Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Electronic Supplementary Information

Layer-by-layer assembly of polycation/$Ti_3C_2T_x$ thin films for use as resistive pH sensors

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S1. Experimental Methods

S1.1 Ti_3AlC_2 MAX Phase Synthesis

Commercial Ti, Al, and TiC powders were combined in a Ti:Al:C = 3:1.2:1.8 ratio. The mixed powders were then ball milled with zirconia beads at 300 rpm for 24 hours in a glass jar and subsequently sintered at 1510 ^oC with a 50 MPa loading for 15 minutes using Pulsed Electric Current System (PECS). The resulting powder was then drill milled and sieved to obtain high purity powder between 20 and 45-micron particle size.

S1.2 $Ti_3C_2T_x$ Clay Synthesis

$Ti_3C_2T_x$ clay was synthesized by selectively etching Al from Ti_3AlC_2. Stock HCl was diluted to 6 M and placed in a polypropylene beaker. LiF was then added and the solution was continuously stirred at room temperature for 5 minutes using a Teflon magnetic stirrer. Ti_3AlC_2 powder was slowly added to the solution and allowed to stir for 45 hours at 40 ^oC. The product was then washed with deionized (DI) water until the pH of the solution reached 6.

S1.3 $Ti_3C_2T_x$ Nanosheet Synthesis

The obtained $Ti_3C_2T_x$ clay was dispersed in 16.67 mL of DMSO per gram of starting MAX phase and subsequently stirred for 20 hours at room temperature. DMSO was then removed by solvent exchange. The intercalated clay was washed with DI water and centrifuged for 4 hours at 5000 rpm. The washed clay was bath sonicated at room temperature for an hour and then centrifuged again at 3500 rpm for an hour. The obtained supernatant contained the $Ti_3C_2T_x$ nanosheets and concentration was determined by vacuum filtration of a known volume of dispersion. NaAsc dissolved in water was then added to the dispersion to obtain a final concentration of 0.5 mg/mL of $Ti_3C_2T_x$ and 1 mg/mL of NaAsc.

S1.4 Graphene Oxide Synthesis

GO was synthesized following Modified Hummers' Method. 3 g of graphite powder and 2.5 g of $NaNO_3$ were added to 120 mL of stock H_2SO_4 and stirred for 5 hours in an ice bath. Afterwards, 15 g of $KMnO_4$ was slowly added to the stirring mixture. 800 mL of cold ultrapure water and 20 mL of H_2O_2 were then added, and the mixture was subsequently washed with 5 wt% HCl and filtered. The mixture was then dispersed in ultrapure water and dialyzed against ultrapure water until the pH of the mixture reached that of the water. The obtained powder was dried at 60 ^oC and redispersed in water to obtain a 0.5 mg/mL solution of GO.

S1.5 X-ray photoelectron spectroscopy

Samples for XPS were prepared by freeze drying in the case of the $Ti_3C_2T_x$ dispersion and used as prepared for the sensors. All samples were dried under vacuum prior to testing.

Ti 2p, C 1s, O 1s, and F 1s spectra were deconvoluted follow previous procedure.[1] CasaXPS software was used for component peak fitting. A Shirley type background function was used to determine background contribution. Spectra for all components were calibrated based on the adventitious carbon peak (C-C, 284.8 eV). Three major constraints were applied for fitting. First, the components of Ti 2p ($2p_{3/2}$ and $2p_{1/2}$) were constrained to an area ratio of 2:1 $2p_{3/2}$:$2p_{1/2}$. Secondly, full width half maximum (FWHM) values were constrained. Lastly, all binding energies (eV) were verified with previous literature results.[1, 2]

Due to the low atomic percentages for nitrogen and chlorine, the Cl 2p and N 1s spectra were not deconvoluted. Ti 2p was separated into 5 component pairs for $2p_{3/2}$ and $2p_{1/2}$: Ti-C, Ti^{2+}, Ti^{3+}, TiO_2, and TiF_x. C 1s was separated into C-Ti-T_x[a], C-Ti-T_x[b], C-C, CH_x/CO, C-OH, and COO. The C-Ti-T_x bond is asymmetric and was fit by splitting into two symmetric peaks. O 1s was separated into TiO_2, C-Ti-O_x, C-Ti-$(OH)_x$, Al_2O_3, and H_2O. F 1s was separated into C-Ti-F_x and AlF_x.

