Supporting Information

Polydimethylsiloxane-Assisted Low-Energy Anodization: A Fluoride-Free Tunable Strategy for Engineering Porous TiO_2 Films

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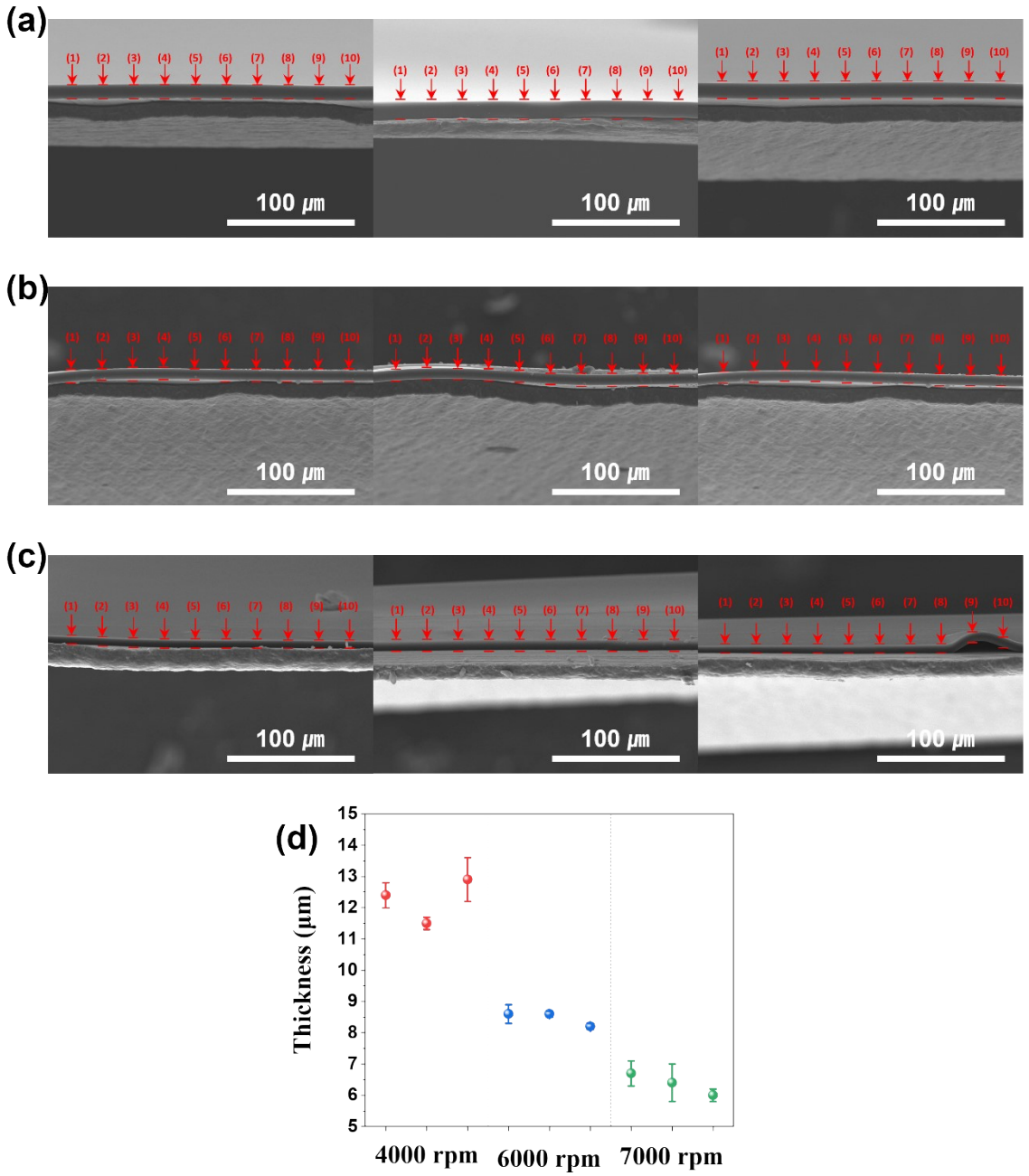


Figure S1. Cross-sectional SEM images of PDMS layers spin-coated on titanium substrates at rotational speeds of (a) 4000 rpm, (b) 6000 rpm, and (c) 7000 rpm. (d) Thickness of PDMS films prepared at spin speeds of 4000, 6000, and 7000 rpm. For each rotational speed, three independent samples were examined, and the film thickness was measured at ten different positions per sample.

Table S1. Numerical values of PDMS film thickness (μm) measured from cross-sectional SEM images at different spin-coating speeds (4000, 6000, and 7000 rpm).

