MXene improves the stability and electrochemical performance of electropolymerized PEDOT films

ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) is the most commonly used conducting polymer in organic bioelectronics. However, electrochemical capacitances exceeding the current state-of-the-art are required for enhanced transduction and stimulation of biological signals. The long-term stability of conducting polymer films during device operation and storage in aqueous environments remains a challenge for routine applications. In this work, we electrochemically synthesize a PEDOT composite comprising the water dispersible two-dimensional conducting material Ti$_3$C$_2$ MXene. We find that incorporating MXene as a co-dopant along with PSS leads to PEDOT:PSS:MXene films with remarkably high volumetric capacitance ($607.0 \pm 85.3$ F cm$^{-3}$) and stability (capacity retention = 78.44% ± 1.75% over 500 cycles), outperforming single dopant-comprising PEDOT films, i.e., PEDOT:PSS and PEDOT:MXene electropolymerized under the same conditions on identical surfaces. The stability of microfabricated PEDOT:PSS:MXene electrodes is evaluated under different conditions, i.e., when the films are exposed to sonication (~100% retention over 6 min), upon immersion in cell culture media for 14 days ($\Delta |Z| = 2.13\%$), as well as after continuous electrical stimulation. Furthermore, we demonstrate the use of a PEDOT:PSS:MXene electrode as an electrochemical sensor for sensitive detection of dopamine (DA). The sensor exhibited an enhanced electrocatalytic activity toward DA in a linear range from 1 $\mu$M to 100 $\mu$M validated in mixtures containing common interferents such as ascorbic acid and uric acid. PEDOT:PSS:MXene composite is easily formed on conductive substrates with various geometries and can serve as a high performance conducting interface for chronic biochemical sensing or stimulation applications.

INTRODUCTION

Organic bioelectronics involves the development of electronic devices that rely on organic electronic materials (e.g., conjugated polymers) for communication with living systems. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has become a flagship conducting polymer for organic bioelectronics because of its biocompatibility, high electrical conductivity (up to 4000 S cm$^{-1}$), ability to transport both ionic and electronic charges in the bulk of the film leading to volumetric capacitances in the range of 39 F cm$^{-3}$ to 327 F cm$^{-3}$, as well as compatibility with various processing methods and softness (down to 2 MPa). Research has focused on improving and tailoring these properties to meet the needs of target applications. For instance, PEDOT films with...
enhanced electrochemical capacitances would lead to neural electrodes that can deliver a large amount of charge at low currents or amplify weak biological signals despite their small footprint.\textsuperscript{19\textendash}21 Similarly, PEDOT films with improved adhesion to their underlying substrates in aqueous media are in demand for chronic applications of implantable organic bioelectronic devices.\textsuperscript{20,21} Thus, the development of organic electronic materials with specifically designed properties is critical for bringing the associated technologies into maturation.

Several polymerization methods have been used to generate PEDOT films with customized properties such as improved capacitance, sensitivity to specific analytes, or enhanced stability.\textsuperscript{17\textendash}21 Among these methods, electropolymerization is a straightforward route, which requires only a small amount of the monomer and short polymerization time to pattern a conducting polymer film on any given conductive surface.\textsuperscript{18} One strategy to modify PEDOT properties via electropolymerization involves the use of EDOT derivatives that contain functional units (e.g., functional groups tethered on the ethylenedioxy ring).\textsuperscript{22\textendash}26 Once the film is formed, molecules of interest can be conjugated to its surface through these units. Another approach relies on the presence of functional molecules in the reaction mixture. These molecules can be integrated into PEDOT as dopant counterions if they bear anions (e.g., lignin, dextran sulfate, heparin, xanthan gum, graphene oxide (GO), and carbon nanotube)\textsuperscript{17\textendash}21 or are entrapped inside the conducting polymer film as it grows on the substrate, such as catalytic enzymes, boronic acid, antibodies, or single-stranded DNA.\textsuperscript{22,26} Furthermore, through electropolymerization of chemically modified EDOT monomers (e.g., carboxylic- and amine-modified EDOT),\textsuperscript{11,22} the electrochemical stability of PEDOT and its adhesion to substrates can be improved. PEDOT can be electropolymerized on surfaces modified with a thin layer of an adhesion promoter (e.g., diphenylamine).\textsuperscript{28} The requirement of special EDOT derivatives and intermediate layers between the substrate and the polymer film may, however, be tedious, inferior to film’s electrical properties, and not feasible for all applications.

An alternative route to enhance stability along with volumetric capacitance is building PEDOT composites that comprise other functional materials. One such material is Ti3C2 MXene, a two-dimensional (2D) material that possesses high volumetric capacitance (1500 F cm\textsuperscript{3})\textsuperscript{29} and electronic conductivity (~10 000 S cm\textsuperscript{1}).\textsuperscript{30} Ti3C2 MXene also has a hydrophilic nature as a result of its negatively charged functional groups (denoted by T\textsubscript{x}) such as hydroxyl (\textsuperscript{\textendash}OH), oxygen (\textsuperscript{\textendash}O), and fluorine (\textsuperscript{\textendash}F).\textsuperscript{31,32} The hydrophilicity of MXene renders it dispersible in aqueous media. Hence, it enables the use of solution processing methods (e.g., spin coating, spray coating, and inkjet printing) to generate Ti3C2 MXene films for diverse applications.\textsuperscript{33,34} Recent work integrated MXenes (Ti3C2 and Mo\textsubscript{1.33}C) with PEDOT:PSS and polypyrrole, leading to polymeric composites with high capacitance and energy density.\textsuperscript{34,37} The composite films were fabricated either by directly mixing the two components followed by filtration or via electropolymerization of EDOT and pyrrole monomers with the MXene as a dopant.\textsuperscript{35,37} The high capacitance of such composites was leveraged to build charge storage devices, while only a few reports focused on bioelectronics applications.\textsuperscript{33,36,39} The chemical instability of Ti3C2 MXene in aqueous solutions may be halting progress in such applications despite the promising features of MXenes.\textsuperscript{39,40} The oxygen in water and the voltage applied in the positive regime (>0.4 V vs Ag/AgCl) were reported to cause chemical degradation of the film and TiO\textsubscript{2} formation.\textsuperscript{35,42} Developing stable MXene based hybrid materials with enhanced electrochemical properties for bioelectronics is, therefore, a compelling task.