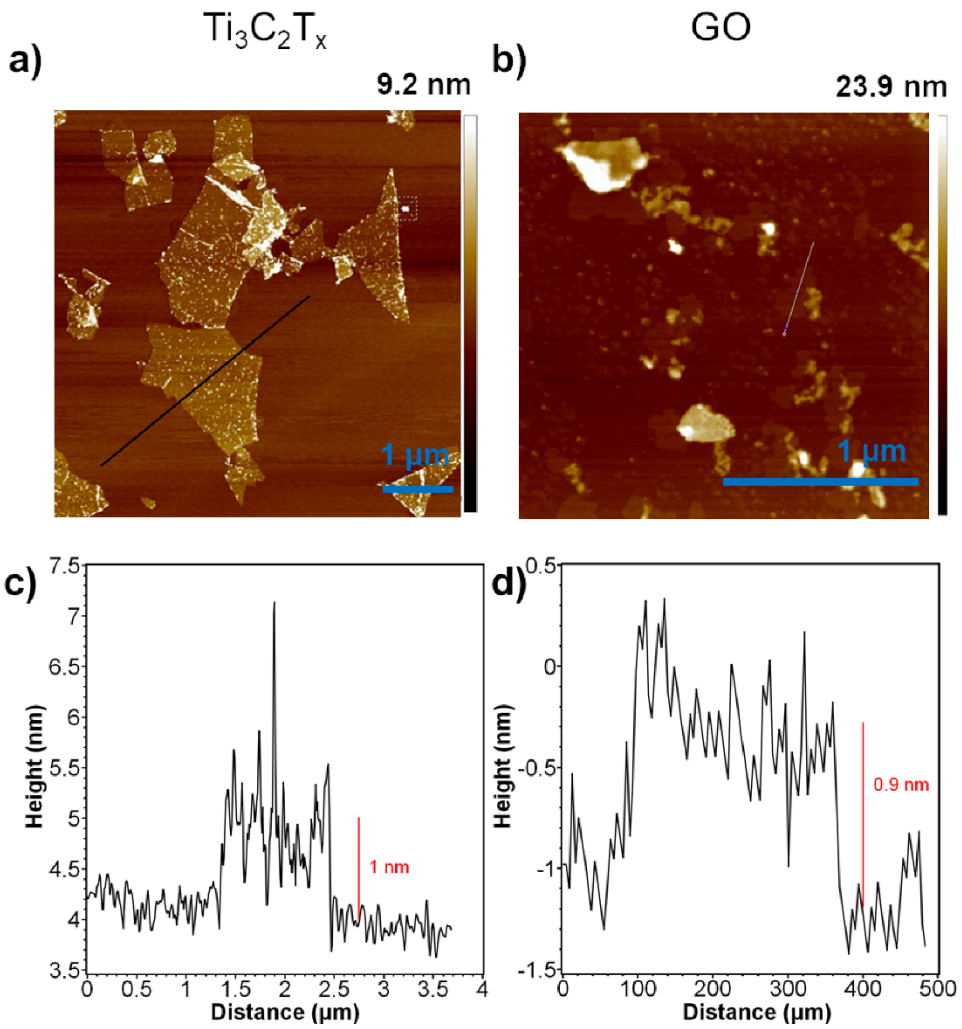

Figure S1 AFM topographical scan of drop-cast (a) $Ti_3C_2T_x$ and (b) GO on mica. Height profile of survey scan for (c) $Ti_3C_2T_x$ and (d) GO.

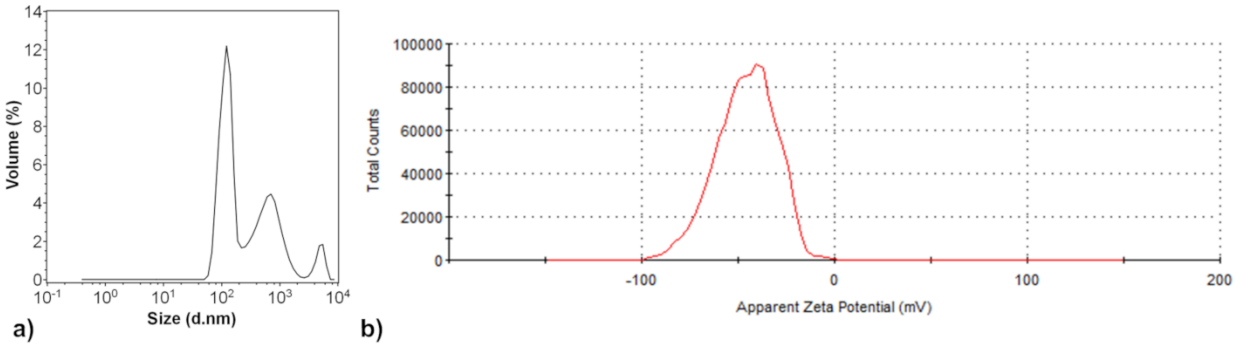

Figure S2 (a) Size distribution from DLS and (b) zeta potential distribution of $Ti_3C_2T_x$. Average size of 304 nm and zeta potential of -46.1 mV.

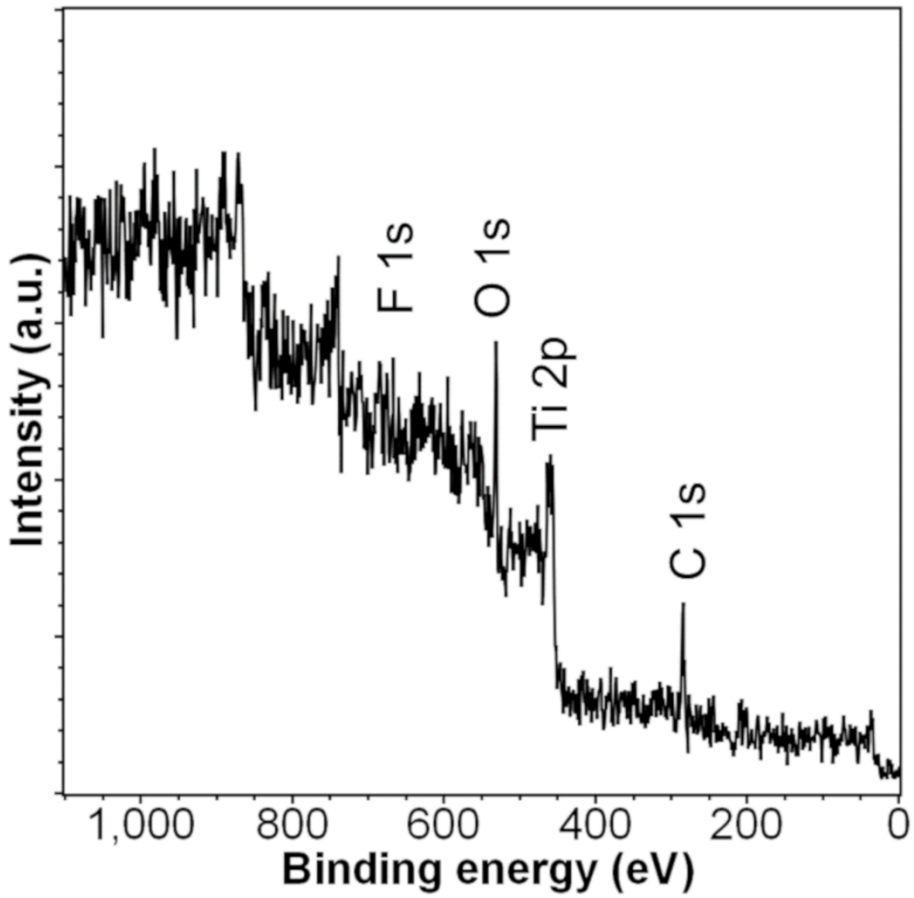

Figure S3 XPS Survey scan of freeze-dried $Ti_3C_2T_x$ powder.

