Inkjet Printing of Self-Assembled 2D Titanium Carbide and Protein Electrodes for Stimuli-Responsive Electromagnetic Shielding

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2D titanium carbides (MXene) possess significant characteristics including high conductivity and electromagnetic interference shielding efficiency (EMI SE) that are important for applications in printed and flexible electronics. However, MXene-based ink formulations are yet to be demonstrated for proper inkjet printing of MXene patterns. Here, tandem repeat synthetic proteins based on squid ring teeth (SRT) are employed as templates of molecular self-assembly to engineer MXene inks that can be printed as stimuli-responsive electrodes on various substrates including cellulose paper, glass, and flexible polyethylene terephthalate (PET). MXene electrodes printed on PET substrates are able to display electrical conductivity values as high as $10^{8} \pm 175$ S cm$^{-1}$, which significantly exceeds electrical conductivity values of state-of-the-art inkjet-printed electrodes composed of other 2D materials including graphene ($250$ S cm$^{-1}$) and reduced graphene oxide ($340$ S cm$^{-1}$). Furthermore, this high electrical conductivity is sustained under excessive bending deformation. These flexible electrodes also exhibit effective EMI SE values reaching 50 dB at films with thicknesses of 1.35 $\mu$m, which mainly originate from their high electrical conductivity and layered structure.

1. Introduction

The significance of printing technologies regarding development and fabrication of novel electronic, photonic, and energy storage devices is increasing rapidly with the expansion in the set of available materials for printing.[1–9] Especially, recent advances in solution processing of 2D crystals including graphene,[10,11] transition metal dichalcogenides,[11] black phosphorus,[12] 2D metal carbides, nitrides, and carbonitrides (MXenes)[13,14] have enabled functional inks that can reflect extraordinary electronic and optical properties of 2D crystals on printed devices. This new family of functional inks was employed to demonstrate printed thin-film photodetectors,[15–19] logic memory devices,[15] transistors,[18–21] photovoltaics,[19,22] and supercapacitors.[23,24] Considering the entire spectrum of printing techniques, inkjet printing is considered as the most potent approach for fabrication of electronic and photonic devices using 2D crystals. Inkjet printing inherits the positive aspects of printing techniques such as compatibility with various substrates including flexible and soft surfaces, low operation temperatures, and the ability to generate large area patterns. In addition to these features shared by other printing techniques, inkjet printing offers additional advantages such as controlled material deposition, rapid multimaterial processing, maskless and high-resolution ($\approx 60$ $\mu$m) digital patterning capability. Even though, the material spectrum for inkjet printing spans many polymers and nanomaterials, it is yet to encompass all 2D crystals.

Current library of printable ink compositions consists of 2D crystals including graphene,[15,16,19,20,22,23,26] graphene oxide,[27,28] molybdenum disulfide,[15,16,18,19] tungsten disulfide,[15,19] hexagonal boron nitride,[19] and black phosphorus.[17] However, functional 2D crystals with exceptional electrochemical,[13,29–33] electromagnetic interference (EMI) shielding,[34–46] performance like MXenes have yet to be processed using inkjet printing. There are several key issues that need to be addressed for developing functional inks of MXenes suitable for inkjet printing.
including i) low viscosity of water-based solvent systems, \[7, 37\], ii) improper adhesion of crystals to substrate, and iii) formation of the coffee-ring effect during solvent evaporation. \[18\]

The low viscosity of water-based solvents employed to stabilize exfoliated MXene sheets can hinder the stability of the jetting process leading to the formation of satellite droplets and jetting deflection. \[7\] Moreover, MXene sheets can accumulate at the edges of the droplets (coffee ring effect) during evaporation due to lack of interactions with the substrate. \[15\] The lack of interaction can also lead to redispersion of deposited materials during printing cycles. \[15\] Similar problems were addressed for other 2D crystals including graphene, molybdenum disulfide, and tungsten disulfide using a binder molecule, which can help increasing viscosity of the ink and facilitating specific interactions between MXene sheets and substrates. \[15\] However, commonly used binder molecules synthesized through chemical routes cannot offer a versatile solution for establishing and controlling sheet-to-sheet \[12, 19–22\] and sheet-to-substrate \[43, 44\] interactions for MXenes. In contrast to chemical binders, proteins can be a better match for MXenes, as both materials can form strong hydrogen bonding interactions. Even though, there are many studies regarding interactions between proteins and 2D crystals, \[45, 46\] the interaction and assembly dynamics of MXenes and proteins remain unexplored.

