Surface-agnostic highly stretchable and bendable conductive MXene multilayers

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Stretchable, bendable, and foldable conductive coatings are crucial for wearable electronics and biometric sensors. These coatings should maintain functionality while simultaneously interfacing with different types of surfaces undergoing mechanical deformation. MXene sheets as conductive two-dimensional nanomaterials are promising for this purpose, but it is still extremely difficult to form surface-agnostic MXene coatings that can withstand extreme mechanical deformation. We report on conductive and conformal MXene multilayer coatings that can undergo large-scale mechanical deformation while maintaining a conductivity as high as 2000 S/m. MXene multilayers are successfully deposited onto flexible polymer sheets, stretchable poly(dimethylsiloxane), nylon fiber, glass, and silicon. The coating shows a recoverable resistance response to bending (up to 2.5-mm bending radius) and stretching (up to 40% tensile strain), which was leveraged for detecting human motion and topographical scanning. We anticipate that this discovery will allow for the implementation of MXene-based coatings onto mechanically deformable objects.

RESULTS AND DISCUSSION

We produced conductive, stretchable, bendable, surface-agnostic MXene coatings through the sequential adsorption of negatively charged MXene sheets and positively charged polyelectrolytes using an aqueous assembly process known as layer-by-layer (LbL) assembly (Fig. 1A) (11–13). Here, we used Ti3C2Tx nanosheets, derived from the parent Ti3AlC2 MAX phase (14). This type of MXene has been used in applications ranging from water desalination to catalysis (15–18). MXene sheets in a stable aqueous dispersion at pH 5 had a negative charge (~32 mV by zeta potential). A transmission electron microscopy (TEM) image of a drop-cast MXene nanosheet showed a slightly wrinkled morphology and a lateral size of several micrometers (fig. S1) (19). The complementary species chosen for LbL assembly was poly(diallyldimethylammonium chloride) (PDAC) because of its positive charge (+18 mV by zeta potential).

The MXene multilayers were first assembled either by alternate immersion (Fig. 1B) or by spraying (Fig. 1C) of the two components onto glass. The color of the coating, which arises from the MXene nanosheets, became successively darker as the number of layer pairs or LbL cycles increased from 0 to 40. This confirms that MXenes may be directly incorporated into multilayer coatings with PDAC using electrostatic interactions. By contrast, when the PDAC adsorption step was removed from the assembly process, no MXene deposition was observed (fig. S2). Furthermore, the MXene multilayer exhibited strong mechanical integrity during tape adhesion tests, whereas a comparable drop-cast MXene film did not (fig. S3). This result further emphasizes the influence of the attractive electrostatic interactions to the multilayer coating’s good adhesion to the underlying surface.

The structure and morphology of the multilayer coating were next examined. Scanning electron microscopy (SEM) and tapping-mode atomic force microscopy verified dense coverage of the MXene nanosheets on the surface, as well as a nacre-like brick-and-mortar cross section (Fig. 1D and figs. S4 and S5). For a 40-layer-pair coating made by immersion, the thickness was 378 ± 33 nm. UV-vis spectroscopy, profilometry, and quartz crystal microbalance (QCM) measurements were conducted to assess the growth behavior (Fig. 1, E to G, and fig. S6). The coating’s UV-vis spectra demonstrate broad adsorption at 770 nm, consistent with...
MXene nanosheets (20, 21). The adsorption at 770 nm increased linearly with the number of layer pairs (Fig. 1, E and F), which is consistent with the linear increase in film thickness (9.7 nm per layer pair for immersion and 2.7 nm per layer pair for spraying; Fig. 1G). QCM also confirmed linear growth and yielded a coating composition of 90–weight % (wt %) MXene and 10–wt % PDAC (fig. S6). Assuming that the average thickness of an MXene sheet is ~1 nm (18, 22) and that the coated polymer’s contribution to thickness is negligible, then each MXene adsorption step deposits 10 layers of MXene nanosheets. The RMS roughness measured using profilometry was consistently <40 nm (Fig. 1H). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) studies support the successful growth of the MXene multilayer (figs. S7 and S8 and table S1), which displayed characteristic features of both PDAC and MXene sheets. X-ray powder diffraction (XRD) analysis shows a decrease in MXene sheet spacing upon inclusion in the multilayer (fig. S9).

