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Electronic Supplementary Information

Chemically tuned, bi-functional polar interlayer for TiO₂ photoanodes in fibre-shaped dye-sensitized solar cells

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Supporting Figures

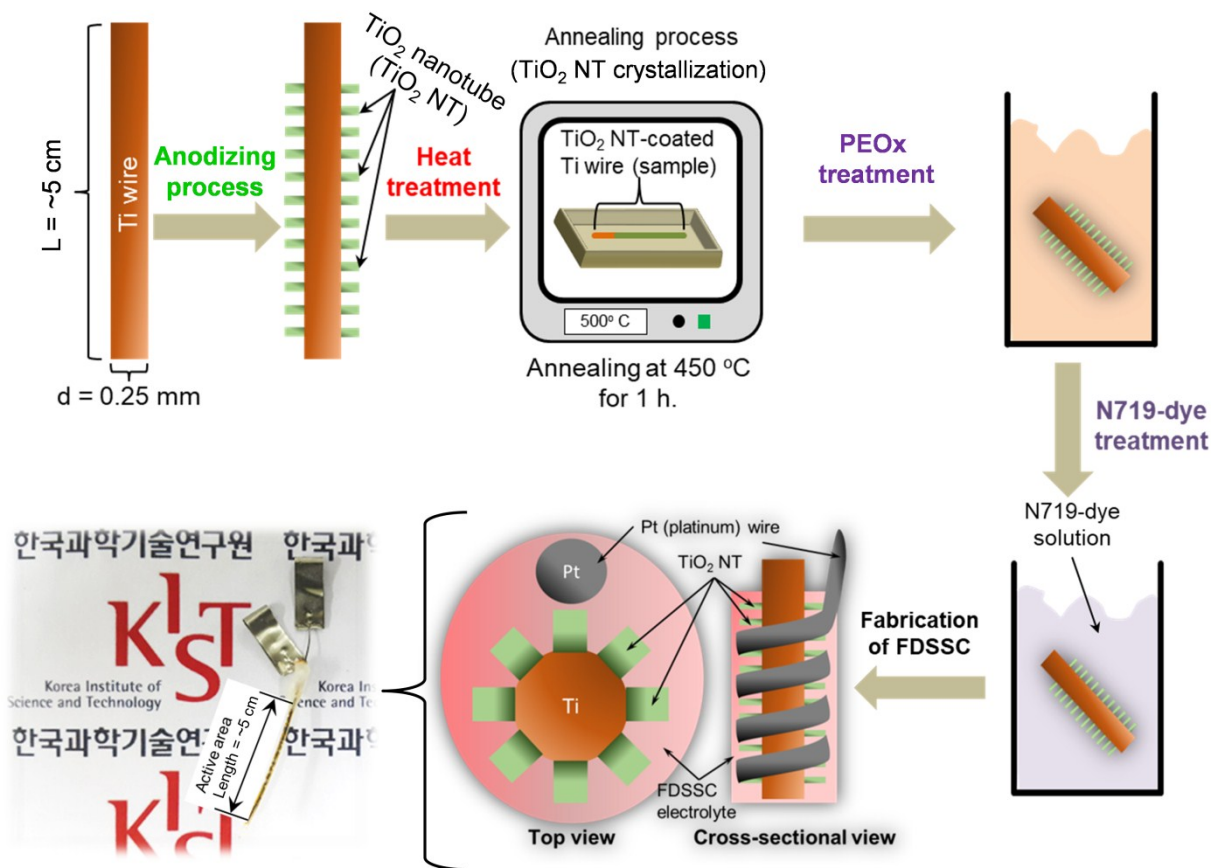
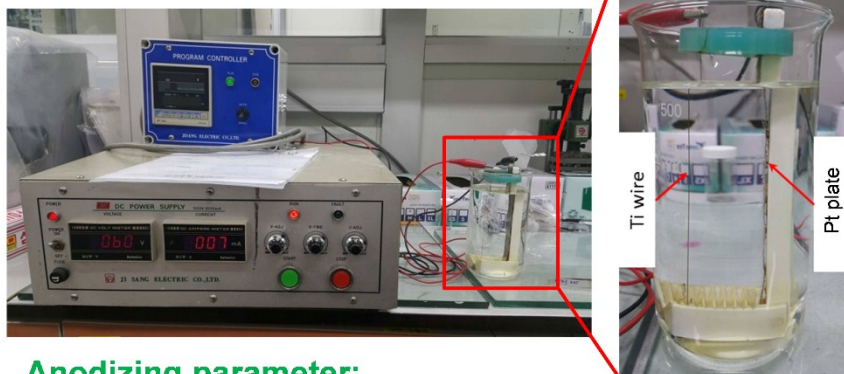
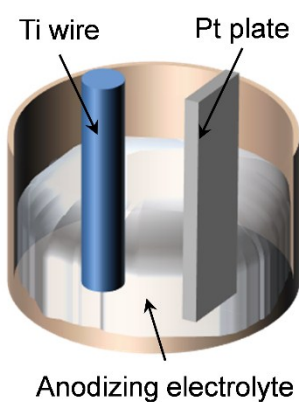


Fig. S1. Schematic of the TiO₂@PEOx-based FDSSC preparation process.