In this work, we demonstrated functional 2D titanium carbide (\(\text{Ti}_3\text{C}_2\text{T}x\)) MXene where \(T\) is a functional group such as O, F, or OH for inkjet printing using binder molecules based on synthetic structural proteins that can form sequence controlled assemblies with hydrogen bonding 2D crystals. \[45\] Synthetic protein-based binders form assemblies with 2D crystals and facilitate controlled aggregation of protein/2D crystal assemblies as the high-viscosity solvent (dimethylsulfoxide, DMSO) evaporates rapidly on heated substrates (70 °C). This promotes uniform deposition of 2D crystals among printing area and impedes formation of coffee ring effect. Proteins with similar amino acid sequences were also known to strongly adhere on a variety of substrates, \[17, 48\] which helps improving the stability of printed MXene patterns. The composition of the MXene ink is optimized to involve minimum amount of binder concentration to sustain unique properties of MXene in printed patterns. These inks were successfully printed on several substrates including cellulose paper, glass, polyethylene terephthalate (PET), and polymethylmethacrylate (PMMA). To highlight the prospect of these inks regarding flexible electronics, we printed MXene patterns on PET films to construct deformable light-emitting diode (LED) circuits and EMI shielding materials. Another interesting aspect of these printed patterns originates from the novel response of proteins to humidity, \[49\] as the conductivity of the printed MXene patterns can be reversibly altered with humidity. This utility can potentially be used to develop humidity-mediated memory systems and sensors, particularly for microfluidic systems.

2. Results and Discussion

2D titanium carbide (Figure 1a) flakes can be delaminated into single/few layer nanosheets using several solvent systems including DMSO and aqueous solutions containing tetraalkylammonium hydroxide (TMAOH) and lithium ions. \[50–52\] Among these methods, DMSO-based delamination methods form the solutions with highest viscosity, and exfoliated MXene concentration, which are both important for sustaining consistent inkjet printing of MXene nanosheets. Despite exhibiting high viscosity (Figure S1, Supporting Information), MXene/DMSO solutions with nanosheet concentrations exceeding 2 mg mL\(^{-1}\) demonstrate satellite drop formation, and consequently poor printing performance (Figure S2, Supporting Information). The assessment of ink quality for MXene/DMSO solutions (2.25 mg mL\(^{-1}\)) can be performed by measuring the inverse Ohnesorge number (\(Z = \sqrt{\rho\alpha\gamma/\eta}\), which describes printability of solutions using various parameters including viscosity (\(\eta\)), surface tension (\(\gamma\)), and density (\(\rho\)) for a given nozzle diameter (\(\alpha\)) (Figures S1 and S2, Supporting Information). \[53\] MXene/DMSO solutions with 2.25 mg mL\(^{-1}\) nanosheet concentration have an average Z value of 27.5 ± 0.02 (Table S1, Supporting Information) for a nozzle diameter of 120 μm, which is high even for inks of 2D materials that can still be printed with Z values above 20. \[15, 16, 20\] High Z values for MXene/DMSO solutions are originating from the high surface tension (51.5 mN m\(^{-1}\)) of these solutions. To decrease the surface tension and Z values, we introduced synthetic polypeptides (proteins) inspired from squid ring teeth (SRT) proteins as macromolecular additives (Figure 1b). \[44\] These block copolymer–like polypeptides are composed of tandem repetitions of amorphous and crystalline regions. Tandem repeat units consisting of hydrophobic and polar amino acids can significantly reduce surface tension. Unlike surfactant additives, these macromolecules with higher molecular weight can also help improving the viscosity of MXene/DMSO solutions, which also reduces Z values. In order to increase viscosity effectively, we employed proteins with high number of tandem repeat units (n = 11) and molecular weight (42 kDa, TR42). \[35, 54–56\] Our ink formulations composed of various TR42 concentrations indicated that these synthetic proteins can increase viscosity and significantly reduce surface tension and Z values for MXene/DMSO solutions, similar to increased MXene concentration (Table S1, Supporting Information). \[57\] MXene/DMSO-based inks with a TR42 concentration of 0.95 mg mL\(^{-1}\) demonstrate a surface tension of 40 mN m\(^{-1}\), a viscosity of 3.4 cP, and a Z value of 21.3 making them suitable for inkjet printing (Table S1, Supporting Information).