In aspiration of combining the features of MXene with PEDOT, in this work, we electrochemically synthesized PEDOT composites with Ti3C2 MXene as a counter anion (PEDOT:PSS:MXene). To evaluate the impact of Ti3C2 MXene on the electrochemical properties, we electropolymerized two other PEDOT films, one grown in the presence of only PSS (PEDOT:PSS) and the other in the presence of only Ti3C2 MXene (PEDOT:MXene). The physicochemical characterization using scanning electron microscopy (SEM), focused-ion beam (FIB) SEM, secondary ion mass spectrometry (SIMS), and x-ray photoelectron spectroscopy (XPS) confirmed that Ti3C2 MXene is distributed throughout the PEDOT matrix in PEDOT:PSS:MXene. We found that PEDOT:PSS:MXene electrodes had the highest volumetric capacitance (607.0 ± 85.3 F cm\textsuperscript{3}) and robust operation with a capacitance retention of ca. 78% after 500 doping–dedoping cycles, outperforming other electropolymerized PEDOT derivatives produced in this work. The films demonstrated remarkable stability: they were resistant to dissolution during a sonication endurance test and maintained their electrical properties upon long-term immersion in phosphate buffer saline (PBS) and cell media and upon repetitive electrical stimulation cycles. Integration into PEDOT via electropolymerization thus rendered Ti3C2 MXene electrochemically stable in a larger electrochemical potential window. Furthermore, we used this composite for electrochemical sensing of dopamine (DA). The PEDOT:PSS:MXene electrode surpassed the performance of the standard PEDOT:PSS as a DA sensor by detecting a few tens of μM of DA in aqueous solutions comprising hundreds of μM of uric acid (UA) and ascorbic acid (AA), two common electro-oxidizable interferents. Our study shows how electropolymerization—a simple, single-step polymerization that omits the use of non-toxic reagents—provides a route to combine the features of two high-performance materials and leads to films directly patterned on conductive substrates of any given geometry.

**EXPERIMENTAL SECTION**

**Materials**

3,4-Ethynediathythiophene (EDOT), poly(sodium 4-styrenesulfonate) (PSS), dopamine (DA), ascorbic acid (AA), uric acid (UA), and 1X phosphate buffer saline (PBS, pH 7.4) were purchased from Sigma-Aldrich and used as received. Si813 and AZ9260 photoresists as well as MF-319 and AZ developers were purchased from MicroChemicals GmbH. All aqueous solutions were prepared using ultrapure water (Millipore Milli-Q). Ti3C2 MXene flakes were synthesized by selectively removing the aluminum layer from the parent layered Ti3AlC2 MAX following previous studies.\textsuperscript{27} For flakes with large lateral dimensions, ~3.5 μm on average, the supernatant solutions were collected at mild centrifuging speeds (~3000 rpm) and reduced sonication times.\textsuperscript{24}
Electropolymerization of the PEDOT derivatives

An aqueous dispersion of 10 mM of EDOT was mixed with 0.8 wt.% NaPSS and/or 0.8 wt.% Ti3C2 MXene in DI water and sonicated for 30 min at room temperature. The pH of EDOT:PSS, EDOT:MXene, and EDOT:PSS:MXene monomer solutions is 5.6, 6.6, and 6.2, respectively, measured using a pH meter (Metrohm). These dispersions were used as the reaction solution. The Au coated electrode (diameter: 7 mm) was placed into a 5 ml beaker that contained this mixture. For microelectrode arrays (MEAs) (diameter: 30 μm) or square shaped micrometer scale gold electrodes (500 μm × 500 μm²), we placed a PDMS well on top of the active area and confined the mixture therein. Ag/AgCl and a Pt wire were also immersed in the solution and used as the reference and counter electrode, respectively. We used a potentiotstatic mode of the potentiostat (Autolab PGSTAT128N, Metrohm) and applied 1 V for 5 min to grow the polymer on top of the working electrode. The electropolymerized film was then washed with deionized water and dried with N₂ spray to remove unreacted monomers as well as any material that was weakly bound to the surface.