To demonstrate the surface-agnostic nature of the MXene multilayers, we assembled the coatings by alternate immersion onto indium tin oxide (ITO)–coated glass, poly(ethylene terephthalate) (PET), In2O3/Au/Ag-coated PET, kirigami-patterned PET, poly(dimethylsiloxane) (PDMS), and nylon fibers (Fig. 2, A to C, and movie S1). These surfaces span different chemistries (oxide, organic, hydrophilic, and hydrophobic) and different geometries (flat versus textured fiber). Figure 2 (A and B) shows the successful deposition of the multilayer onto all of these surfaces, which is impressive considering that this could not have been achieved by other means (for example, vacuum filtration and dip-coating). It is also demonstrated that these coatings retain their conductive nature. Figure 2C shows that the nylon fiber was rendered conductive by the multilayer coating. Figure 2D quantifies the sheet resistance with the number of layers pairs. A five-layer-pair multilayer had a sheet resistance of 17 kilohm per square, which decreased and stabilized to 5 to 8 kilohm per square because more layer pairs were deposited. This is because more continuous pathways for charge transport developed as additional layer pairs were added. The sheet resistance values here were higher than that of pure Ti3C2 MXene sheets (7, 8) because of the presence of insulating PDAC in the multilayer coatings. To demonstrate conductivity, the multilayer coating on PET operated an LED even under extreme bending and folding from 180° to 0° (Fig. 2E and movie S2).
Because the conductive MXene multilayers can be incorporated into flexible (PET) and stretchable (PDMS) objects, we next examined how the resistance changes during extreme bending and stretching (fig. S10).

There is a general increase in resistance upon bending to smaller radii, for which resistance doubled at a bending radius of 2.5 mm versus the flattened state (Fig. 3A and fig. S11A). A similar result was obtained for the case of stretching MXene-coated PDMS, where increasing tensile strain resulted in up to a ninefold increase in resistance at 40% strain (Fig. 3B and fig. S11B). This result is remarkable in that the film maintains its conductance at such extreme deformations; for comparison, MXene-based papers made by vacuum filtration cannot withstand these high strains (only 1.0%) (8). To our knowledge, this is one of the first reports of extremely stretchable surface-agnostic MXene composites (table S2).

To understand the stability of resistance with mechanical cycling, we repeatedly bent and stretched both MXene-coated PET and PDMS, respectively (Fig. 3, C and D, and movie S3). Over the course of 2000 cycles of bending from a radius of 4.4 mm to a flattened state, the resistance was fairly stable (increasing by 0.05% \( \frac{R}{R_0} \) per cycle) (table S3 and fig. S12A). There was some initial nonrecoverable change in resistance in the first cycle, which we attribute to the initial formation of defects. We observed similar stability (0.03% \( \frac{R}{R_0} \) per cycle) for MXene-coated PDMS with repeated stretching (table S4 and fig. S12B). These MXene-based coatings endured other types of deformations, such as twisting and kirigami stretching, reversibly responding to strain without forming large-scale visible cracks (fig. S13 and movies S4 to S8).

To understand the underlying mechanism of the electromechanical coupling, we monitored structural changes in the MXene multilayer coating before and after bending and stretching (Fig. 3, E and F, and fig. S14). The as-prepared MXene multilayer exhibited no cracks or defects by SEM. Upon initial bending or stretching, microcracks and gaps irreversibly formed, explaining the initial increase in the normalized resistance in Fig. 3 (C and D). The gaps and cracks are not so large as to completely destroy the conductive network; rather, this lengthens the pathway for electron conduction. Upon release, the cracks and gaps close and recover, and the conductive pathway is reformed. This is confirmed by a geometric analysis that accounts for the average island and gap size under deformed and released states, as well as for the tortuous conduction path that results from it. (figs. S15 and S16 and analysis shown in Supplementary Materials). This mechanism has been observed elsewhere for carbon nanotube strain sensors (23, 24), a crack-based Pt sensor (25), and a microcracked organic semiconductor (26).