Following the initial characterization of ink formulations, we investigated the assembly mechanics of MXene nanosheets and proteins. MXene nanosheets possess functional groups at their surface, which can facilitate several physical interactions including hydrogen bonding (Figure 1a). Proteins can form connections with these 2D crystals via hydrogen bonding; however, governing the ultimate structure of this assembly requires a specific amino acid sequence that can be modulated using synthetic biology. Recently, we demonstrated that it is possible to control the assembly and interconnectivity of hydrogen bonding 2D crystals (graphene oxide) using proteins consisting of tandem repetitions (Figure 1b). \[45\] We modulated our MXene ink formulations to initiate formation of this assembly during solvent evaporation of printed patterns (Figure 1c). Initial pristine MXene solutions consisting of exfoliated sheets of MXene in DMSO (2.25 mg mL\(^{-1}\)) remain stable for an extended period of time (~6 months). As we increase the
concentration of synthetic proteins (TR42), the rate of sheet aggregation/assembly increases (Figure 1d). We observed that instant aggregation (~10 s) occurs at a critical protein concentration of 1 mg mL\(^{-1}\). For inks with protein concentrations slightly lower than 1 mg mL\(^{-1}\), the assembly process takes 12 h at room temperature without agitation, stirring, or sonication. In light of this assessment, we prepared ink solutions with protein concentrations of 0.5 mg mL\(^{-1}\) (P7) and 0.95 mg mL\(^{-1}\) (P5) from initial the MXene/DMSO solutions (2.25 mg mL\(^{-1}\)) (Figure 1d; Figure S4, Supporting Information). Monitoring the jetting sequence of respective ink formulations shows the formation of satellite droplets during printing of pristine MXene/DMSO (control) solutions, as inferred from the initial characterization of Z values (Figure 1e; Figure S1, Supporting Information). On the other hand, solutions containing proteins (ink P5 and ink P7) exhibit stable droplet formation and printing (Figure 1e).

The initial printing performance of pristine and protein-based (P5 and P7) MXene inks is evaluated by printing circles with 1 cm diameter on cellulose paper (Figure 2a). Each printed sample goes darker with an increasing number of passes, which is indicative of uniform printing. The higher-magnification images of printed samples at the edges of circles indicate a better stability for patterns printed using protein-based MXene inks. Circles printed with pristine MXene inks exhibit splattered droplets at the edge of circles (Figure 2a(ii)), which is potentially originated from satellite droplets observed during the printing process (Figure 1e). On the other hand, there is no indication of droplet splash for circles printed using protein-based MXene inks (P5 and P7) (Figure 2a(iii)). Microstructure characterization by X-ray diffraction (XRD) from the printed samples on cellulose paper indicates MXene inks form an intercalated sheet structure in which MXene layers are stacked on top of each other\(^{[50,52,54]}\) and separated by water.\(^{[50,52,54]}\)
DMSO[50,58] and protein molecules (Figure 2b,c). Samples printed from pristine MXene inks demonstrate stacked MXene layers with intercalated water ($2\theta = 7^\circ \pm 0.15^\circ$) and DMSO ($2\theta = 5.75^\circ \pm 0.1^\circ$) molecules represented by the (002) peak in the XRD pattern (Figure 2c). The influence of protein-mediated assembly of MXene sheets begins to show in samples printed from P7 inks, as the intercalation of protein molecules adds a tertiary periodicity ($2\theta = 4.75^\circ \pm 0.1^\circ$) for the (002) peak of MXene (Figure 2c). Additionally, diffraction peaks originating from the crystalline (100) plane of synthetic proteins ($2\theta = 9.15^\circ$) also become apparent (Figure 2c). These protein-mediated diffraction signals become more dominant for samples printed from P5, potentially due to increased protein concentration (Figure 2c). The changes in spacing between MXene sheets are quantified using XRD data (Figure 2d). This analysis reveals that protein-mediated assembly increases separation between sheets (Figure 2d). The characterization of sheet resistance of inks printed on cellulose paper substrates shows resistance values higher than those of the patterns processed using pristine MXene inks, possibly due to percolative effects facilitated by the presence of protein (Figure 2e). The presence of proteins can lead to an increase in planar intersheet separation and formation of protein inclusions in between sheets.[52] This moderate difference between sheet resistance values...
of MXene patterns potentially originates from the improved interconnectivity of MXene sheets, which can be facilitated by protein-mediated assembly. Even though the sheet resistance values are increased for the MXene–protein ink-printed patterns on cellulose paper, these values (220 Ω sq⁻¹, 50 pass) are significantly lower than the state-of-the-art graphene-based inkjetted electrodes (≈600 Ω sq⁻¹, 50 pass) without any need for further treatment.