Physiochemical characterizations

The morphology of the PEDOT films was visualized by using a FEI Nova nano scanning electron microscope (SEM) with an accelerating voltage of 3 kV and a working distance of 5 mm. The films were mounted onto aluminum stubs and attached with a conductive double-sided tape. We used a focused-ion beam (FIB) to create a precise cross section of the samples with subsequent imaging via scanning electron microscopy (SEM). Cross-sectional images were taken with a focused ion beam (FIB)/SEM (FEI Helios NanoLab 400S). The FIB/SEM dual-beam system was equipped with a Ga⁺ ion source. Platinum layers were deposited on the surface region of interest by an electron and ion beam for sample protection. To characterize the elemental composition of the films, secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS) studies were performed. Depth profiling experiments were performed on a Dynamic SIMS instrument from Hiden Analytical Company (Warrington, UK) operated under ultrahigh vacuum conditions, typically 10⁻⁹ Torr. A continuous Ar⁺ beam of 4 keV energy was employed to sputter the surface while the selected ions were sequentially collected using a MAXIM spectrometer equipped with a quadrupole analyzer. The raster of the sputtered area is estimated to be 750 × 750 μm². In order to avoid the edge effect during depth profiling experiments, it is necessary to acquire data from a small area located in the middle of the eroded region. Using an adequate electronic gating, the acquisition area from which the depth profiling data are obtained was ~75 × 75 μm². XPS analysis was performed on a Kratos Axis Supra instrument equipped with a monochromatic Al Kα x-ray source (hv = 1486.6 eV) operated at 75 W under UHV conditions (~10⁻⁹ mbar). The spectra were recorded in a hybrid mode using electrostatic and magnetic lenses and an aperture slot of 300 × 700 μm². The survey and high-resolution spectra were acquired at fixed analyzer pass energies of 80 eV and 20 eV, respectively. The samples were mounted in a floating mode to avoid differential charging. The spectra were acquired under charge neutralization conditions. Atomic Force Microscopy (AFM) images were obtained using a Veeco Dimension 3100 scanning probe system. The morphological images were acquired with RTESPA-300 (nominal resonant frequency: 300 kHz; spring constant: 40 N m⁻¹) and PFTUNA (nominal resonant frequency: 70 kHz; spring constant: 0.4 N m⁻¹) probes (Bruker). Image post-treatment and statistical data were performed and collected using the Gwyddion software.

Electrochemical measurements

We measured the electrochemical performance of the PEDOT films by using a three-electrode configuration and a potentiostat (Autolab PGSTAT128N, Metrohm). A Pt wire was used as the counter electrode and an Ag/AgCl electrode (in 3M KCl) was used as the reference electrode, while the electrolyte was a 10 mM PBS solution (pH 7.4). For the cyclic voltammetry (CV) measurements, the potential was swept from −0.6 V to +0.6 V at a scan rate of 100 mV s⁻¹. The impedance measurements were performed by applying 10 mV sinusoidal perturbations onto a DC potential fixed at 0 V vs an open-circuit potential (VOC) in the range of 0.1 Hz–10 000 Hz. All measurements were performed at room temperature inside a grounded Faraday cage and in air unless stated otherwise. For the data analysis, the frequency cutoff (fcut-off) was defined at the point where the data showed capacitor-like behavior, which we observe to be at 6.3 Hz for PEDOT:PSS, 1.26 Hz for PEDOT:MXene, and 0.5 Hz for PEDOT:PSS:MXene. The capacitance was calculated from the impedance spectra by using the following equation:

\[ C = \frac{1}{2\pi f Z''} \]

where f is the frequency and Z” is the imaginary part of the impedance. The data can be represented as −Z” vs 1/f, where the slope of that line is \( \frac{1}{\text{fcut-off}} \).

Fabrication of microelectrodes

The micrometer-sized electrodes (the circular microelectrode array, MEA, or square shaped electrodes) were fabricated on glass wafers (D 263 T eco, Schott) using photolithography, as described in the literature. Briefly, the first layer of the photoresist (S1813) was deposited and exposed under UV light using a contact aligner to create the electrodes and interconnection pads. The photoresist pattern was generated using a MF-319 developer, followed by metal sputtering of 10 nm of Cr and 100 nm of Au and a lift-off process. The next step involved the deposition of a parylene-C layer as an insulator layer of the gold interconnects. The second layer of photoresist AZ9260 was then spin-coated on the substrates and developed using an AZ developer. The micrometer-sized electrode areas and the contact pads were opened by reactive ion etching (RIE).