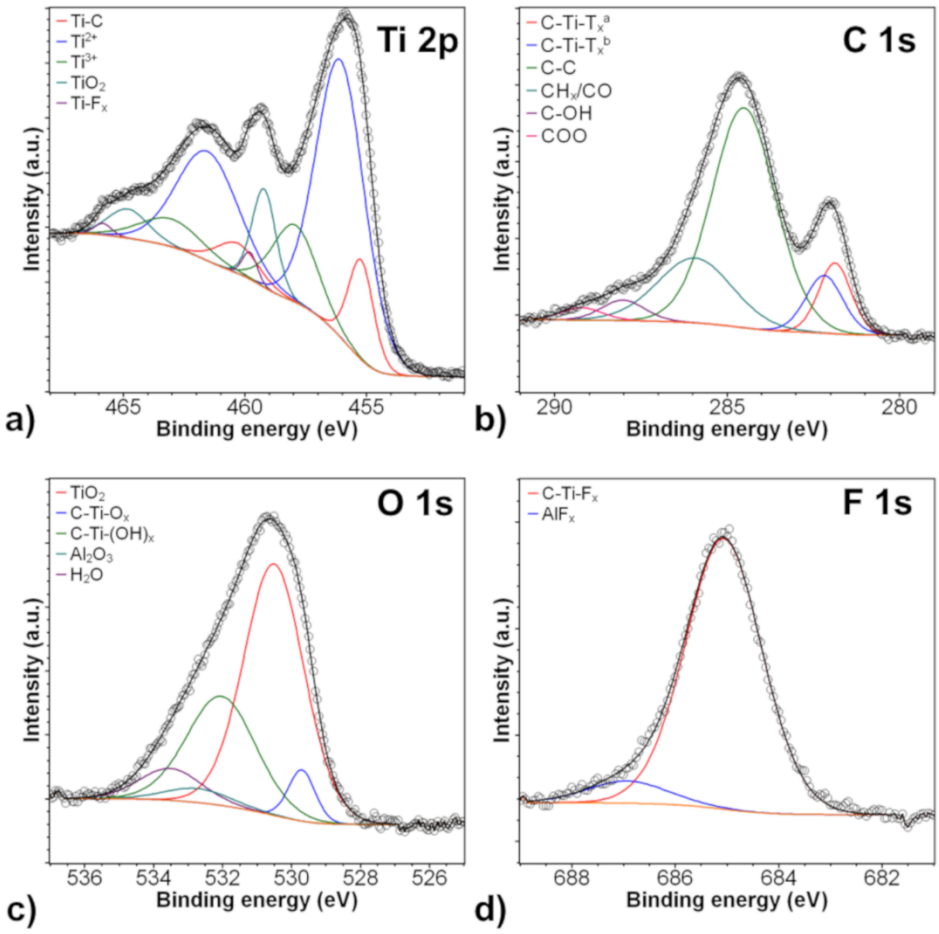

Figure S4 Component peak fittings of freeze-dried $Ti_3C_2T_x$ powder for (a) Ti 2p, (b) C 1s, (c) O 1s, and (d) F 1s.

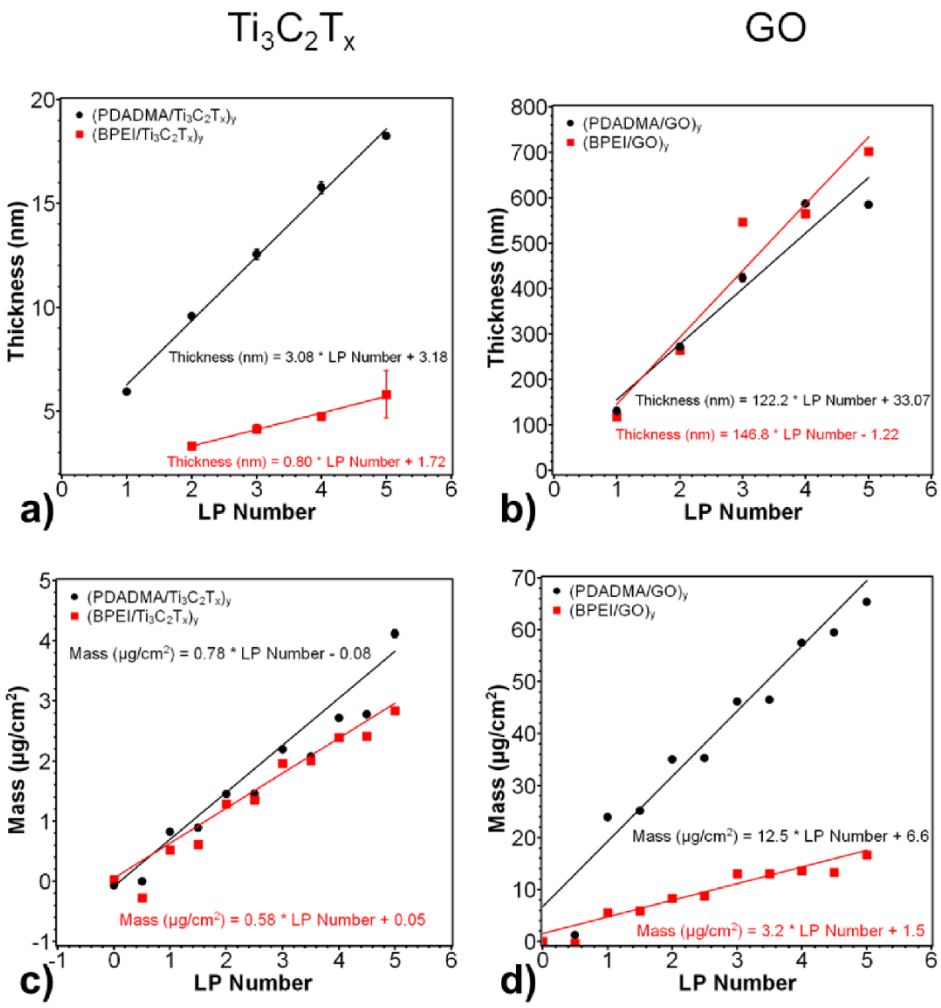

Figure S5 Thickness of (a) $Ti_3C_2T_x$ and (b) GO multilayers measured using ellipsometry. Areal mass of (c) $Ti_3C_2T_x$ and (d) GO multilayers measured using QCM.