Besides cellulose paper substrates, the printing performance of pristine and protein-based MXene inks is examined for other substrates relevant for inkjet printing including glass, PET, PMMA, and polydimethylsiloxane (PDMS). The printing performance assessment of PMMA provided inconsistent results, as DMSO effectively dissolves PMMA. In addition, contact angle measurements performed for PDMS substrates showed insufficient wetting of MXene inks of PDMS surface. Consequently, the printing performance analysis focuses on most potent substrate candidates including fused silica glass, and particularly PET, due to potential applications in flexible electronics. To investigate printing capabilities of pristine and protein-based MXene inks on glass and PET substrates, large circles (d = 1 cm) were printed using pristine MXene ink and ink P5 formulation. Pristine MXene inks demonstrated irregular material deposition for both glass and PET substrates. Pristine MXene inks are absorbed more homogeneously by the surface, because of the rapid dissipation of DMSO solvent in cellulose paper. However, relatively flat and nonporous glass and PET substrates necessitate an additional mechanism of adhesion for MXene sheets to be deposited uniformly. The printed circles using ink P5 offered a much better coverage.

![Figure 3](image_url)

**Figure 3.** a) Low-magnification optical images of circles inkjet-printed on PET substrates using i) pristine MXene ink and ii) P5 ink (30 passes/cycles); high-magnification optical images of the edge of circles inkjet-printed on PET substrates using iii) pristine MXene ink and iv) P5 ink (30 passes/cycles); high-magnification optical images of the center of circles inkjet-printed on PET substrates using v) pristine MXene ink and vi) P5 ink (30 passes/cycles); and high-magnification optical image of conductive lines (width: 120 µm, length: 2 cm) inkjet-printed on PET using ink P5 with an interline spacing of vii) 40 µm and viii) 150 µm. b-i) Low-magnification and ii) high-magnification SEM images of circles inkjet-printed on PET substrates using ink P5; iii) cross-sectional SEM image of circles inkjet-printed on PET substrates using ink P5. c) Sheet resistance values of circles inkjet-printed on various substrates using ink P5 as a function of printing passes/cycles. d) Average thickness of circles inkjet-printed on glass and PET as a function of printing passes/cycles. The inset shows the data for the thin pattern inkjet-printed on glass.
and shape confirmation in comparison to pristine MXene ink (Figure 3a(ii,iv,vii)). To exploit protein-mediated adhesive capabilities of these MXene inks, parallel electrodes with a width of 120 µm were printed with separation distances of 40 µm (30 µm is the resolution of the printer moving stage) and 150 µm (Figure 3a(vi,vi,vi)). The resulting electrodes were continuous for 2 cm and can conduct electricity \((R = 40 \, \text{k} \Omega \text{ each})\), which highlights printing capabilities of protein-based MXene inks for devices patterned on flexible substrates for soft electronics. Further assessment of surface characteristics by scanning electron microscopy (SEM) imaging of circles printed from the protein-based MXene ink P5 reveals relatively uniform deposition of MXene flakes across the printed areas (Figure 3b(ii)). SEM images with higher magnifications present the planar structural arrangement of MXene sheets and protein assemblies (bright spots) located on MXene sheets (Figure 3b(iii)). The