Examination of electrode stability

The stability of the electrodes was tested by measuring the magnitude of electrochemical impedance. Electrochemical measurements related with the stability before and after stimulation were
PERFORMED USING THE INTAN RHS SYSTEM. 3D PRINTED POLYLAGID ACID (PLA) RECTANGULAR CHAMBERS MOUNTED ON MEAS WERE FILLED WITH PBS OR GROWTH MEDIA (NEUROBASAL MEDIA). NEUROBASAL MEDIUM (GIBCO) WAS ADDED WITH B27 SUPPLEMENT (GIBCO), 500 μM L-GLUTAMINE (SIGMA), AND 2.5% PENICILLIN/STREPTOMYCIN (GIBCO). DISK-SHAPED GOLD MICROELECTRODES (30 μM IN DIAMETER) FABRICATED ON A 4-IN. GLASS WAVER WERE USED AS THE WORKING ELECTRODE, WITH A REFERENCE BEING ALSO FABRICATED ON THE SAME DEVICE. THE MEA WAS PLACED IN AN INCUBATOR AT 37 °C, 95% HUMIDITY, AND 5% CO2. GROWTH MEDIA AND PBS WERE CHANGED AFTER EACH MEASUREMENT. FOR STIMULATION STABILITY, THE MEAS WERE STIMULATED WITH 10000 PULSES CONSECUTIVELY AT A 100 μA BIPHASIC PULSE WITH A WIDTH OF 100 μS AND AN INTER-PULSE DELAY OF 100 μS USING AN INTAN RHS SYSTEM. THE IMPEDANCE WAS MEASURED AT A SINGLE FREQUENCY (1 KHz) BEFORE AND AFTER ELECTRICAL STIMULATION TO MONITOR THE STABILITY OF THE MATERIAL. THE STATISTICAL SIGNIFICANCE OF THE TWO DATASETS HAD THE SAME DISTRIBUTION COULD NOT BE REJECTED AT THE 5% SIGNIFICANCE LEVEL WITH P = 0.0819. THE TWO DATASETS EACH HAD AN AVERAGE MASS (~43 μG) AND A THICKNESS OF ABOUT 302.89 ± 9.94 NM WERE GENERATED (Fig. S1). FROM THE CHRONOAMPEROMETRY CURVE, WE CALCULATED THE CHARGE CONSUMED DURING THE ELECTROPOLYMERIZATION (Qpol) TO BE AROUND 0.139 C CM–2. PEDOT FILMS SHOWED NO NOTICEABLE DIFFERENCE IN THEIR APPEARANCE EVALUATED BY THE NAKED EYE [FIG. 1(b)]. THE PEDOT:MXENE FILM IS, HOWEVER, THE LEAST HOMOGENEOUS ONE COMPARED TO THE OTHER TWO FILMS THAT CONTAIN PSS WITH A THICKNESS OF 246.24 ± 49.37 NM, AS DEPICTED IN FIB-SEM IMAGES [FIGS. 1(c)–1(e)]. THE TOP VIEW SEM [FIGS. 1(f)–1(h)] AND AFM IMAGES (Fig. S2) REVEALED A ROUGH, WRINKLED SURFACE FOR THE PEDOT:MXENE FILM. PEDOT:PSS:MXENE, ON THE OTHER HAND, HAD A THICKNESS OF 278.17 ± 15.73 NM AND AGGLOMERATES WITH A SIZE OF ~1 μM–5 μM ON ITS SURFACE, WHICH IS SIMILAR TO THE ESTIMATED LATERAL DIMENSIONS OF Ti3C2 MXENE FLAKES (1 μM–6 μM).26 THE topography of the PEDOT:PSS film was quite uniform, in agreement with other studies.27–29 THE PRESENCE OF FLEXIBLE AND SOFT PSS SEEMS TO PROMOTE THE UNIFORMITY OF THE COATINGS.

WHILE MICROSCOPY IMAGES SHOW DIFFERENCES IN THESE FILMS’ SURFACES DUE TO THE PRESENCE OF Ti3C2 MXENE IN THE ELECTROPOLYMERIZATION SOLUTION, THEY DO NOT PROVE THAT Ti3C2 MXENE IS SUCCESSFULLY INCORPORATED IN THE PEDOT NETWORK. WE THEREFORE SAW THE DISTRIBUTION OF Ti3C2 MXENE IN THE FILMS AS WELL AS THE ELEMENTAL STATE AND CHEMICAL BONDING OF THE UPPERMOST SURFACE (3 NM–10 NM IN DEPTH). THE FILM’S SURFACE ANALYSIS IS IMPORTANT AS THIS PART WILL HAVE DIRECT CONTACT WITH BIOLOGICAL SPECIES. WE FIRST ACQUIRED HIGH-RESOLUTION Ti 2p XPS SPECTRA OF PEDOT:MXENE AND PEDOT:PSS:MXENE [FIG. 2(a)]. COMPARED TO THE STANDARD SPECTRA OF THE Ti3C2 MXENE-ONLY FILM, THE Ti SIGNALS OF PEDOT FILMS WERE STRONGER BUT PRESENT. FOR BOTH OF THESE FILMS, THE HIGH-RESOLUTION XPS SPECTRA OF S 2p SHOWED SIGNALS OF PEDOT (162 eV–166 eV) AND, FOR PEDOT:PSS:MXENE, A THIRD PEAK AROUND 169 eV WAS FOUND, WHICH IS ATtributed TO SULFUR ATOMS OF PSS [FIG. 2(b)].27–49 WE ALSO PERFORMED CONTACT ANGLE MEASUREMENTS TO INVESTIGATE THE EFFECT OF Ti3C2 MXENE ON THE WETTABILITY OF THE FILMS. FROM FIG. S3, WE EXTRACTED A LOW WATER CONTACT ANGLE FOR THE PEDOT:PSS FILM (26.0°), WHICH INCREASED FOR PEDOT:PSS:MXENE TO 34.3° AND FURTHER TO 80.2° FOR PEDOT:MXENE. THESE RESULTS SUGGEST THAT PSS IS THE COMPONENT THAT MAKES THE FILMS HYDROPHILIC, AND IT IS PREFERENTIALLY ON THE SURFACE OF PEDOT:PSS AND PEDOT:PSS:MXENE. THE SURFACE OF PEDOT:MXENE IS, ON THE OTHER HAND, PRIMARILY COVERED BY PEDOT, WHICH renders THE FILM HYDROPHOBIC (CONTACT ANGLE = 80.2°). THE PEDOT:PSS:MXENE FILM SURFACE IS MOSTLY POPULATED BY PEDOT AND PSS ALONG WITH A FEW Ti3C2 MXENE FLAKES. THE SPARSELY LOCALIZED STRUCTURES OF PEDOT:PSS:MXENE OBSERVED IN THE SEM IMAGES [FIG. 2(b)] ARE, THEREFORE, ATTRIBUTED TO THE INDIVIDUAL OR AGGLOMERATES OF Ti3C2 MXENE FLAKES SURROUNDED BY A PEDOT SHELL.