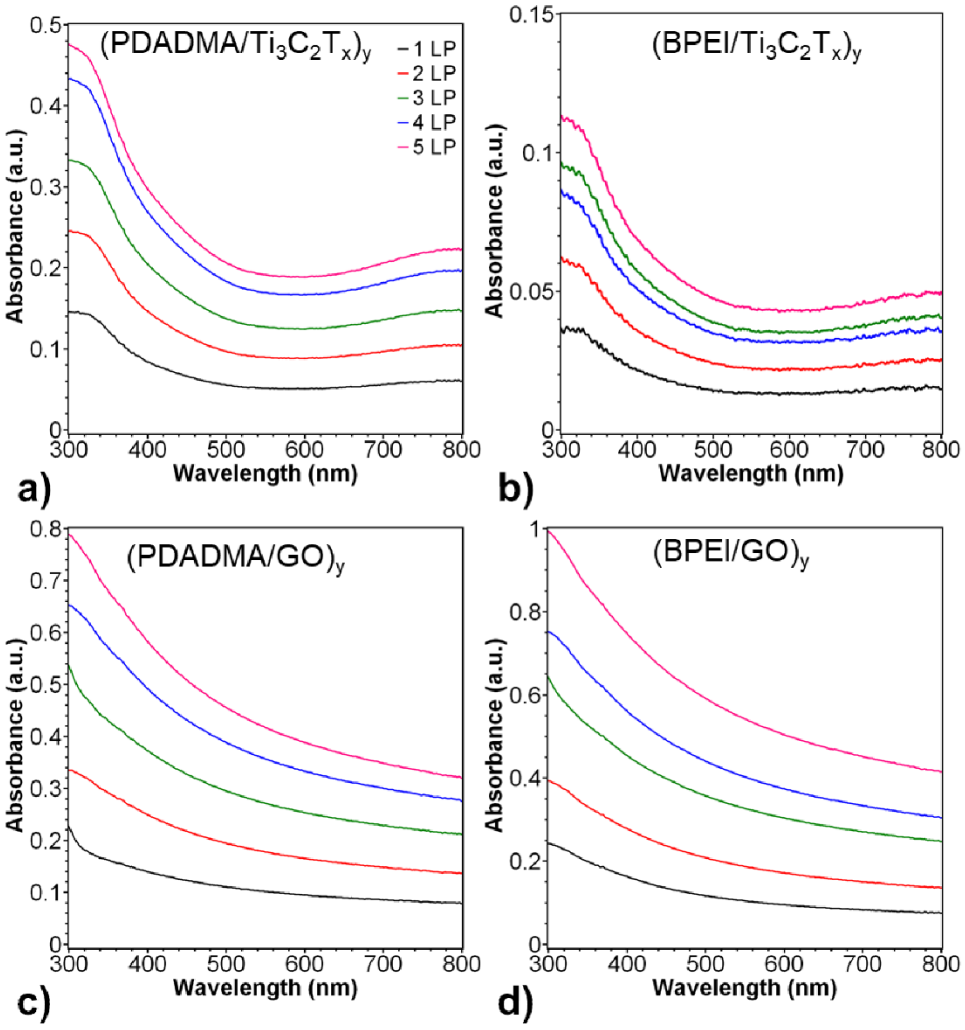

Figure S6 UV-VIS spectra for (a) $(PDADMA/Ti_3C_2T_x)_y$, (b) $(BPEI/Ti_3C_2T_x)_y$, (c) $(PDADMA/GO)_y$, and (d) $(BPEI/GO)_y$. The legend in (a) applies to all panels.

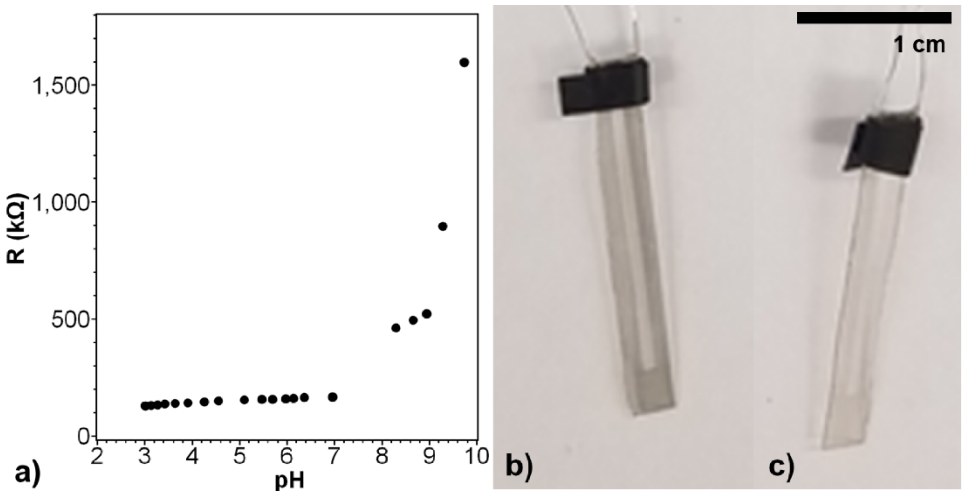

Figure S7 (a) pH Response of (BPEI/$Ti_3C_2T_x$)$_5$ film over extended pH range. Digital image of sensor (b) before and (c) after exposure to basic environment.