planar stacking of MXene sheets is also confirmed by the cross-sectional SEM image acquired from the printed samples of ink P5 (Figure 3b(iii)). The detailed characterization of electrical properties of MXene patterns inkjet-printed using ink P5 on fused silica glass, PMMA, and PET was performed to further evaluate inkjet printing performance of protein-based MXene inks on nonporous substrates (Figure 3c). MXene patterns (circles) inkjet-printed using ink P5 on these nonporous substrates demonstrated sheet resistance values significantly lower than the patterns inkjet-printed on porous substrates like cellulose paper using same ink formulation (P5). These nonporous substrates with more regular surface morphology except PMMA are excellent for the assessment of geometry-independent electrical properties like electrical resistivity or conductivity, which is particularly important for electronic device performance and design. To identify electrical resistivity/conductivity of MXene patterns inkjet-printed on fused silica glass and PET, thickness values of each printed feature were measured using surface profilometry (Figure 3d). Measured sheet resistance and thickness values were employed to calculate resistivity and conductivity values for MXene patterns, which correspond to resistivity values of \((0.85 \pm 0.17) \times 10^{-3} \, \Omega \text{ cm}\) and \((1.17 \pm 0.19) \times 10^{-3} \, \Omega \text{ cm}\), and conductivity values of \(1215.9 \pm 250\) and \(870.5 \pm 140 \, \text{S cm}^{-1}\) for MXene patterns inkjet-printed on fused silica glass and PET, respectively. These conductivity values are significantly higher compared to conductivity values of state-of-the-art graphene-based electrodes \((250 \, \text{S cm}^{-1})^{[25]}\) deposited on glass and PET substrates using inkjet printing.

Device performance of printed patterns using protein-based MXene ink (P5) is also characterized by assembling an LED circuit using printed electrodes on PET substrate (McMaster-Carr, 250 µm). To evaluate performance of LED circuit under mechanical deformation, the printed MXene electrodes were subjected to bending corresponding to a specific radius of curvature (Figure 4a,b). The voltage passing across LED was measured during bending deformation, which remained stable up to a radius of curvature of 5 mm and demonstrated negligible decrease at maximum radius of curvature of 3.6 mm (Figure 4a,b). This experiment highlights the mechanical stability of printed electrodes and robust attachment of MXene sheets on PET substrates, which is facilitated by TR proteins.

Beyond stabilizing the printing process for MXene sheets on various substrates, TR proteins induce reversible structural changes in response to specific stimuli such as humidity. An increase in humidity initiates swelling of proteins,\(^{[47,49]}\) which leads to an increase in volume of proteins and consequently a decrease in volumetric fraction of conductive MXene sheets in composite-printed electrodes. The reduced volumetric fraction of conductive MXene sheets results in a decrease in electrical conductivity. Because the structural changes originating from the humidity are reversible, it is possible to alter the resistivity of printed patterns on PET substrates (Figure 4c; Figure S6, Supporting Information). The most drastic change in resistance by increasing humidity occurs in the thinner electrodes (10 pass), yet, deviation in sheet resistance is also far greater for thinner electrodes (Figure 4c).

