the effect of additional polymeric component on material or device properties of MXene systems. Meanwhile, the incorporation of polymeric composites into MXene films has revealed that they can boost both the mechanical and environmental stability. To test both aspects, MXene@PCE composite films fabricated with SW were used for EMI shielding applications. The morphologies of the bare MXene and PCE-MXene composite films are compared in Fig. 4 (A and B) and fig. S15. Without the protection of PCE, many large holes (~100 $\mu$m) and small holes (~3 $\mu$m) were observed using optical microscopy (fig. S15) and scanning electron microscopy (fig. S16), respectively, owing to the severe aggregation of MXene in SW. The smoothness and compactness of MXene@PCE hybrid composite film can improve the conductivity, EMI shielding efficiency (SE), and mechanical stability of the film. The pristine MXene film made by HPW exhibited high EMI SE (47.4 dB on average) over a broad frequency range (0.5 to 18 GHz), but the MXene film made using SW degraded to only 13.1 dB (Fig. 4A). The low EMI SE of the aggregated MXene was attributed to the non-uniform film thickness and electromagnetic radiation penetrating through the holes in the film. Adding the PCE polymer can effectively improve the dispersion of MXene in the ionic solution, thereby improving the film quality. The EMI SE of the film recovered from 13.1 to 24.2, 33.7, and 42.2 dB, as the proportion of PCE polymer increased from 0 to 10, 20, and 30%, respectively. The addition of PCE expanded the layer distance of MXene, resulting in more internal reflection and absorption of electromagnetic wave (EM) waves. However, a further increase in the PCE fraction degraded the EMI shielding performance because of increased interference from the insulating polymeric part in the film. Figure 4B shows the EMI shielding mechanism from reflection (SE_R) and absorption (SE_A) in the MXene and 30% MXene@PCE composite at 9 GHz. Pristine MXene presented a reflection-dominated shielding mechanism ($\approx 37$), while the intercalation of PCE afforded notable multiple reflections between MXene layers, thereby improving the absorption mechanism ($\approx 38$). The electrical conductivity of 30% MXene@PCE composite film remained high (466.1 S cm$^{-1}$) (fig. S18).

To investigate the mechanical robustness of composite film, we fabricated a large-area (diameter of 13.0 cm) composite film with artificial SW by vacuum-assisted filtration, and a pristine MXene film was fabricated with HPW as the control sample. A fatigue bending test was performed to quantitatively observe the robustness with the motorized equipment described in fig. S19. Figure 4C
Fig. 4. EMI shielding properties and stability measurements. (A) EMI shielding efficiency (SE) of MXene films fabricated with HPW and SW. (B) Total EMI SE (EMI SE$_T$), absorption (SE$_A$), and reflection (SE$_R$) mechanism in pristine MXene and 30 wt % MXene@PCE at 8 GHz. (C) Normalized EMI SE of pristine MXene and 30 wt % MXene@PCE composite film as a function of the bending cycle. (D) Humidity stability of MXene@PCE composite films under 40% relative humidity (RH) at 20°C as a function of the exposure time. Photo credit: Dong Hae Ho, Yonsei University.

shows the changing EMI SE with increasing bending cycles of the pristine MXene film fabricated with HPW and 30% MXene@PCE composite film fabricated with artificial SW. The EMI SE of pristine MXene film decreased by 34.15% after 1000 bending cycles under a strain of 1.46%, while only 4.27% degradation was detected in the 30% MXene@PCE composite film, indicating that the uniform intercalation of PCE polymers improved the bending endurance of MXene. The conductivity, on the other hand, showed that MXene@PCE composite film can withstand 1.5% of bending strain (fig. S21). Furthermore, in addition to mechanical stability, the MXene@PCE composite film can exhibit stability against both oxidation and moisture in film. The environmental stability of the films was tested under relative humidities of 40 and 100% at 20°C, as shown in Fig. 4D and fig. S20. The protection of MXene surface by PEG segments of PCE from the exposure to air and moisture is the likely cause of the enhanced stability, in contrast to a previous report on the composite film based on a more hydrophilic polymer, PVA (39, 40). This result further corroborates the strong amorphous entanglement of PEG segments in the solid states, which can provide a passivation shield against the infiltration of vapors together with the hydrophobicity of PEG segments.