Ti signals were weaker in the PEDOT composites compared to the bare MXene, indicating that most of MXenes should be inside the film and covered by the PEDOT:PSS shell in the first 10 nm from the outermost surface. To validate this hypothesis, we employed positive mode SIMS that identifies the positive ion species related to the elements within a film. As shown in Figs. 2(c) and 2(d), we detected Ti⁺ signals across PEDOT:PSS:MXENE and PEDOT:MXENE films, respectively. The Ti⁺ signals exhibited an increase in the first minute of etching, suggesting that the MXene was not dominantly located in the outermost surface and accumulated mostly about 13.9 nm under the surface. The difference between the Ti profiles of

RESULTS AND DISCUSSION

Physicochemical and electrochemical characterization of PEDOT films

We electropolymerized our PEDOT derivatives on Au coated flexible polyimide substrates. We applied a constant potential of 1 V vs Ag/AgCl (corresponding to a stabilized current of 0.17 mA) to initiate the polymerization of three distinct PEDOT films in aqueous media in the presence of PSS (PEDOT:PSS) and Ti3C2 MXENE (PEDOT:MXENE) and in the co-presence of these countercations (PEDOT:PSS:MXENE) [FIG. 1(a)]. The hydrophilic nature of Ti3C2 MXENE allows us to use it along with the EDOT monomer in water. Figure S1 displays typical chronoamperometric curves recorded during the polymerization of PEDOT derivatives, which showed a sharp increase in current at the beginning, characteristic of the oxidation of the monomer and the nucleation stage, followed by a stabilized current indicating of the chain-growth polymerization through the diffusion of dimers and oligomers toward the substrate. During electropolymerization, the applied voltage oxidizes the EDOT monomer into a cation radical, and chain-growth proceeds on the electrode surface. The cation radicals emerge on the chains as protons are removed, and the holes on PEDOT are charge-balanced by the anionic counter ions (PSS and/or Ti3C2 MXENE). After 5-min-long electrodeposition, PEDOT:PSS films with an average mass (~43 μG) and a thickness of about 302.89 ± 9.94 nm were generated (Fig. S1). From the chronoamperogram curve, we calculated the charge consumed during the electropolymerization (Qpol) to be around 0.139 C cm–2. PEDOT films showed no noticeable difference in their appearance evaluated by the naked eye [FIG. 1(b)]. The PEDOT:MXENE film is, however, the least homogeneous one compared to the other two films that contain PSS with a thickness of 246.24 ± 49.37 nm, as depicted in FIB-SEM images [FIGS. 1(c)–1(e)]. The top view SEM [FIGS. 1(f)–1(h)] and AFM images (Fig. S2) revealed a rough, wrinkled surface for the PEDOT:MXENE film. PEDOT:PSS:MXENE, on the other hand, had a thickness of 278.17 ± 15.73 nm and agglomerates with a size of ~1 μM–5 μM on its surface, which is similar to the estimated lateral dimensions of Ti3C2 MXENE flakes (1 μM–6 μM).26 The topography of the PEDOT:PSS film was quite uniform, in agreement with other studies.27–29 The presence of flexible and soft PSS seems to promote the uniformity of the coatings.

While microscopy images show differences in these films’ surfaces due to the presence of Ti3C2 MXENE in the electropolymeryzation solution, they do not prove that Ti3C2 MXENE is successfully incorporated in the PEDOT network. We, however, observed the distribution of Ti3C2 MXENE in the films as well as the elemental state and chemical bonding of the uppermost film surface (3 nm–10 nm in depth). The film’s surface analysis is important as this part will have direct contact with biological species. We, therefore, acquired high-resolution Ti 2p XPS spectra of PEDOT:MXENE and PEDOT:PSS:MXENE [FIG. 2(a)]. Compared to the standard spectra of the Ti3C2 MXENE-only film, the Ti signals of PEDOT films were weak but present. For both of these films, the high-resolution XPS spectra of S 2p showed signals of PEDOT (162 eV–166 eV) and, for PEDOT:PSS:MXENE, a third peak around 169 eV was found, which is attributed to sulfur atoms of PSS [FIG. 2(b)].27–49 We also performed contact angle measurements to investigate the effect of Ti3C2 MXENE on the wettability of the films. From Fig. S3, we extracted a low water contact angle for the PEDOT:PSS film (26.0°), which increased for PEDOT:PSS:MXENE to 34.3° and further to 80.2° for PEDOT:MXENE. These results suggest that PSS is the component that makes the films hydrophilic, and it is present on the surface of PEDOT:PSS and PEDOT:PSS:MXENE. The surface of PEDOT:MXENE is, on the other hand, predominantly covered by PEDOT, which renders the film hydrophobic (contact angle = 80.2°). The PEDOT:PSS:MXENE film surface is mostly populated by PEDOT and PSS along with a few Ti3C2 MXENE flakes. The sparsely localized structures of PEDOT:PSS:MXENE observed in the SEM images [FIG. 2(b)] are, therefore, attributed to the individual or agglomerates of Ti3C2 MXENE flakes surrounded by a PEDOT shell.

Ti signals were weaker in the PEDOT composites compared to the bare MXene, indicating that most of MXenes should be inside the film and covered by the PEDOT:PSS shell in the first 10 nm from the outermost surface. To validate this hypothesis, we employed positive mode SIMS that identifies the positive ion species related to the elements within a film. As shown in Figs. 2(c) and 2(d), we detected Ti⁺ signals across PEDOT:PSS:MXENE and PEDOT:MXENE films, respectively. The Ti⁺ signals exhibited an increase in the first minute of etching, suggesting that the MXene was not dominantly located in the outermost surface and accumulated mostly about 13.9 nm under the surface. The difference between the Ti profiles of
FIG. 1. (a) Chemical structure of the electropolymerized polymers. For simplicity, PEDOT is drawn in its neutral state, and counterions of the dopants are not shown. (b) Optical images of PEDOT:PSS (1), PEDOT:MXene (2), and PEDOT:PSS:MXene (3) films coated on flexible Au/Kapton substrates. FIB:SEM [(c)–(e)] and top view SEM [(f)–(h)] images of PEDOT:PSS, PEDOT:MXene, and PEDOT:PSS:MXene, from left to right. The Pt coatings in FIB:SEM experiments were deposited as protective layers. The scale bar is 400 nm for (c)–(e) and 3 μm for (f)–(h).