4000 rpm			6000 rpm			7000 rpm		
Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
12.0	11.3	12.7	8.7	8.5	8.3	6.4	6.5	5.9
12.4	11.3	12.3	8.5	8.6	8.1	6.6	6.5	5.9
12.6	11.4	13.2	9.0	8.7	8.2	6.8	6.2	6.0
12.4	11.6	13.7	8.6	8.8	8.2	6.7	6.2	6.0
12.6	11.6	13.3	8.5	8.6	8.2	7.0	6.0	6.2
12.6	11.7	13.1	8.5	8.6	8.2	6.9	6.9	6.1
12.4	11.4	13.2	8.5	8.5	8.2	6.8	6.6	5.9
12.4	11.3	12.5	8.7	8.6	8.2	6.4	6.5	6.0
12.4	11.7	12.7	8.9	8.6	8.3	7.0	6.2	6.0
12.2	11.6	12.6	8.6	8.6	8.2	6.3	5.9	5.8
Average: 12.67 ± 0.67			Average: 8.49 ± 0.04			Average: 6.41 ± 0.38		

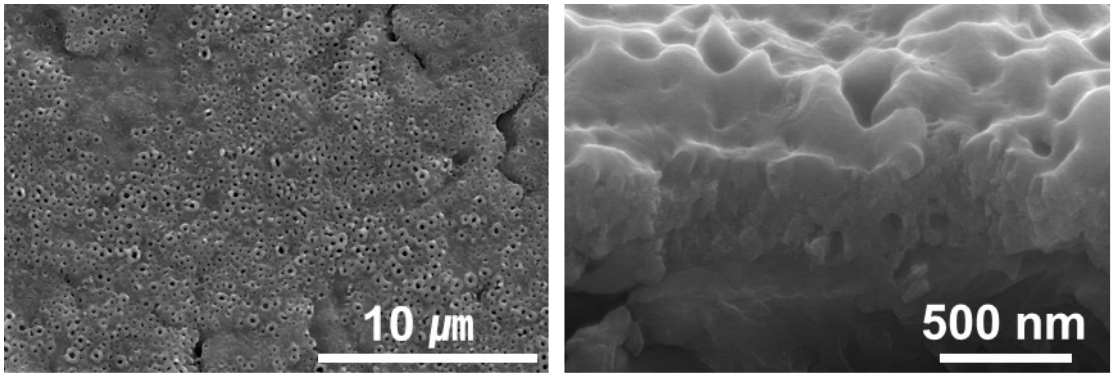


Figure S2. Top-view and cross-sectional SEM images of oxide layers formed on bare Ti pre-cathodic treated at 100 mA cm^{-2} for 10 min and anodized at 150 V for 30 min in 0.2 M H_2SO_4.

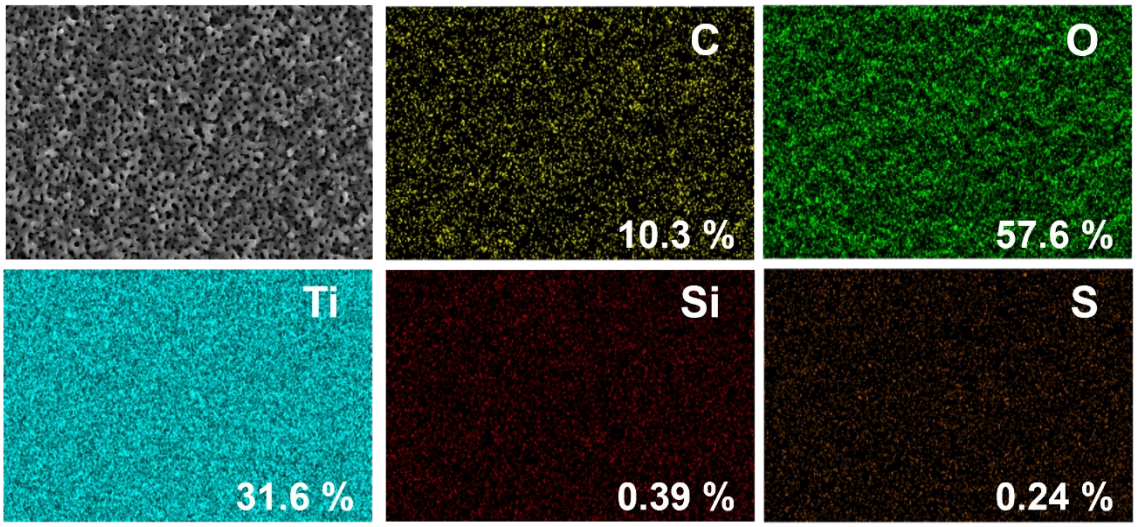


Figure S3. EDS elemental mapping and elemental composition of the oxide layer formed on PDMS-Ti anodized in 0.2 M H_2SO_4 at 150 V for 30 min.