In summary, we developed a superdispersant for Ti$_3$C$_2$T$_x$ MXene nanosheets that can simultaneously provide largely enhanced sedimentation times in an unprecedented broad dispersibility window, ranging from polar to nonpolar and even ionic solvents, as well as superior mechanical and moisture stabilities in the solid state. A comb-type PCE was introduced to MXene to form MXene@PCE hybrids, where the PAA segments strongly anchor onto the MXene surface, while flexible PEG segments provide a steric spacing as semidilute grafted chains to shield against strong vdW interactions that dissipate 1 nm from the surface. The resulting hybrids demonstrated a broad Hildebrand solubility window from 48 MPa$^{0.5}$ (water) to 18.5 MPa$^{0.5}$ (chloroform), which can simultaneously include various polar, nonpolar, and low–boiling point organic solvents. Because of the shielding effect, the precipitation of MXene@PCE hybrid colloids exhibited a reduced Avrami process, where their agglomeration probability was reduced by an order of magnitude of $10^{-3}$ in nonpolar organic solvents compared to MXene dispersed with linear-type PEG. The PCE further facilitated a persistent dispersibility in various high-concentration ionic aqueous solvents such as acid, base, and artificial SW, which shows that the comb-type design of PCE is indeed a one-of-a-kind dispersant material. Furthermore, the incorporation of polymeric dispersant leads to MXene@PCE composite films exhibiting highly robust EMI shielding capability under both mechanical and humidity stresses. It should be noted that the incorporation of polymeric component leads to a degree of retardation in the properties of final materials and devices such as the electrical conductivity, as commonly observed in the previous reports in other low-dimensional materials. Depending on the applications, those aspects might be detrimental in practical usages and therefore should be considered as one of the key parameters in finding the balance in their trade-offs with respect to the distinct advantages of polymer inclusion, such as the facile solution fabrication and improved mechanical/environmental stability. Further
studies on the minimization of the dispersant component and development of proper postprocessing methods would be highly beneficial in acquiring the better practical applicability of polymer-assisted dispersion approaches. On the basis of our study, we believe that the results reported herein will open up a new window for harnessing the diverse processing potential of MXenes adequate for broader applications.

MATERIALS AND METHODS

Synthesis of Ti3C2Tx MXene and MXene-polymer composites

In a 250-ml Teflon beaker, the etchant solution was prepared by dissolving 3.2 g of LiF (99.9%; Sigma-Aldrich) in 40 ml of 9 M HCl aqueous solution and then cooled to below 5°C using an ice-water bath. After the etchant was deoxygenated with ultrahigh-purity N2, 2.0 g of the MAX phase (Ti3AlC2 powder, 99%, 325 mesh; Forsman) was gradually added into the etchant under gentle stirring. The mixture was then deoxygenated once more and protected under an inert atmosphere. Etching was conducted for 48 hours in an oil bath at 25°C to remove most of the Al layer from the MAX phase. The product was washed and delaminated in two 50-ml centrifuge tubes with deoxygenated water using five to six centrifuge-shaking (vortex shaker) cycles. Last, the delaminated MXene was sonicated in an ice bath for 30 min and then centrifuged at 3500 rpm for 1 hour to obtain a single-layer MXene-dominated supernatant. The concentration of as-prepared MXene dispersion was determined using freeze drying. The PCE polymer aqueous solution (MW: 50 k, 55.0%; L’BESTE GAT) was mixed with the MXene dispersion according to the experimental design ratio (10, 20, 30, 50, 70, and 90 wt%). PEO (MW: 60 k), SA (MW: 10 k to 1 M), PAA (MW: 15 k), and PVA (MW: 50 k) were purchased from Sigma-Aldrich and dissolved in deionized water before mixing with MXene. The mixture of MXene and polymers was thoroughly shaken for 30 min to obtain uniform MXene-polymer composite materials.

Characterization

A UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) was used to monitor the concentration of dispersed MXene or MXene-polymer in various salt solutions. DLS (Microtrac, Nanotrac Wave) was conducted to measure the particle sizes of MXene and MXene-polymer dispersions. An x-ray photoelectron spectrometer (Thermo Fisher Scientific, ESCALAB250) was operated using an aluminum anode as the source with a spot size of 100 μm. A cross-sectional transmission electron microscope (JEOL, JEM-2100F) and XRD (Bruker, D8 ADVANCE) were used to detect the differences in the interlayer spacing of the MXene and MXene-PCE composite films. An optical microscope (Nikon, Eclipse-LV100ND) and a scanning electron microscope (Hitachi, S-5000) were used to characterize the surface morphologies of the MXene and MXene-PCE composite films.

EMI shielding characterization

The MXene or desired MXene-PCE composite dispersion was diluted with HPW or SW (1:510 volume ratio). The MXene films and MXene-PCE films were prepared by vacuum-assisted filtration using a polyvinyl difluoride (PVDF) membrane (0.45-μm pore size) and then cut into circular specimens with a 12.2-mm diameter. All the films were dried and stored in vacuum at room temperature before further measurement. EMI shielding characterization of all films was carried out using a two-port network analyzer (E8364B, Agilent) in the wide X-band frequency range (0.5 to 18 GHz). A bending test was carried out to evaluate the mechanical robustness of MXene and MXene-PCE films using a stepper motor controller (ECOPIA, BM-111). The bending strain (S) was fixed at 1.46%, according to the following equation: 

\[ S = 0.5 \times \left( \frac{t_{\text{membrane}} + t_{\text{film}}}{R} \right) \]

where \( t_{\text{membrane}} \) and \( t_{\text{film}} \) are the thicknesses of the PVDF membrane (~115 μm) and the MXene film (~1.68 μm) and 30% PCE-MXene composite film (~2.21 μm), respectively, and \( R \) is the bending radius (~4 mm).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at https://science.sciencemag.org/content/sciadv/sciadv.1ab5299.

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