the two films is that for PEDOT:PSS:MXene, Ti₃C₂ MXene seems to be more homogeneously distributed throughout the film as its content decreased less monotonically toward the substrate. Moreover, for PEDOT:PSS:MXene, the relative concentration of S⁺ ions (stemming from PEDOT and PSS) was similar from top to bottom. This characterization proves that Ti₃C₂ MXene blends very well with PEDOT, instead of agglomerating only at the surface or at the bottom.

Verifying that Ti₃C₂ MXene is well distributed inside the PEDOT-rich network, we next investigated the impact of Ti₃C₂ MXene on the electrochemical properties of PEDOT. Figures 3(a) and 3(b) show the cyclic voltammetry (CV) curves and electrochemical impedance spectra of the three PEDOT derivatives, respectively. The CV curves were obtained in the range of −0.6 to 0.6 vs Ag/AgCl within the water window to avoid interference from electrolysis reactions. The volumetric capacitance was calculated according to the following equation:

\[ C = \frac{\int I(dV)}{\nu \Delta V A}, \]

where \( I \) is the current (A), \( \nu \) is the scan rate (V s⁻¹), \( \Delta V \) is the potential window (V), and \( A \) is the volume of the composite (cm³). Analyzing the square-shaped CV curves and the thickness of each PEDOT composite (N = 3), we found that the PEDOT:PSS:MXene films exhibited the highest volumetric capacitance (607 ± 85.3 F cm⁻³). The electrochemical capacitances of PEDOT:MXene and PEDOT:PSS were calculated to be 358.9 ± 16.7 F cm⁻³ and 195.6 ± 1 F cm⁻³, respectively. These values outperform other PEDOT films reported in the literature, such as organic framework-incorporated PEDOT and acid-treated PEDOT films.⁵⁴–⁵⁷ Figure 3(b) shows that both PEDOT:MXene and PEDOT:PSS:MXene films have a lower electrochemical impedance magnitude below ~10 Hz than PEDOT:PSS. Note that all three electrodes used in these experiments had the same dimensions. Analysis of the spectra revealed that all films exhibited capacitor behavior, which can be seen more clearly in the Nyquist plots exhibiting a nearly vertical line (Fig. S4a). At low frequencies (below \( \nu_{\text{cutoff}} \)), the data can be approximated with a simple RC (resistor in series with a capacitor) circuit where the capacitance represents the double layer capacitance (Fig. S4b). In agreement with CV results, we found that the PEDOT composites with Ti₃C₂ MXene had higher double layer capacitance compared to PEDOT:PSS (Fig. S4c; see the section titled Experimental Section for the details of analysis).

Next, to find out the doping (oxidation) level of PEDOT in the films and whether Ti₃C₂ MXene fulfilled its role of a countercion, we recorded Raman spectra. The Raman spectra in the range
FIG. 2 Chemical characterization of the PEDOT films. (a) High-resolution Ti 2p XPS spectra of PEDOT:MXene and PEDOT:PSS:MXene along with that of the Ti$_3$C$_2$ MXene only film (drop cast) in the inset. (b) High-resolution S 2p XPS spectra of PEDOT:MXene, PEDOT:PSS:MXene, and the Ti$_3$C$_2$ MXene film. SIMS spectra of (c) PEDOT:PSS:MXene and (d) PEDOT:MXene. Ti$^+$ signal stems from Ti$_3$C$_2$ MXene, while S$^+$ is attributed to the sulfur atoms in the thiophene ring of PEDOT. O$^+$ and C$^+$ signals stem from both PEDOT and Ti$_3$C$_2$ MXene.

of 1100 cm$^{-1}$–1700 cm$^{-1}$ mainly contain the vibrational modes of carbon atoms (C$\alpha$ and C$\beta$) on the thiophene ring of PEDOT [Fig. 3(c)]. The peaks in the range of 1500 cm$^{-1}$ to 1570 cm$^{-1}$ are related to the asymmetrical stretching of C$\alpha$ = C$\beta$, while those between 1420 cm$^{-1}$ and 1445 cm$^{-1}$ refer to the symmetrical stretching of C$\alpha$ = C$\beta$. C$\alpha$–C$\alpha$ inter-ring stretching and C$\beta$–C$\beta$ stretching appear at $\sim$1251 cm$^{-1}$–1267 cm$^{-1}$ and 1360 cm$^{-1}$–1368 cm$^{-1}$, respectively [Fig. 3(d)]. From the deconvoluted Raman spectra, we extracted the ratio of oxidized to neutral chains (O:N ratio) by calculating the contribution of peaks associated with the oxidized thiophene (at 1444 cm$^{-1}$) and with the neutral thiophene (at 1425 cm$^{-1}$) located in the region of C$\alpha$ = C$\beta$ symmetric stretching [Fig. 3(e)]. For a full summary of the Raman peak assignments and their relative contributions, see Table S1. The Raman results suggest that Ti$_3$C$_2$ MXene alone (in the absence of PSS) is able to dope PEDOT. The coupling is thought to occur between PEDOT holes and the negatively charged groups of Ti$_3$C$_2$ MXene [recall Fig. 1(a)]. Second, while Ti$_3$C$_2$ MXene is an effective counter ion for PEDOT, PSS enables more PEDOT units to be oxidized. We found that the PEDOT:PSS:MXene film has the highest O:N ratio of 1.56, suggesting that the best doping level has been achieved by using the double dopants. With an O:N of 0.62, PEDOT:MXene is less oxidized than PEDOT:PSS (O:N = 0.92). The higher doping efficiency of films comprising PSS can be explained by the flexibility of PSS and the higher amount of negative charge that the backbone bears compared to the MXene. On the other hand, MXene increases the overall electrochemical capacitance of the film. Despite the lower oxidation of PEDOT in PEDOT:MXene compared to PEDOT:PSS, the capacitance of the former is higher. Hence, MXene not only charge compensates PEDOT but it is also electrochemically active, in agreement with the EIS and CV results. These results justify the use of Ti$_3$C$_2$ MXene as a conducting dopant along with PSS.