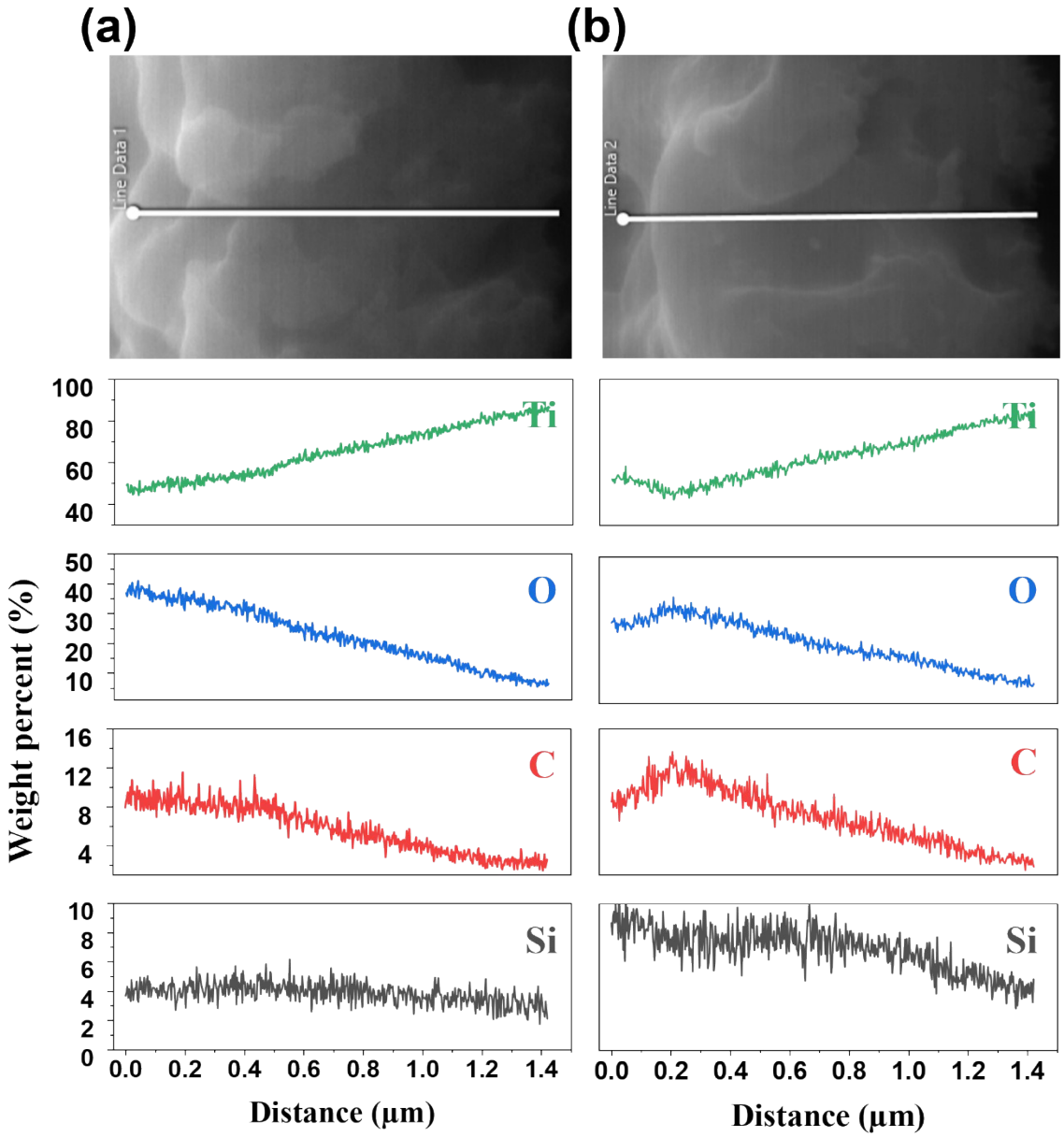


Figure S4. EDS line scanning of the oxide layer formed on PDMS-Ti anodized in (a) 0.2 M H_2SO_4 and (b) mixed electrolyte of 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3 at 150 V for 30 min.

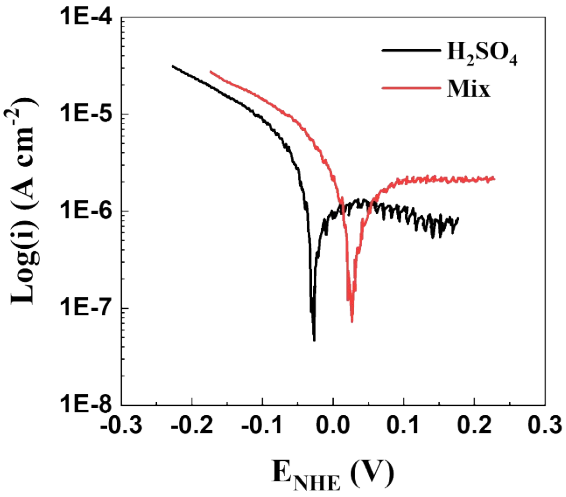


Figure S5. Tafel polarization curves of PDMS-Ti anodized at 150 V for 30min in 0.2 M H_2SO_4 and a mixed electrolyte of 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3.

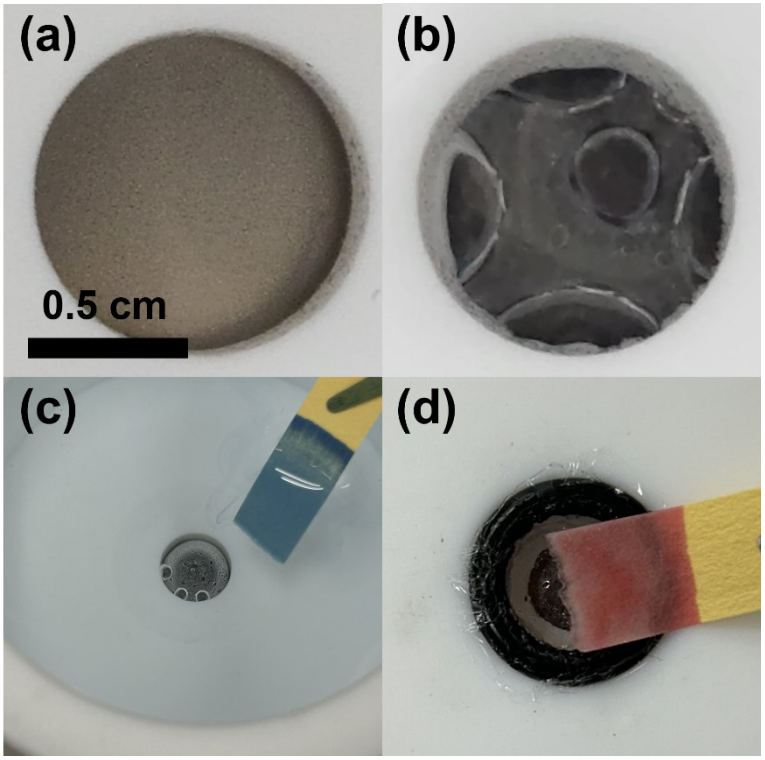


Figure S6. Surface images of the PDMS-Ti electrode (a) before and (b) after anodization. (c) pH indicators result for the electrolyte and (d) the localized pH inside the PDMS layer following anodization.