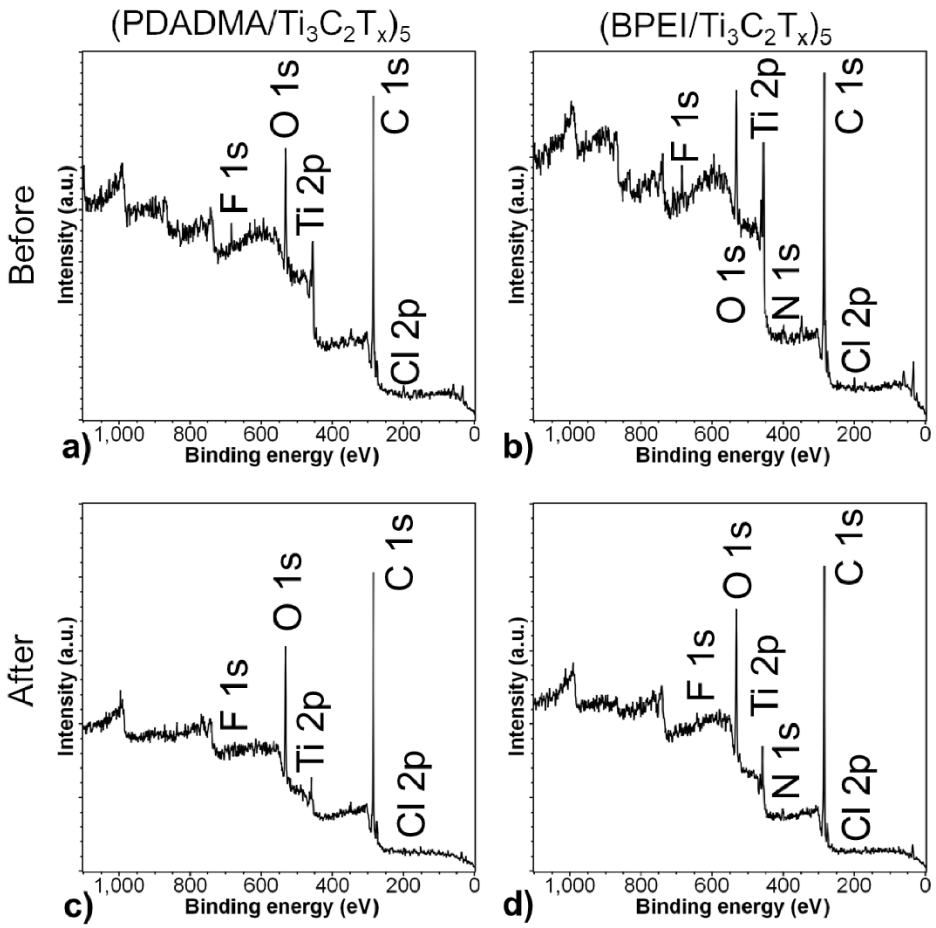

Figure S8 XPS survey scan of $(PDADMA/Ti_3C_2T_x)_5$ films (a) before and (b) after pH response tests and $(BPEI/Ti_3C_2T_x)_5$ films (c) before and (d) after pH response tests.

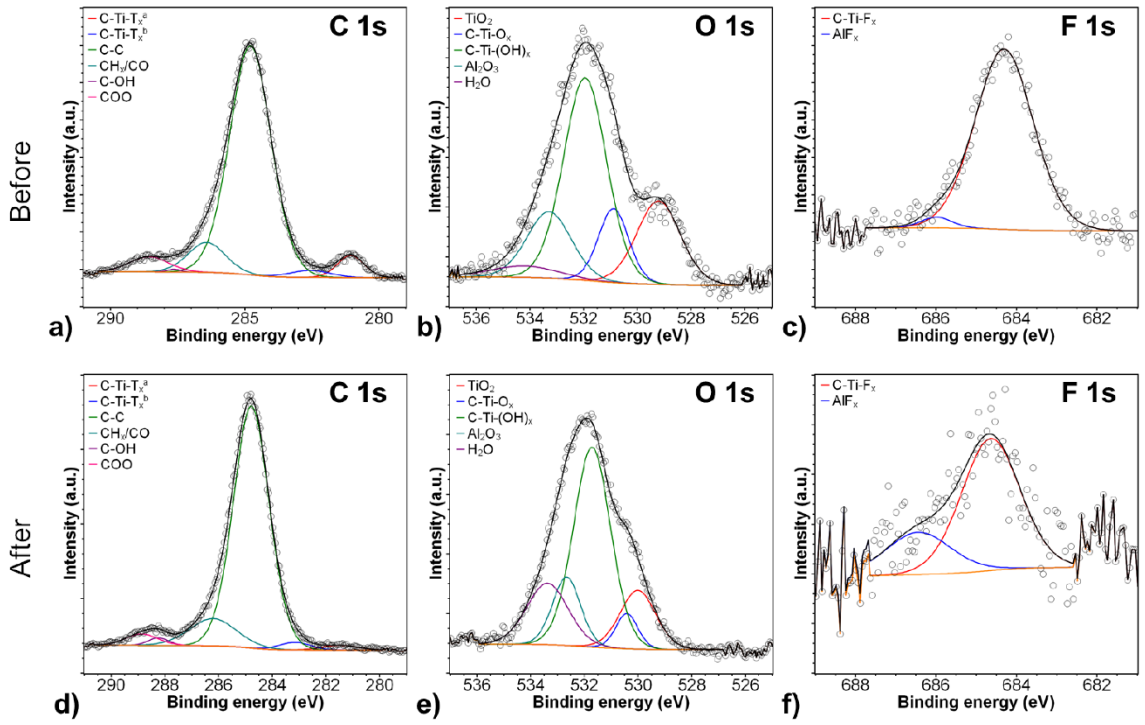

Figure S9 Deconvoluted XPS of $(PDADMA/Ti_3C_2T_x)_5$ films for (a) C 1s, (b) O 1s, (c) F 1s before and (d) C 1s, (e) O 1s, (f) F 1s after pH response tests.