To estimate humidity response of electrodes printed from protein-based MXene inks, a stimuli response is defined from initial resistance \((R_0)\) and saturation resistance \((R_s = \text{resistance values at } 100\% \text{ relative humidity})\). Figure 4d depicts that thicker electrodes reach saturation resistance at lower levels of humidity, while thinner electrodes demonstrate a gradual increase in resistance up to 90% humidity. Our results show that thicker electrodes exhibit binary-like response (on/off) and thinner electrodes are more suitable for humidity sensing. The binary-like response of thicker electrodes is more visible for sheet resistance measurements performed during continuous humidity cycles for various humidity conditions (Figure 4e–g). Thin electrodes (10 pass) cannot reach saturation resistance and present inconsistent resistance cycles during changes of humidity. However, thick printed electrodes (20 and 30 pass) reach saturation values at relatively low changes in humidity (10%), and exhibit more consistent changes in resistance during consecutive humidity changes. Unlike conductive patterns of ink P5, the conductive patterns inkjet-printed using pristine MXene inks demonstrate electrical properties with minimal dependence on changes in humidity conditions (Figure S6, Supporting Information).

Following the characterization of flexible device performance and stimuli response of inkjet-printed MXene electrodes, the EMI shielding capabilities of electrodes printed using pristine MXene ink and ink P5 were also evaluated. EMI shielding samples were prepared by inkjet printing of large circles \((d = 2 \, \text{cm})\) using MXene ink and ink P5 on PET substrates (Figure S7, Supporting Information). Inkjet printing of pristine MXene ink resulted in circles with discontinuous coverage similar to smaller circles printed using pristine MXene ink for characterization of electrical properties (Figure 3a(i)); Figure S7a, Supporting Information). Consequently, it is not possible to obtain a representative electrical conductivity and thickness measurement from electrodes printed using pristine MXene inks. However, circular electrodes inkjet-printed with ink P5 exhibit better coverage and more consistent electrical conductivity values that increase with the increasing number of printing passes (Figure 5a; Figure S7b, Supporting Information). The electrical conductivity of three inkjet-printed electrodes used for EMI shielding efficiency (EMI SE) analysis (30 passes) had an average conductivity of \(750 \pm 200 \, \text{S cm}^{-1}\) and a thickness of \(1.45 \pm 0.2 \, \mu\text{m}\), which were employed to generate a theoretical EMI SE performance using Simon formalism.

\(R = 40 \, \text{k} \Omega \text{ each} \)
Due to discontinuous coverage, experimental EMI SE values of the electrodes printed from the pristine MXene ink are inferior to electrodes printed using ink P5 under ambient humidity conditions (60% relative humidity (RH)) (Figure 5a). Electrodes inkjet-printed using ink P5 offer EMI SE values reaching 50 dB with an electrode thickness of 1.35 µm in frequencies between 8 and 12 GHz at ambient humidity conditions (60% RH) (Figure 5a). These EMI SE properties are close to the state-of-the-art EMI shielding materials demonstrated recently from free-standing MXene films,[34,60] which highlights the potential of these protein-based MXene inks as EMI shielding materials for printed electronics.

The influence of stimuli responsive nature of the electrodes printed using protein-based ink (ink P5) was also investigated for EMI SE properties. To evaluate the impact of humidity on EMI SE, both electrodes printed from pristine MXene ink and ink P5 were exposed to water until they reach ≈100% RH. The EMI shielding performance of electrodes printed from pristine
MXene inks remains relatively unchanged under 100% RH (Figure 5b), even though water can potentially diffuse more effectively throughout the electrodes, due to larger surface area stemming from discontinuous MXene coverage. However, EMI SE of electrodes printed using ink P5 decreased from 50 to 40 dB after reaching 100% RH (Figure 5b). The decrease in EMI SE values can be explained by the increase in resistivity of the samples, which was observed during analysis of the stimuli response of printed electrodes (Figure 4c). Even though proteins facilitate swelling corresponding to an increase in volume (≈20%) [47,49] which is known to improve EMI SE of swollen MXene nanostructures [60], it cannot compensate for the drop in EMI SE originating from the increase in resistivity and consequently a decrease in electrical conductivity.