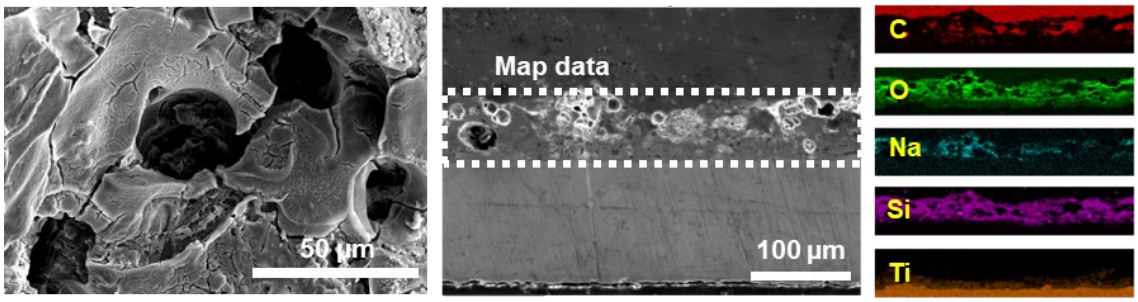


Figure S7. Top-view and cross-sectional SEM images of the oxide layer formed on PDMS-Ti after PEO treatment at 200 V, along with cross-sectional EDS elemental mapping confirming the elemental distribution within the oxide film (reproduced with permission from [1]).

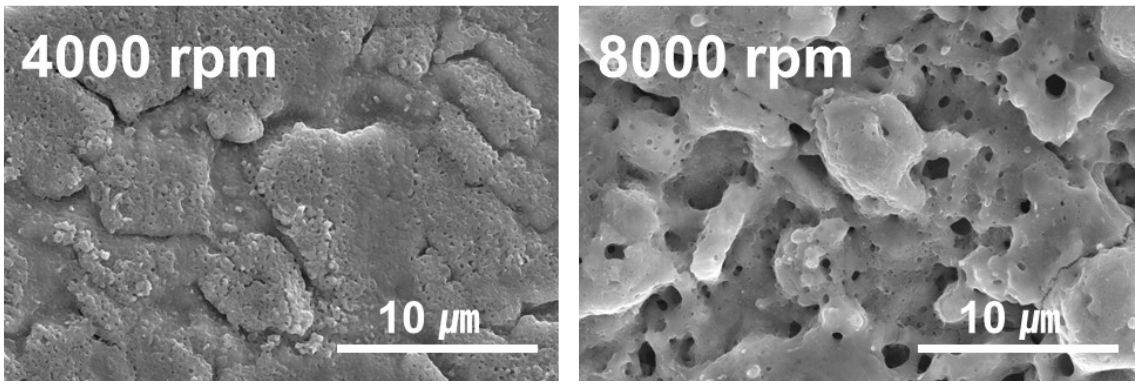


Figure S8. Top-view SEM images of oxide layers formed on PDMS-coated Ti, spin-coated at 4000 and 8000 rpm, after anodization at 150 V for 30 min in a mixed electrolyte of 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3.

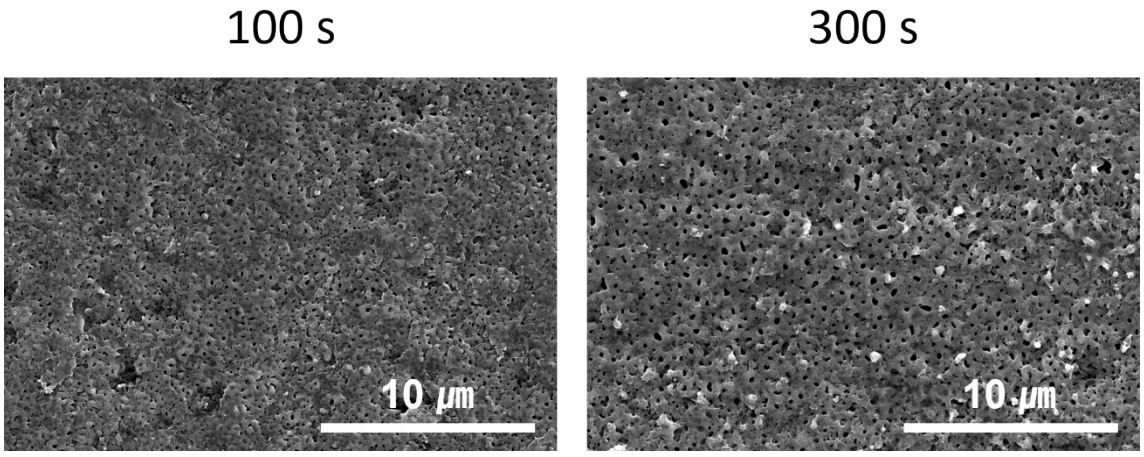


Figure S9. Top-view SEM images of oxide layers formed on PDMS-Ti anodized in 0.2 M H_2SO_4 at 150 V for 100 s and 300 s.