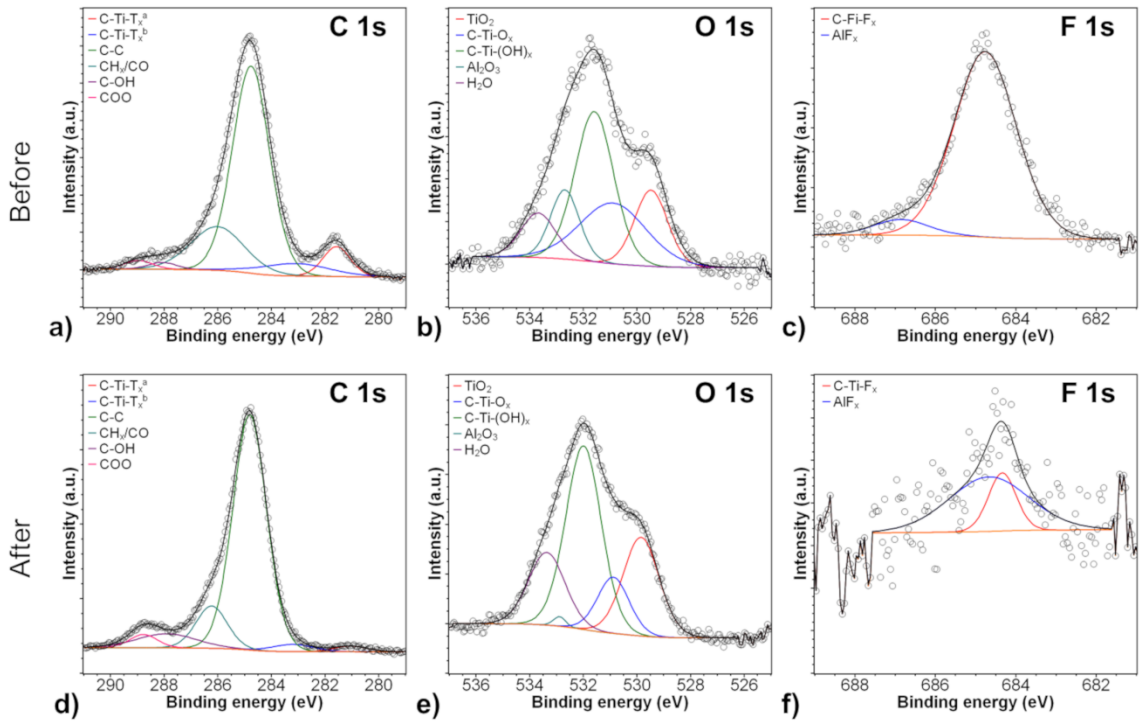

Figure S10 Deconvoluted XPS of $(BPEI/Ti_3C_2T_x)_5$ films for (a) C 1s, (b) O 1s, (c) F 1s before and (d) C 1s, (e) O 1s, (f) F 1s after pH response tests.

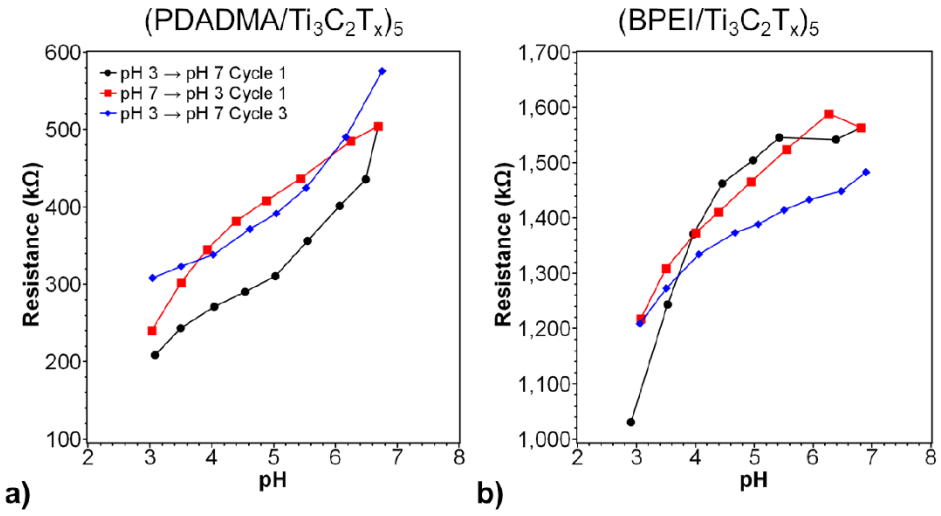

Figure S11 pH Response of (a) (PDADMA/$Ti_3C_2T_x$)$_5$ and (b) (BPEI/$Ti_3C_2T_x$)$_5$ films. pH sensitivity of 72 kΩ/pH and 68 kΩ/pH for cycles 1 and 3, respectively, for (a). pH sensitivity of 120 kΩ/pH and 65 kΩ/pH for cycles 1 and 3, respectively, for (b). *$Ti_3C_2T_x$ was not treated with NaAsc for these tests.*