These results suggest that the MXene multilayer films could be used as strain sensors to topographically sense objects or materials deformation. For demonstration, a topographic scanner was fabricated using a patterned MXene multilayer–coated PET film (Fig. 4A, fig. S1, and...
The MXene-coated PET bent and deformed as small objects passed through the scanner, resulting in a change in normalized resistance $R/R_0$ (Fig. 4, A and B, and movie S10). The topographic scanner (Fig. 4C) was even able to map complex shapes, such as T, A, M, and U letters (Fig. 4, D and E). A soft human motion sensor was fabricated using MXene-coated PDMS (Fig. 4F). The sensor detected the angle of a bent index finger with little hysteresis (Fig. 4G and fig. S18). As the bending angle increased to 35°, the normalized resistance $R/R_0$ also increased more than double, showing a large gauge factor (GF, the sensitivity to bending) defined as $GF = (\Delta R/R)/\varepsilon = 11.5$; in comparison, common metal-foil gauges have a GF of 2.0 (5% maximum strain) (27). In summary, these results demonstrate that MXene nanosheets can form mechanically responsive conductive coatings, having implications for soft, flexible, and stretchable conductors that could enable organic electronics or biometric sensing on a variety of surfaces and interfaces.

Fig. 3. Strain sensor behavior under bending and stretching. (A) Normalized resistance ($R/R_0$) versus bending radius for 20-layer-pair MXene multilayer on PET and (B) versus strain for 20-layer-pair MXene multilayer on PDMS. $R_0 = 22.4$ kilohm (bending) and 1.66 megohm (stretching). Cycling performance under (C) bending and (D) stretching. SEM images of the surface structure of the 20-layer-pair MXene multilayer on (E) PET (bending) and (F) PDMS (stretching). The deformed coatings on PET and PDMS are under bending ($r = 4.4$ mm) and stretching ($\varepsilon = 20\%$), respectively.
MATERIALS AND METHODS

Materials

PDAC [molecular weight (Mw) = 200,000 to 350,000 g/mol, 20 wt % in water], linear poly(ethyleneimine) (Mw = 50,000 g/mol), hydrochloric acid [HCl; ACS reagent; 37% (w/w)], and dimethyl sulfoxide (DMSO; ReagentPlus; >99.5%) were purchased from Sigma-Aldrich. Ti (44-μm average particle size, 99.5% purity), Al (44-μm average particle size, 99.5% purity), TiC powders (2- to 3-μm average particle size, 99.5% purity), and lithium fluoride (LiF, 98+% purity) were purchased from Alfa Aesar. Substrates for LbL deposition included slide glass (VWR International), ITO-coated glass (R < 20 ohm per square; Delta Technologies), In2O3/Au/Ag coated PET (R < 10 ohm per square; Delta Technologies), nylon fiber (Artiste), PDMS (Sylgard 184, Dow Corning), and PET (Melinex ST505, Tekra).

Synthesis of Ti\textsubscript{3}AlC\textsubscript{2} MAX phase

Commercial Ti, Al, and TiC powders were used as starting raw materials to synthesize Ti\textsubscript{3}AlC\textsubscript{2} MAX phase. To prepare homogeneous powder mixtures, Ti, Al, and TiC powders were first weighed to achieve Ti/Al/C = 3.0:1.2:1.8 ratio and mixed them together using ball-milling with zirconia beads in a glass jar at the speed of 300 rpm for 24 hours (18, 28). Then, the bulk high-purity Ti\textsubscript{3}AlC\textsubscript{2} samples were sintered at a temperature of 1510°C for 15 min with a loading of 50 MPa using pulsed electric current sintering (PECS). To fabricate high-purity Ti\textsubscript{3}AlC\textsubscript{2} powder, the sample sintered using PECS was first drill-milled and sieved to obtain powder with particle sizes below 44 μm.

Synthesis of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene clay

Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene clay was synthesized by etching Al from the MAX phase using the technique described by Ghidiu et al. (18). Concentrated HCl [37% (w/w)] was diluted with deionized (DI) water to obtain 30 ml of 6 M HCl solution. This solution was transferred to a polypropylene (PP) beaker, and 1.98 g of LiF was added to it. This dispersion was stirred for 5 min using a Teflon (polytetrafluoroethylene) magnetic stirrer at room temperature. Ti\textsubscript{3}AlC\textsubscript{2} MAX phase powder was slowly added to the HCl + LiF solution to prevent overheating because the reaction is highly exothermic. The PP beaker was capped to prevent evaporation of water, and a hole was made in the cap to avoid buildup of gases. The reaction mixture was stirred at 40°C for about 45 hours. The slurry product was filtered and washed with DI water in a polyvinyl difluoride (PVDF) filtration unit with pore size of 0.22 μm (SCGVU10RE Stericup GV; Millipore) to remove the unreacted HF and water soluble salts. This washing process was repeated until the pH of the filtrate reached a value of about 6. Reaction product collected over the PVDF filter was extracted as Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene clay.