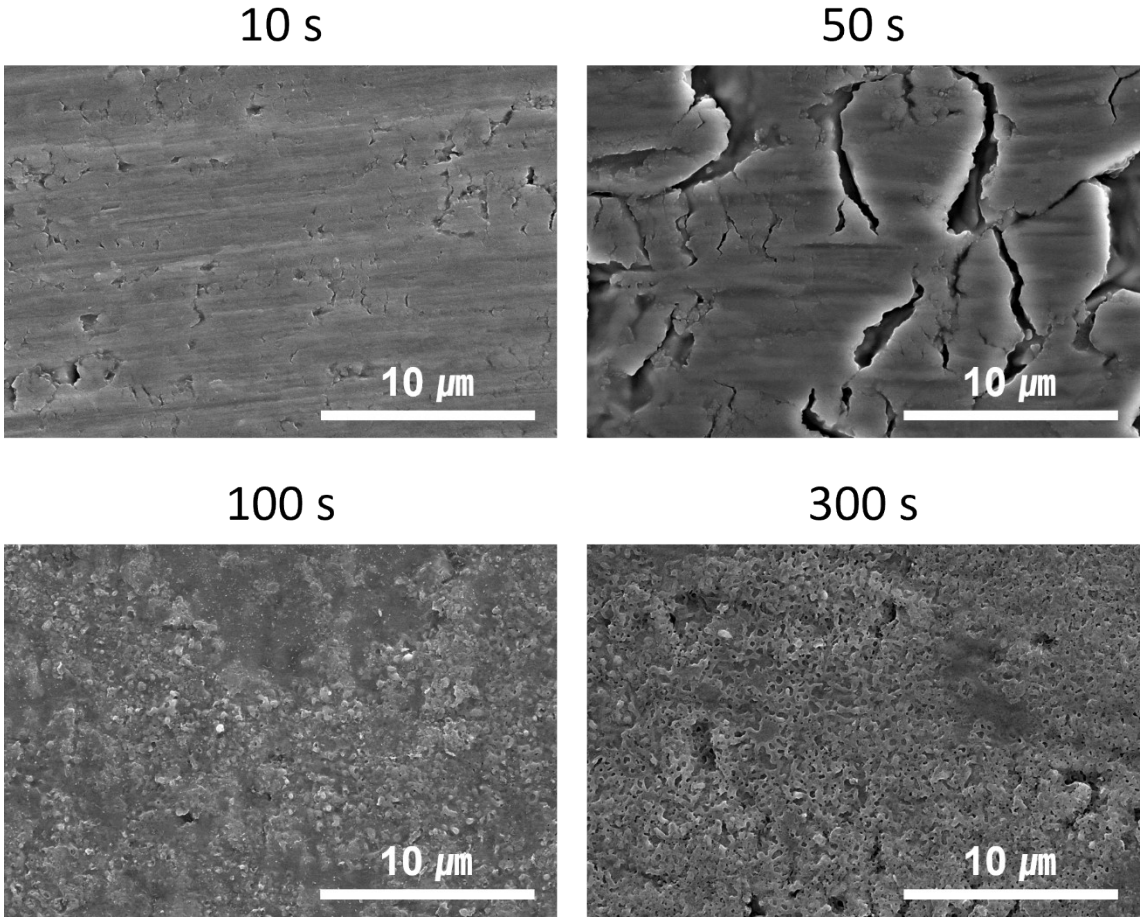


Figure S10. Top-view SEM images of oxide layers formed on PDMS-Ti anodized in mixed electrolyte of 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3 at 150 V for 0, 10, 50, and 300 s.

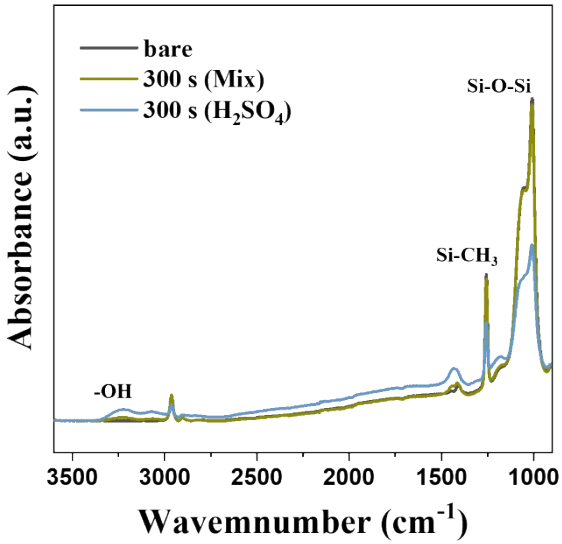


Figure S11. FT-IR spectra of the PDMS layer treated in 0.2 M H_2SO_4 and mixed electrolyte of 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3 at 150 V for 300 s