Electrochemical stability and mechanical durability of PEDOT:PSS:MXene

An important property for any electronic film developed for use at the interface with electrolytes is their electrochemical stability during device operation and ability to retain their mechanical integrity. We first examined the electrochemical durability of the films subjected to 500 CV cycles at a scan rate of 100 mV s$^{-1}$ in 1 x PBS. Figure 4 shows the selected CV cycles (i.e., 1st, 50th, 100th, 200th, 300th, 400th, and 500th) of each PEDOT film and the capacitance retention measured at the end of cycles. We found that PEDOT:PSS:MXene exhibited the highest capacitance retention, $\sim$78% after 500 CV cycles, while the PEDOT:PSS film lost nearly half of its charging ability upon continuous cycling (retention is 37% at 500 CV cycles). Previous reports observed a similar instability behavior for PEDOT:PSS. The electrochemical instability was attributed to the fact that PSS swells in water, and even more during continuous uptake and release of electrolyte ions, which leads to its dissolution and de-coupling from PEDOT. Ti$_3$C$_2$ MXene, therefore, not only increases the charge
FIG. 3. The electrochemical characteristics and chemical analysis of the PEDOT films. (a) The CV curves of the PEDOT films obtained at a scan rate of 0.1 V s\(^{-1}\) over a potential window of −0.6 V to 0.6 V vs Ag/AgCl in 1X PBS at 25° C. (b) The magnitude and phase of the impedance of the PEDOT films. The electrochemical impedance spectroscopy (EIS) measurements were performed at the open-circuit potential (\(V_{oc}\)) vs Ag/AgCl. (c) The chemical structure of PEDOT showing α and β carbon atoms in the thiophene ring. (d) Raman spectra of PEDOT:PSS with the deconvoluted peaks showing the assigned vibrations. (e) Zoomed-in view of Raman spectra of PEDOT:PSS, PEDOT:MXene, and PEDOT:PSS:MXene to show the peaks at 1425 cm\(^{-1}\) and 1444 cm\(^{-1}\) representing vibrations of the neutral and the charged PEDOT chains, respectively.

FIG. 4. Electrochemical stability and capacitance retention of [(a) and (d)] PEDOT:PSS, [(b) and (e)] PEDOT:MXene, and [(c) and (f)] PEDOT:PSS:MXene upon 500 CV cycles. The CV curves were recorded at a scan rate of 100 mV s\(^{-1}\) in 1X PBS. Error bars are obtained from three different films (N = 3).
storage capability of the PEDOT film but also improves its electrochemical stability. Importantly, the Ti$_3$C$_2$ MXene film alone (drop-cast, in the absence of PEDOT) degraded under these conditions only after 25 cycles (Fig. S5). Such degradation was observed by other researchers and attributed to the electrochemical oxidation of Ti.

Next, we evaluated the mechanical stability of the best performer, PEDOT:PSS:MXene. An ultrasonication test was used to monitor the adhesion strength of the film to the Au substrate. The polymer electrodes were immersed into a vial filled with DI water and sonicated in the ultrasonic chamber. Figures 5(a) and 5(b) display the optical images of these PEDOT:PSS and PEDOT:PSS:MXene films, respectively, electropolymerized on micrometer scale Au electrode patterns (500 × 500 μm$^2$). As sonication started, the PEDOT:PSS film disintegrated gradually, and ~80% of the initial coating was lost after 6 min as it fragmented into small flakes. PEDOT:PSS:MXene, on the other hand, remained intact during the sonication. The excellent adhesion of PEDOT:PSS:MXene on Au is independent of the size of the electrode geometry or the underlying substrate used, which is proven by the similar results that we obtained with millimeter scale flexible Au coated polymide substrates (Fig. S6). These results suggest that besides improving the overall film capacitance and its stability against successive cycles, Ti$_3$C$_2$ MXene promotes film’s mechanical integrity. The strong adherence of the PEDOT:PSS:MXene film to the substrate also led to stable electrical performance, which is eminent from the impedance profile of the films coated on microelectrodes with a diameter of 30 μm [Fig. 5(c)]. Over two weeks of incubation in cell media or PBS at 37 °C, the electrodes showed no change in their impedance magnitudes [Fig. 5(d)]. Furthermore, passing a biphasic current at 100 μA over 10 000 cycles (higher than standard stimulation conditions) caused no statistically significant change in the impedance characteristics of the electrodes, monitored over 44 samples [Fig. 5(e)].