Fig. 4. An object scanner and human motion sensor. (A) Digital image of a topographical scanner using the MXene multilayer–coated PET (LbL sensor). (B) The topographical map by normalized resistance variations with various cube patterns. (C) Topographical scanner with the five MXene multilayer–coated PET sensors and (D) T, A, M, and U patterns using cubes. (E) Topographical maps of normalized resistance variations for the T, A, M, and U patterns. (F) Digital image of the human motion strain sensor. (G) Response to finger motion.
Intercalation and delamination of Ti$_3$C$_2$T$_x$ MXene clay

Ti$_3$C$_2$T$_x$ MXene clay was intercalated with DMSO and subsequently bath sonicated to obtain an aqueous dispersion of delaminated Ti$_3$C$_2$T$_x$ MXenes. DMSO was added to Ti$_3$C$_2$T$_x$ MXene clay (dried in vacuum oven for about 24 hours at 40°C) to form a suspension (60 mg/ml) followed by about 18 hours of stirring at room temperature. After intercalation, excess DMSO was removed by several cycles of washing with DI water and centrifugation at 5000 rpm for 4 hours. The intercalated Ti$_3$C$_2$T$_x$ MXene suspension in DI water was bath sonicated for 1 hour at room temperature followed by centrifugation at 3500 rpm for 1 hour to separate the heavier components. The supernatant contained the stable Ti$_3$C$_2$T$_x$ nanosheet dispersion.

Preparation of dip-assisted MXene-based multilayers

Multilayers were deposited at the surface of various substrates, slide glass, ITO-coated glass, pure PET, In$_2$O$_3$/Au/Ag-coated PET, PDMS, and nylon fiber. The PDAC and MXene sheets were diluted to a concentration of 1.0 mg/ml in DI water (18.2 megohm). The pH values of the PDAC solution and MXene dispersion were 5.00 and 5.03, respectively, and both solutions were used without adjusting the pH. For PDAC/MXene LbL film on bare glass, a slide glass was cut into 1.25 cm × 5.00 cm and then cleaned by sequential sonication in isopropyl alcohol, water, and acetone for 15 min each. After washing, the glass was dried with nitrogen. Plasma treatment (Harrick PDC-32G) was conducted for 5 min. Plasma-treated glass substrates were immersed in PDAC solution for 15 min and rinsed with DI water for 2, 1, and 1 min each. Then, the substrates were immersed in MXene dispersion for 15 min and rinsed with DI water for 2, 1, and 1 min each. The same procedure was repeated until the desired thickness was obtained. For deposition onto ITO glass and PDMS, all procedures were identical. For LbL deposition onto pure PET, In$_2$O$_3$/Au/Ag-coated PET, and nylon fiber, isopropyl alcohol and water were used to clean the substrates, whereas all other processing steps were the same as in the case of deposition on slide glass. For mechanical-electrical tests, the films were cut into 50 mm × 3.15 mm.

Preparation of spray-assisted MXene-based multilayers

The identical PDAC and MXene solution-dispersions were used for spray-assisted LbL deposition. A slide glass was cut into 1.25 cm × 1.25 cm. Cleaning and drying processes were identical to those used in the dip-assisted method. Plasma treatment (Harrick PDC-32G) was conducted for 5 min. One layer of linear poly(ethyleneimine) was deposited by immersing substrates into the poly(ethyleneimine) solution (1 mg/ml) for 1 min, followed by rinsing with DI water three times. After washing, the glass was dried with nitrogen. PDAC solution was sprayed onto the substrates for 5 s at a flow rate of 0.4 ml/s, followed by spraying of DI water for 20 s. Air was blown for 30 s. Subsequently, MXene dispersion was sprayed for 5 s at a flow rate of 0.4 ml/s, followed by spraying of DI water for 20 s. Air was blown for 30 s. The procedure was repeated until the desired number of layer pairs was obtained.

Preparation of U-shaped patterned PDAC/MXene multilayers

To make a U-shaped pattern, a 1-mm-wide tape was put on PET substrate before LbL assembly. After LbL coating, the tape was removed. Other procedures were identical to the dip-assisted LbL preparation.