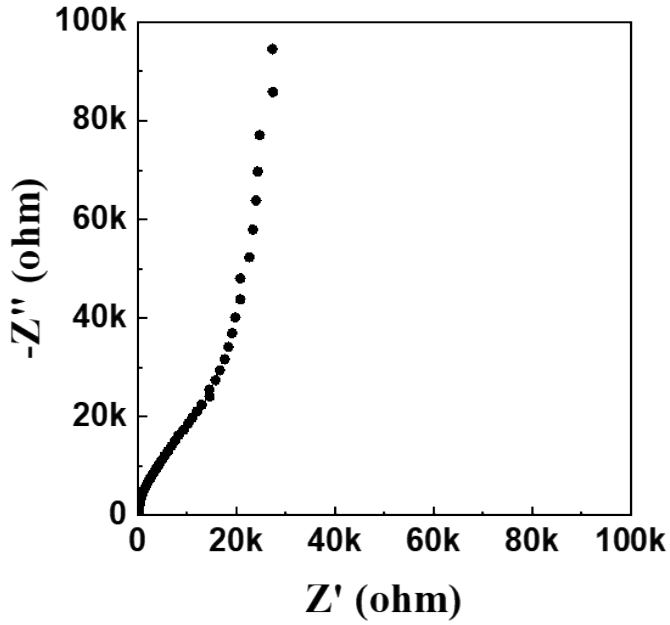


Figure S12. Nyquist plots of PDMS–Ti immersed in the mixed electrolyte for 30 min without an applied voltage.

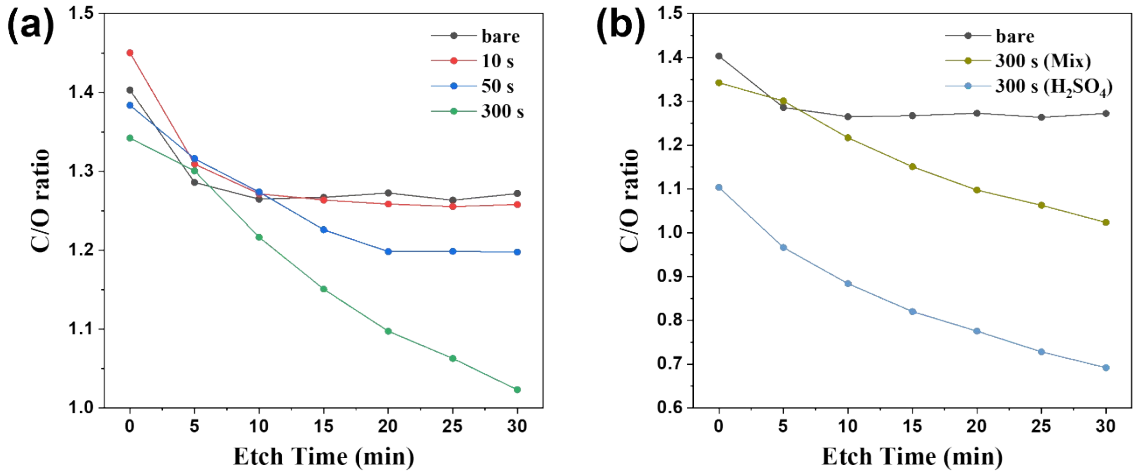


Figure S13. (a) C/O ratio depth profiles of PDMS layers treated at 150 V for 0, 10, 50, and 300 s in a mixed electrolyte containing 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3. (b) C/O ratio depth profiles of PDMS layers treated at 150 V for 300 s in 0.2 M H_2SO_4 and in a mixed electrolyte containing 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3.