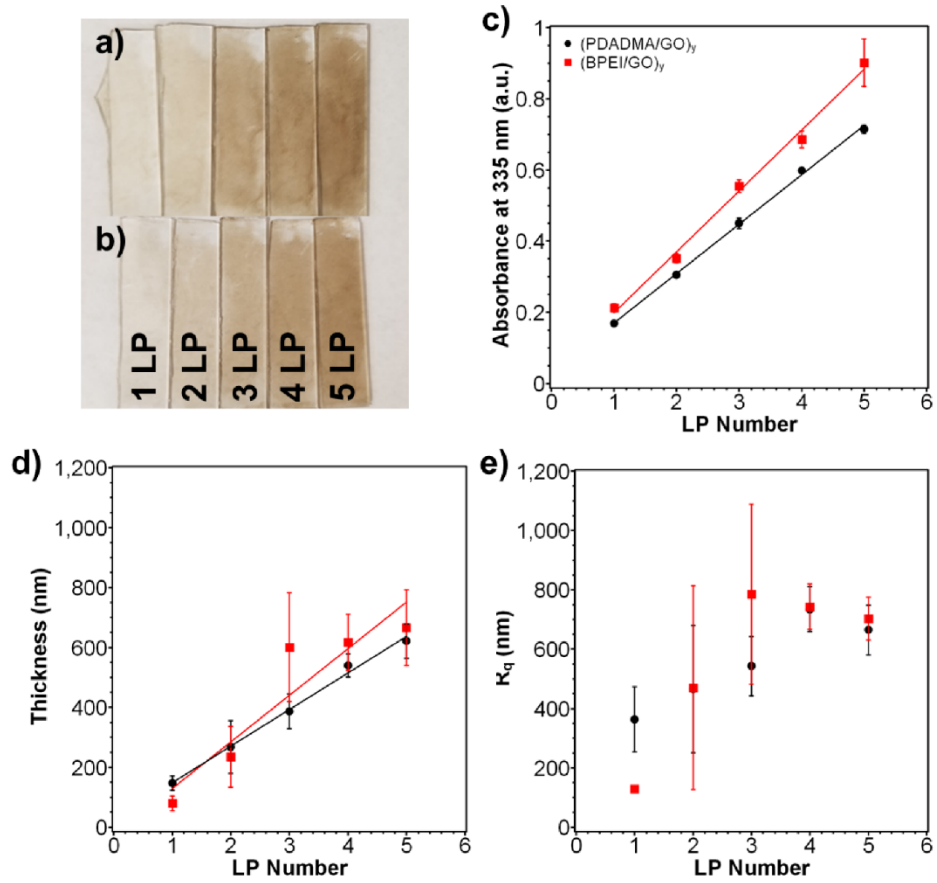

Figure S12 Digital images of (a) $(PDADMA/GO)_y$ and (b) $(BPEI/GO)_y$ films. (c) Absorbance at 335 nm, (d) thickness, and (e) roughness of GO multilayers. Absorbance at 335 nm grows as 0.14 a.u./LP and 0.17 a.u./LP for $(PDADMA/GO)_y$ and $(BPEI/GO)_y$, respectively. Thickness grows as 122 nm/LP and 155 nm/LP for $(PDADMA/GO)_y$ and $(BPEI/GO)_y$ films, respectively.

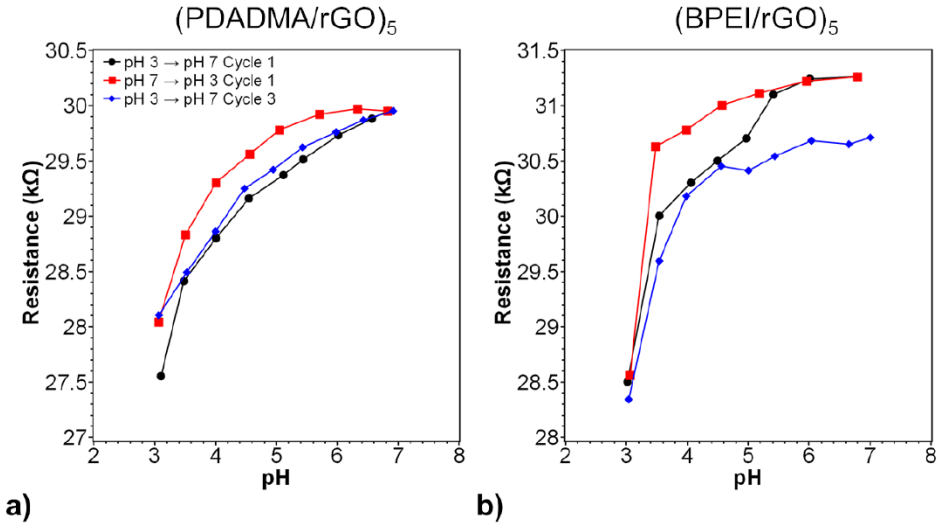

Figure S13 pH Response of (a) $(PDADMA/rGO)_5$ and (b) $(BPEI/rGO)_5$ films. pH sensitivity of 0.6 kΩ/pH and 0.5 kΩ/pH for cycles 1 and 3, respectively, for (a). pH sensitivity of 0.6 kΩ/pH and 0.5 kΩ/pH for cycles 1 and 3, respectively, for (b).

Table S1 XPS peak fitting results for $Ti_3C_2T_x$.[a]

Element	Element at%	Binding energy (eV)	Component name	Component AT%	FWHM
Ti $2p_{3/2}$ ($2p_{1/2}$)	17.7	455.2 (460.3)[a]	Ti-C	11.3	1.2 (2.0)
		456.1 (461.5)	Ti^{2+}	60.8	2.3 (3.0)
		457.9 (463.0)	Ti^{3+}	15.5	2.2 (3.0)
		459.2 (464.8)	TiO_2	10.6	1.2 (2.0)
		459.8 (465.8)	Ti-F_x	1.8	0.7 (0.8)
C 1s	54.2	281.9	C-Ti-T_x	9.3	1.1
		282.2	C-Ti-T_x	8.7	1.3
		284.5	C-C	56.7	2.2
		285.9	CH_x/CO	19.7	2.6
		288.0	C-OH	3.6	1.5
		289.2	COO	2.1	1.4
O 1s	22.9	529.7	TiO_2	5.1	0.9
		530.5	C-Ti-O_x	56.4	2.1
		532.0	C-Ti-$(OH)_x$	27.8	2.4
		532.7	Al_2O_3	3.4	2.2
		533.5	H_2O	7.3	2.1
F 1s	5.2	685.1	C-Ti-F_x	92.1	1.7
		686.9	AlF_x	7.9	1.8

[a]The numbers in parentheses correspond to the $2p_{1/2}$ component of the Ti spectra.