![Image](https://example.com/image.png)

**FIG. 5.** Adherence and impedance stability tests. Optical microscope images of (a) PEDOT:PSS and (b) PEDOT:PSS:MXene microelectrodes (500 × 500 μm$^2$). From left to right: upon 0 min, 3 min, and 6 min of ultrasonication. The scale bar is 100 μm. (c) An optical image of the electrodeposited PEDOT:PSS:MXene films on the microelectrode arrays. The device also contains bare gold electrodes without polymer coating (bottom). The electrode size is 30 μm in diameter. The scale bar is 100 μm. (d) The impedance magnitude of micro electrodes obtained in PBS and cell media. The impedance was recorded at 1 kHz as the electrode arrays were exposed to the media in an incubator (37 °C) for two weeks (n = 13). (e) Impedance magnitudes of PEDOT:PSS:MXene electrodes recorded in cell media before and after 10 000 cycles of biphasic current stimulation at 100 μA (n = 44).
PEDOT:PSS:MXene for electrochemical detection of dopamine

Dopamine (DA) is a neurotransmitter that plays an essential role in central nervous and cardiovascular systems and metabolism. Abnormal levels of DA in plasma of cerebrospinal fluid and blood have been used as a biomarker for neurodegenerative diseases such as Parkinson’s and Alzheimer’s. Dopamine is an electroactive molecule, which means that certain electronic materials can catalyze it upon application of an appropriate voltage. The most frequently used electronic materials in electrochemical sensing of DA are noble metals such as gold and platinum, which are expensive and scarce. Conducting polymers blended with nanomaterials such as carbon nanotubes and graphene oxide have been proposed as alternative materials with high sensitivity toward DA. While the detection of DA with electrochemical techniques has been rather straightforward, the interference from other electroactive molecules present in biological media, such as uric acid (UA) and ascorbic acid (AA), typically overshadows the electrochemical peak of DA, reducing the specificity of such sensors. A convenient method that offers enhanced Faradaic current resolution is differential pulse voltammetry (DPV), which minimizes capacitive current contributions.

Figures 6(a) and 6(b) show the Faradaic currents that PEDOT:PSS and PEDOT:PSS:MXene films generate upon the oxidation of DA added to the electrolyte at various concentrations. Both films experienced an increase in their peak currents, observed at ~0.2 V vs Ag/AgCl. On the contrary, the Ti3C2 MXene film, drop-casted on top of an identical substrate, showed no particular peak in the potential window of 0 V–0.4 V when exposed to DA [Fig. 6(c)]. Therefore, we conclude that DA detection is governed by PEDOT. Importantly, Fig. 6(d) shows that the PEDOT:PSS:MXene electrode has superior sensitivity (143.9 µA mM⁻¹) toward DA compared to the standard PEDOT:PSS (69.5 µA mM⁻¹) and the bare gold electrode (see also Fig. S7a). The DA detection sensitivity of PEDOT:PSS:MXene is among the highest compared to other conducting polymer/nanomaterial based composite electrodes (Table S2).

Next, we recorded the response of PEDOT:PSS:MXene and PEDOT:PSS electrodes to various concentrations of uric acid (UA) and ascorbic acid (AA) at their physiologically relevant concentrations (Fig. S8). Both electrodes were sensitive to these species, yet the calibration plots in Fig. 6(d) evidence the distinct response of PEDOT:PSS:MXene toward DA. The enhanced response of PEDOT:PSS:MXene toward positively charged DA compared to PEDOT:PSS may be due to the presence of negatively charged Ti3C2 MXene in the film. Such an improvement was also observed in other electrochemical sensors that contain negatively charged nanomaterials. Finally, we examined the performance of PEDOT:PSS:MXene in detecting DA in a solution that contains AA and UA. To mimic a complex in vivo environment, we prepared solutions containing 400 μM of AA and 400 μM of UA and then varied the concentration of DA therein. Figures 6(e) and 6(f) show the response of the electrodes to increasing levels of DA in...
these mixtures. The sensitivity of PEDOT:PSS:MXene to DA was not affected by the species in the background, while PEDOT:PSS had a hindered response. In such complex media, the superiority of PEDOT:PSS:MXene becomes more evident: the film displays a higher sensitivity and selectivity compared to PEDOT:PSS, with performance identical to the buffer where we spiked only DA (see Figs. S7b and S7c for calibration curves). Combined with the excellent electrochemical and mechanical stability of the electrodes, these results reveal the potential of PEDOT:PSS:MXene for the development of implantable electrochemical DA sensors.

CONCLUSION

In this work, we electropolymerized a PEDOT composite with Ti₃C₂ MXene. The use of double dopants, i.e., Ti₃C₂ MXene and PSS, improved the electrochemical properties and stability of PEDOT films and led to strong adherence to the Au substrate. The PEDOT:PSS:MXene film had a high volumetric capacitance (607.0 ± 85.3 F cm⁻³) and remarkable electrochemical and mechanical stability (i.e., ca. 78% capacitance retention upon 500 CV cycles, no delamination upon sonication, and no change in impedance upon immersion in cell media for 14 days and electrical stimulation for 10,000 times). We confirmed the successful incorporation of the Ti₃C₂ MXene within the PEDOT films by XPS and SIMS measurements and verified its ability to act as a counterion by Raman spectroscopy. The PEDOT:PSS:MXene electrode surpassed the performance of the standard PEDOT:PSS as a DA sensor by detecting a few tens of μM of DA in aqueous solutions comprising hundreds of μMs of UA and AA, two common electro-oxidizable interferents in biological media. With its high capacitance, adherence, and durability, we suggest the PEDOT:PSS:MXene film to be a promising electrode material for chronic and implantable bioelectronics.

SUPPLEMENTARY MATERIAL

The electropolymerization profile, AFM analysis, wettability study, EIS analysis, adherence test, and DPV curves of the electrochemical sensors are provided in the supplementary material.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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