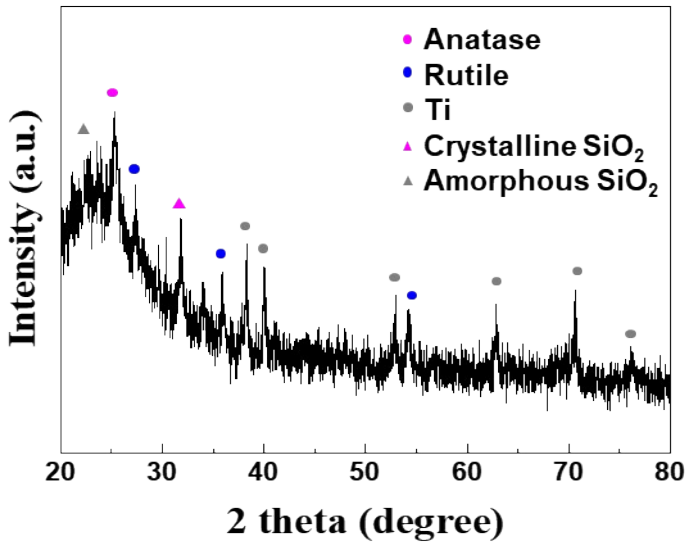
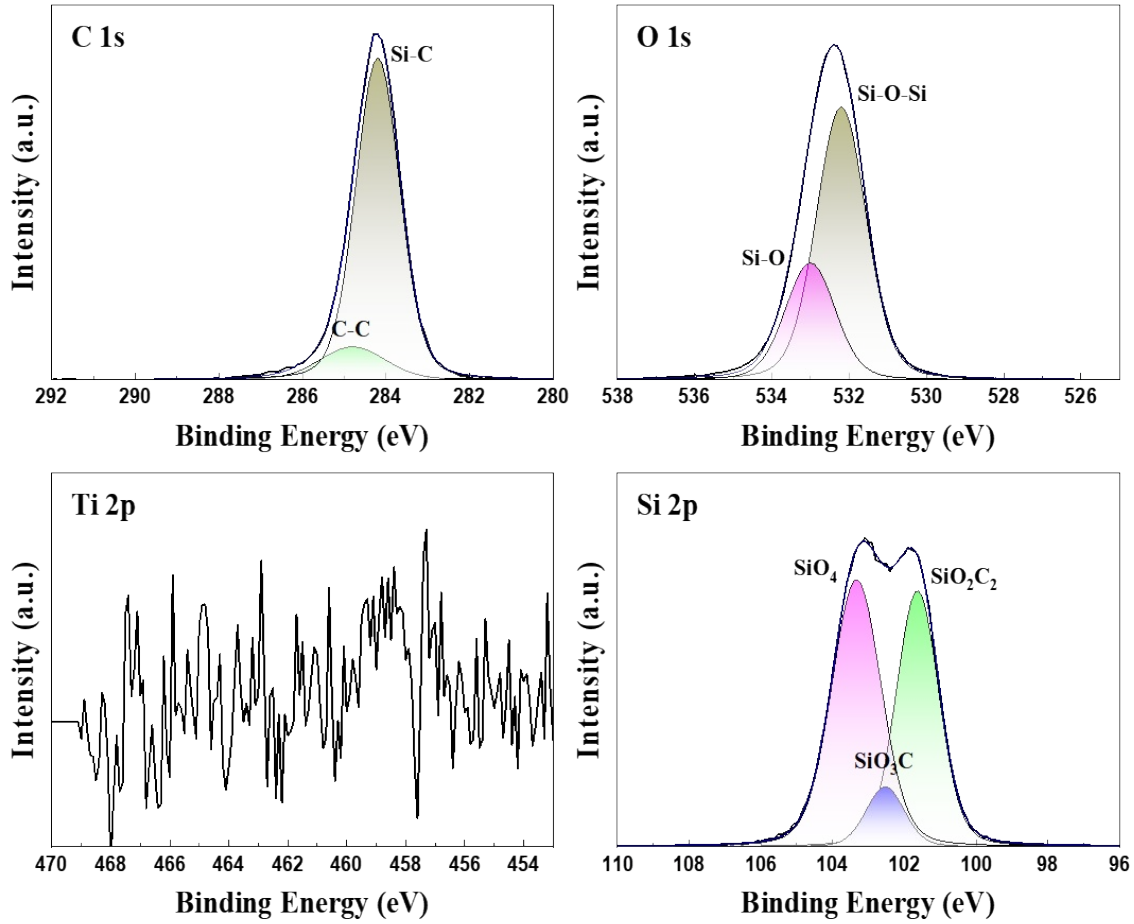


Figure S14. XRD pattern of PDMS-Ti after PEO treatment at 200 V (reproduced with permission from [1]).



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88 **Figure S15.** XPS spectra of C 1s, O 1s, Ti 2p, and Si 2P of PDMS-Ti after PEO treatment at

89 200 V (reproduced with permission from [1]).

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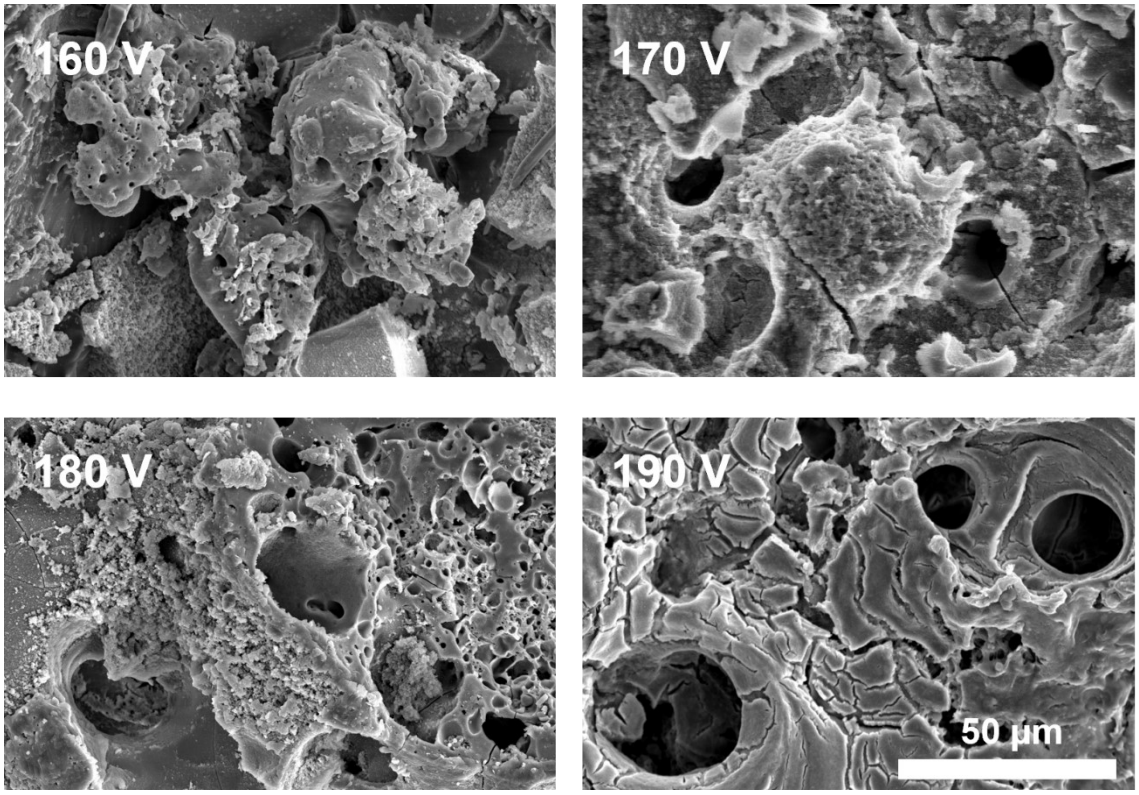


Figure S16. Top-view SEM images of PDMS-Ti after PEO treatment at voltages ranging from 160 V to 190 V.