Table S2 XPS peak fitting results for (PDADMA/$Ti_3C_2T_x$)$_5$ before pH response test.[a]

Element	Element at%	Binding energy (eV)	Component name	Component AT%	FWHM
Ti $2p_{3/2}$ ($2p_{1/2}$)	4.9	454.4 (459.8)[a]	Ti-C	46.7	1.6 (2.5)
		455.5 (460.9)	Ti^{2+}	23.8	1.5 (1.6)
		456.6 (462.2)	Ti^{3+}	27.6	2.1 (2.0)
		458.2 (464.5)	TiO_2	1.5	1.0 (1.0)
		459.0 (465.8)	Ti-F_x	0.9	1.6 (1.0)
C 1s	77.6	281.0	C-Ti-T_x	4.9	1.2
		282.6	C-Ti-T_x	2.2	1.7
		284.8	C-C	78.6	1.8
		286.4	CH_x/CO	9.2	1.6
		287.6	C-OH	0.3	0.6
		288.6	COO	4.8	1.7
O 1s	15.4	529.2	TiO_2	20.0	1.9
		530.9	C-Ti-O_x	12.2	1.3
		531.9	C-Ti-$(OH)_x$	47.6	1.9
		533.3	Al_2O_3	16.1	2.0
		534.2	H_2O	4.2	3.0
F 1s	1.1	684.3	C-Ti-F_x	96.7	1.7
		686.0	AlF_x	3.3	1.0
Cl 2p	1.0	-	-	-	-

[a]The numbers in parentheses correspond to the $2p_{1/2}$ component of the Ti spectra.

Table S3 XPS peak fitting results for $(BPEI/Ti_3C_2T_x)_5$ before pH response test.[a]

Element	Element at%	Binding energy (eV)	Component name	Component AT%	FWHM
Ti $2p_{3/2}$ ($2p_{1/2}$)	7.3	455.0 (460.0)[a]	Ti-C	46.3	1.8 (3.0)
		455.9 (461.4)	Ti^{2+}	33.5	2.4 (1.6)
		456.8 (462.8)	Ti^{3+}	17.9	2.0 (1.6)
		458.2 (464.5)	TiO_2	1.7	0.9 (1.2)
		459.1 (466.2)	Ti-F_x	0.6	1.9 (0.7)
C 1s	73.0	281.6	C-Ti-T_x	6.8	1.2
		283.1	C-Ti-T_x	7.0	3.0
		284.8	C-C	63.3	1.6
		286.0	CH_x/CO	19.2	2.3
		288.1	C-OH	1.6	1.3
		289.0	COO	2.0	1.2
O 1s	14.5	529.5	TiO_2	15.9	1.5
		530.9	C-Ti-O_x	25.3	2.9
		531.6	C-Ti-$(OH)_x$	36.4	1.7
		532.7	Al_2O_3	12.5	1.3
		533.7	H_2O	9.9	1.5
F 1s	1.8	684.8	C-Ti-F_x	93.1	1.8
		686.9	AlF_x	6.9	1.6
Cl 2p	1.3	-	-	-	-
N 1s	2.0	-	-	-	-

[a]The numbers in parentheses correspond to the $2p_{1/2}$ component of the Ti spectra.

Table S4 XPS peak fitting results for (PDADMA/$Ti_3C_2T_x$)$_5$ after pH response test.[a]

Element	Element at%	Binding energy (eV)	Component name	Component AT%	FWHM
Ti $2p_{3/2}$ ($2p_{1/2}$)	2.3	455.0 (460.0)[a]	Ti-C	23.7	1.9 (3.0)
		456.1 (461.2)	Ti^{2+}	7.6	2.0 (1.3)
		457.1 (462.7)	Ti^{3+}	19.8	3.0 (2.8)
		458.7 (464.8)	TiO_2	47.1	1.3 (2.1)
		459.1 (466)	Ti-F_x	1.9	1.7 (1.4)
C 1s	77.7	281.5	C-Ti-T_x	1.5	1.5
		283.1	C-Ti-T_x	2.1	1.3
		284.8	C-C	79.8	1.6
		286.2	CH_x/CO	11.8	2.1
		288.2	COH	1.4	0.9
		288.9	COO	3.4	1.4
O 1s	19.0	530.0	TiO_2	14.2	1.6
		530.4	C-Ti-O_x	5.3	1.0
		531.7	C-Ti-$(OH)_x$	50.3	1.6
		532.7	Al_2O_3	13.0	1.2
		533.4	H_2O	17.3	1.8
F 1s	0.4	684.6	C-Ti-F_x	73.6	1.7
		686.4	AlF_x	26.4	1.9
Cl 2p	0.6	-	-	-	-

[a]The numbers in parentheses correspond to the $2p_{1/2}$ component of the Ti spectra.

Table S5 XPS peak fitting results for $(BPEI/Ti_3C_2T_x)_5$ after pH response test.[a]

Element	Element at%	Binding energy (eV)	Component name	Component AT%	FWHM
Ti $2p_{3/2}$ ($2p_{1/2}$)	3.7	454.8 (460.2)[a]	Ti-C	18.1	1.9 (2.8)
		456.1 (460.8)	Ti^{2+}	16.6	2.4 (3.0)
		457.6 (462.7)	Ti^{3+}	8.6	2.1 (2.2)
		458.5 (464.2)	TiO_2	55.0	1.3 (2.1)
		459.2 (464.8)	Ti-F_x	1.7	0.9 (1.1)
C 1s	72.7	281.0	C-Ti-T_x	1.7	1.4
		283.2	C-Ti-T_x	2.7	1.8
		284.8	C-C	72.6	1.5
		286.2	CH_x/CO	12.1	1.4
		287.9	C-OH	7.6	2.6
		288.8	COO	3.3	1.2
O 1s	21.5	529.8	TiO_2	24.4	1.6
		530.9	C-Ti-O_x	12.2	1.4
		532.0	C-Ti-$(OH)_x$	44.5	1.6
		532.9	Al_2O_3	0.8	0.5
		533.4	H_2O	18.2	1.6
F 1s	0.5	684.3	C-Ti-F_x	26.9	0.8
		684.7	AlF_x	73.1	2.3
Cl 2p	0.4	-	-	-	-
N 1s	1.2	-	-	-	-

[a]The numbers in parentheses correspond to the $2p_{1/2}$ component of the Ti spectra.

References

1. X. Zhao, A. Vashisth, E. Prehn, W. Sun, S. A. Shah, T. Habib, Y. Chen, Z. Tan, J. L. Lutkenhaus, M. Radovic and M. J. Green, *Matter*, **1**, 513-526.
2. S. A. Shah, T. Habib, H. Gao, P. Gao, W. Sun, M. J. Green and M. Radovic, *Chem. Commun.*, 2017, **53**, 400-403.