3. Conclusions

We demonstrated inkjet printing of 2D MXene. MXene sheets in DMSO solution provide a basis for generating printable inks once supported with tandem repeat proteins. The resulting ink formulations can be effectively printed on many substrates including cellulose paper, glass, PET, and PMMA to generate electrode patterns. The conductive MXene electrodes printed on flexible PET substrates can reach electrical conductivity of $10^{80} \pm 175$ S cm$^{-1}$ for films with an average thickness of 2.25 µm. This value corresponds to the highest electrical conductivity reported among electrodes that are inkjet-printed using 2D materials. Furthermore, these highly conductive electrodes printed on flexible PET substrates remain intact and maintain their electrical conductivity under bending deformation, which is particularly important for applications in flexible electronics. The robust and highly conductive electrodes printed from MXenes also provide efficient electromagnetic interference shielding (50 dB, a film thickness of 1.35 µm), matching the state-of-the-art shielding materials composed of MXene films. In addition, the prominent electrical and electromagnetic shielding properties of patterned electrodes respond to changes in humidity, which expand the spectrum of applications for these 2D inks.

4. Experimental Section

Synthesis of MXene from Ti$_3$AlC$_2$ (MAX Phase): Ti$_3$C$_2$T$_x$ was synthesized through selective etching of Ti$_3$AlC$_2$ powders as described elsewhere [50,52]. About 1 g of Ti$_3$AlC$_2$ powder was added to a 10 mL of aqueous solution of 9 m hydrochloric acid (HCl, Fisher Scientific) and 1 g of lithium fluoride (LiF, Alfa Aesar 98+%). The mixture was then stirred for 24 h at 35 °C. The acidic product was washed several times with deionized (DI) water (H$_2$O) via centrifugation at 3500 rpm for 5 min per cycle and supernatant was decanted each time. This process was repeated until supernatant solution of pH ≥ 5 was reached. Resultant sediment was collected and redispersed in DI water then bath sonicated for 1 h. Finally, the mixture was centrifuged for 1 h and the supernatant containing delaminated Ti$_3$C$_2$T$_x$ was collected. Stable colloidal solution of Ti$_3$C$_2$T$_x$ in DI water was obtained for further processing.

Expression of Tandem Repeat Proteins: Binder tandem repeat protein composed of 11 repetitions was constructed and expressed using rolling circle amplification (RCA). The detailed protocols describing the amino acid sequence and expression methods are presented in the earlier works [45,54].

Figure 5. a) Electrical conductivity of large area electrodes inkjet-printed on PET. Electromagnetic Interference shielding efficiency (EMI SE) of large area (circle, $d = 2$ cm) electrodes inkjet-printed on PET using various ink solutions (MXene ink, ink P5) at b) dry (60% relative humidity) and c) wet (100% relative humidity) conditions.
Preparation of MXene Inks: Solutions consisting of MXene sheets exfoliated in water (4.5 mg mL\(^{-1}\)) were centrifuged (13 200 rpm, 15 min), and water was exchanged with either DMSO or TR42 protein/DMSO solutions (TR42 protein concentration of 0.5 mg mL\(^{-1}\) for ink P7 and 0.95 mg mL\(^{-1}\) for ink P5). For the preparation of pristine MXene inks, centrifuged MXene sheets were redispersed in DMSO using bath sonication under controlled temperature (25 °C) for 2 h. This centrifugation, solvent exchange, and redispersion cycle was performed three times to ensure complete solvent exchange to DMSO. The concentration of the resulting MXene/DMSO solution was diluted to 2.25 mg mL\(^{-1}\) for generating pristine MXene inks that can be printed without clogging printer tips. For preparation of ink P7 and P5, centrifuged MXene sheets were redispersed in respective TR42 protein/DMSO solutions using bath sonication under controlled temperature (25 °C) for 2 h. This protocol consisting of centrifugation, solvent exchange, and redispersion was performed for three cycles, and MXene concentration of these inks were diluted to 2.25 mg mL\(^{-1}\) to ensure continuous printing.