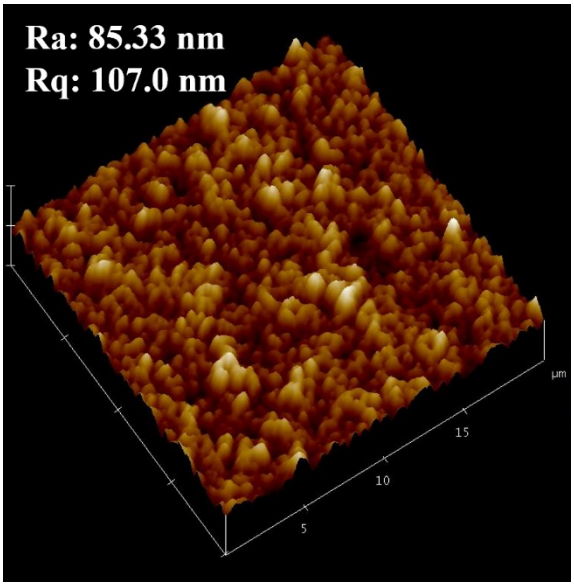


Figure S17. AFM surface morphology and roughness maps of oxide layers formed on PDMS-Ti anodized in 0.2 M H_2SO_4 at 150 V for 30 min.

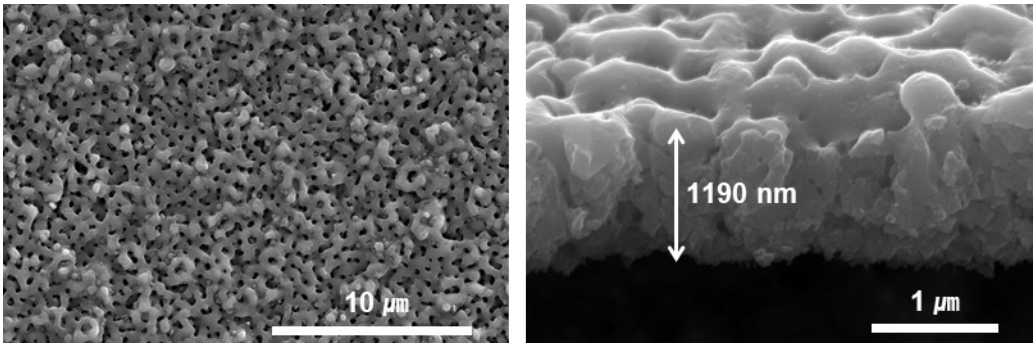
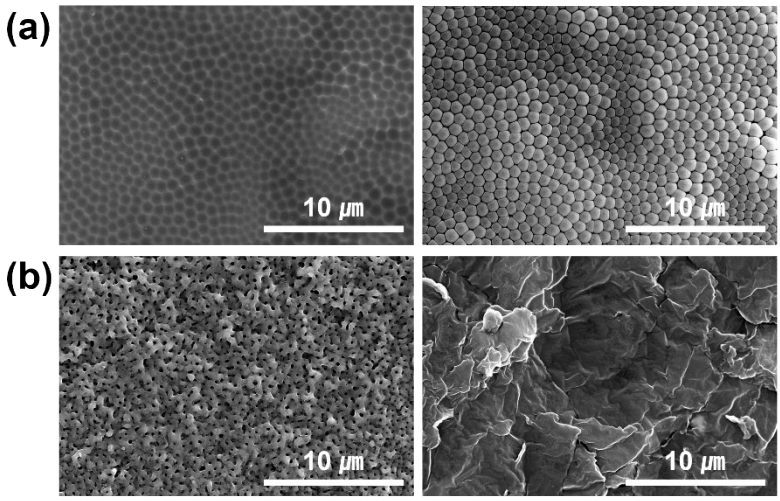


Figure S18. Top-view and cross-sectional SEM images of PDMS-Ti anodized at 150 V for 3 hr.



(c)

Element (at%)	Tubular (substrate)	Tubular (tape)	PDMS-Ti (tape)
C	17.4	17.42	92.59
O	-	48.10	7.35
F	1.29	6.92	-
Ti	81.31	27.56	0.05

Figure S19 Top-view SEM images of the substrate and tape surfaces after the tape test: (a) bare Ti anodized at 60 V for 20 min in an ethylene-glycol-based electrolyte containing 0.3 wt% NH_4F and 7.5 wt% DI water, and (b) PDMS–Ti anodized at 150 V for 30 min in an electrolyte containing 0.2 M H_2SO_4 and 0.4 M Na_2SiO_3. (c) Atomic percentages of C, O, F, and Ti for each sample obtained from EDX analysis.

References

1. H.-G. Gim, Y.-T. Kim and J. Choi, *Electrochem. Commun.*, 2023, **148**, 107455.