Characterization

TEM (FEI Tecnai F20) was used to investigate morphologies of the Ti$_3$C$_2$ MXene nanosheet. The Ti$_3$C$_2$ MXene dispersion was diluted down to 0.01 mg/ml. Then, a portion of the dispersion was collected in a dropper and poured onto a holey carbon grid. The grid was allowed to dry in air before it was examined under TEM. SEM (JEOL JSM-7500F) was used to investigate morphologies of the multilayer films. Three nanometers of platinum/palladium alloy was sputter-coated onto samples before imaging. Profilometry (P-6, KLA-Tencor) was used to measure the thickness of the MXene-based multilayers. The thickness was measured in at least five different locations. The mass of the multilayer was measured using QCM. First, plasma treatment was carried out on a 5-MHz Ti/Au quartz crystal for 5 min. The multilayer was deposited onto the quartz crystal using the LbL assembly procedure described above. The composition of the multilayer was determined by monitoring the frequency changes during each layer deposition from 10 to 15 layer pairs. Mass was calculated from the measured frequency using the Sauerbrey equation. UV-vis spectroscopy was conducted using a Shimadzu UV-2401 PC spectrometer over a wavelength range of 300 to 900 nm. XPS was performed using an Mg K$_\alpha$ x-ray (energy source of 1253.6 eV) and a charge neutralizer (Omicron CN10). For the survey scan, a pass energy of 100 eV and an energy step size of −1.0 eV were used. A linear-type background subtraction was used to isolate the photoemission lines. A manual four-point resistivity probe (Lucas Labs S-302-4) was used to measure and calculate the conductivity of the multilayer. Multimeter (Velleman DVM890F) was used to measure the resistance under various deformations (bending, stretching, twisting, and folding). ATR-FTIR spectroscopy (Nicolet 6700 ATR-FTIR, Thermo Fisher Scientific) was used with a germanium crystal. The IR spectra were obtained at a wave number range of 650 to 4000 cm$^{-1}$ at a resolution of 1 cm$^{-1}$. Mechanical-electrical property characterization of the multilayer was performed on a homemade actuating tester. A multimeter (Velleman DVM890F) was used to measure the resistance of the LbL films.

Fabrication of an object scanner

Five-layer-pair multilayers (50 mm × 3.15 mm) with U-shaped pattern were used. Copper wires were connected to both ends of the U shape–patterned LbL film using silver paste. The object scanner was fixed between two metal frames with Kapton tape (VWR International) for electrical insulation. For object scanning, the copper wires were connected to the multimeter.

Fabrication of a human motion sensor

Twenty-layer-pair multilayers (30 mm × 3.15 mm) were used. Aluminum ribbons were connected to both ends of the multilayer using electrical tape (VWR International). The human motion sensor was fixed on a finger using an electrical tape. For human motion sensing, the aluminum ribbons of the sensors were connected to the multimeter.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/3/eaaq0118/DC1

fig. S1. TEM image of a Ti$_3$C$_2$ MXene nanosheet on a perforated carbon grid.

fig. S2. Digital images of (left) bare glass, (middle) the result of LbL assembly using only MXene sheets (without PDAC solution), and (right) 10-layer-pair MXene/PDAC multilayer coating.

fig. S3. Adhesion testing with tape.

fig. S4. A cross-sectional SEM image of the MXene multilayer prepared by spray-assisted LbL assembly on glass.

fig. S5. AFM images of PDAC/MXene multilayers.

fig. S6. Thickness of the multilayers as a function of the number of layer pairs.

fig. S7. ATR-FTIR spectra of MXene, PDAC, and 20-layer-pair MXene multilayer coating.

fig. S8. XPS survey spectra of MXene, (PDAC/MXene)$_{20}$ multilayer finished with MXene, and (PDAC/MXene)$_{20}$, multilayer finished with PDAC.
PET film. movie S10. A topographic scanner was fabricated using a patterned MXene multilayer with rapid response. movie S8. An MXene multilayer on PDMS detects a twisting deformation. movie S7. An MXene multilayer on PDMS detects stretching deformations.

REFERENCES AND NOTES

table S1. Atomic composition at the surface of cast MXene sheets, (PDAC/MXene)$_{20}$ multilayer.

fig. S14. SEM images of MXene multilayers after bending and stretching.

fig. S12. Comparison of resistance drift in literature.

fig. S10. Digital images of MXene multilayers bending and stretching.

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movie S4. An MXene multilayer on PET detects bending deformations.

movie S3. Cyclic bending of a MXene multilayer on PET shows rapid and reversible response.

table S3. Characteristics of reported bendable conductors.

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