Printing Process and Device Fabrication: Prepared inks were printed using a commercial printer, jetlab 4 (MicroFab Technologies Inc., Plano, TX). The piezo-inkjet dispensing device orifice diameter is 120 µm (MJ-ABL01-120-8MX, MicroFab). It is a multichannel piezo inkjet printer and deposited on substrates heated to 70 °C to facilitate rapid evaporation of solvent. Due to large flake size of MXene sheets (3–6 µm),\(^{[31]}\) a single nozzle with a diameter of 125 µm was used during printing processes. The resolution, defined as the smallest width of printed line, was 120 µm on PET (McMaster-Carr, 250 µm) (Figure 3a(vii,viii)). The minimum distance between two parallel lines for successful printing was 40 µm (the resolution of the moving stage was 30 µm) (Figure 3a(vii)). The entire printing processes were carried out at an operational frequency of 200 Hz. The droplet spacings for printed electrode patterns including lines, circles, rectangles, and circuits on different substrates using different inks can be found in Table S1 in the Supporting Information. The printing process and droplet spacing for EMI shielding samples printed on PET substrates can also be found in the Supporting Information. The flexible LED circuit consists of two rectangular MXene lines printed on PET substrates (McMaster-Carr, 250 µm) as electrodes and a commercially available red LED with an operation voltage of 3 V. This circuit was powered with a Keithley 2400 Sourcemeter and the output voltage was set to 12 V.

Characterization: X-ray diffraction experiments were performed using reflection mode with PANalytical Xpert Pro MPD (Cu Kα radiation, λ = 1.5406 Å, operating at 40 kV, and a cathode current of 20 mA) under standard laboratory conditions. Raman spectroscopy experiments were performed using LabRam system (Horiba Jobin-Yvon, France) using an excitation wavelength of 633.82 nm (He–Ne laser) and 3.5 mW power (10% of peak power). A 50x long working distance objective with a numerical aperture of 0.50 was used, and the corresponding spot size was 30 µm × 30 µm. The spectral resolution of the experiments was set to 2 cm\(^{-1}\). Surface tension measurements of ink formulations were analyzed using a standard contact angle measurement system (First Ten Angstroms, FTA1000 B Class). Viscosity measurements of ink formulations were characterized by TA Instruments Discovery hybrid rheometer HR-2 at room temperature using a concentric cylinder geometry. Viscosity values were measured across a shear rate range of 5–200 s\(^{-1}\). Optical images were acquired using benchtop optical imaging system (Thermofisher Scientific, EVO FL Auto Imaging System). SEM images were acquired using ZEISS 55 Ultra FESEM at 3 kV beam voltage. The thickness of printed patterns was measured using Veeco Dektak 6M profilometer. The sheet resistance and electrical conductivity values of the printed electrodes and EMI samples were measured using a custom-built automated four-point probe measurement system connected to a Keithley 2400 Sourcemeter (n = 3, error bars represent standard deviation). Conductive thin lines printed using MXene inks were measured using a probe station connected to Keithley 2400 Sourcemeter. LED circuit-bending experiments were performed in two-point probe configuration using a deformation stage custom-built from optical mechanical stages. The LED circuit was powered by HP/Agilent 34461A Sourcemeter. The voltage readout on LED was acquired using HP/Agilent Sourcemeter. Sensor response measurements were also performed in two-point probe configuration using a digital multi-meter. Samples were incubated in vacuum chamber for 10 min prior to measurements.

Electromagnetic Interference Shielding Measurements: EMI shielding measurements of electrode samples printed on PET using pristine MXene inks and protein-based MXene inks (ink P5) were carried out using coaxial transmission lines with a two-port network analyzer (8720ES, Keysight, USA) in X-band frequency range (8.2–12.4 GHz). The equipment was calibrated using a standard procedure with short offset, short, and load on both ports 1 and 2. The samples were punched into circular shape with diameters of 1.2 cm slightly smaller than the opening of the sample holder (1.5 cm). Electromagnetic wave had an incident power of 0 dB. The average thickness of printed samples was (1.15 ± 0.31 µm) for samples printed using MXene–DMSO inks and 1.45 ± 0.2 µm for samples printed using ink P5.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
M.C.D. and M.V. have a pending patent application on protein based 2d materials assembly.

Keywords
electromagnetic interference shielding, inkjet printing, MXene, responsive electrodes, synthetic protein

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