Anodizing apparatus:



Anodizing parameter:



Anodizing electrolyte contains

- ✓ Ethylene glycol (EG),
- ✓ 2 vol% of H₂O, and
- ✓ 0.25 wt% of NH₄F.

Anodizing condition

- ✓ 60 V of DC voltage
- ✓ 6 hours of anodizing time.
- ✓ ~27 °C.

Fig. S2. Anodizing apparatus to prepare the TiO₂ nanotube photoanodes used in this work.

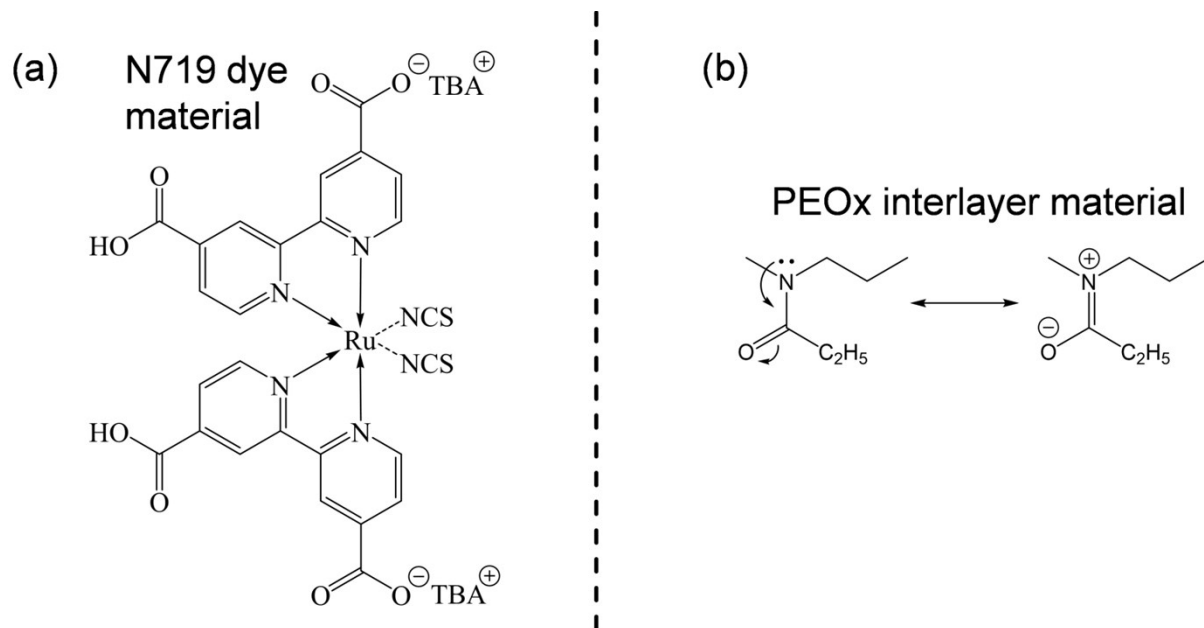


Fig. S3. Chemical structures of the (a) N719 dye and (b) PEOx interlayer materials.

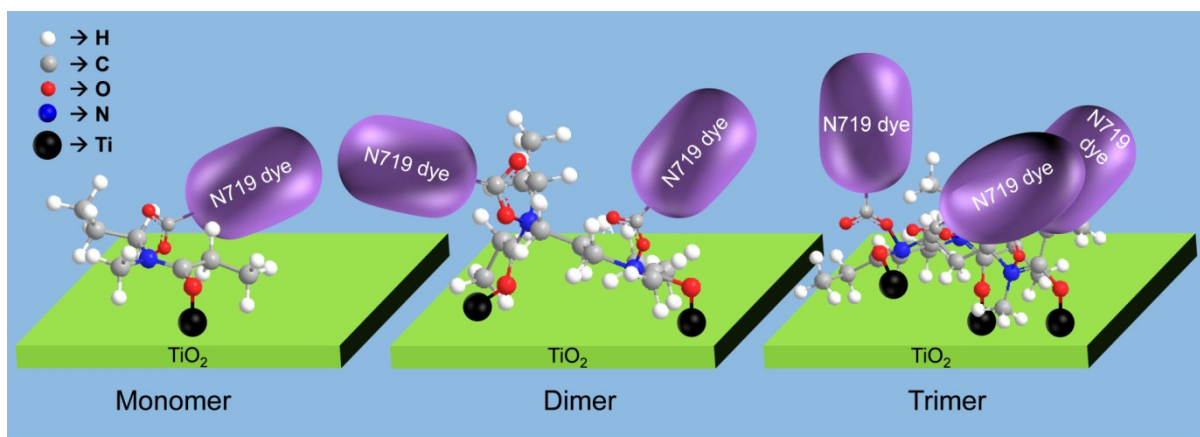


Fig. S4. 3D molecular model of the PEOx interlayer material, binding at the TiO₂/N719 dye interface, with monomer, dimer, and trimer configurations.

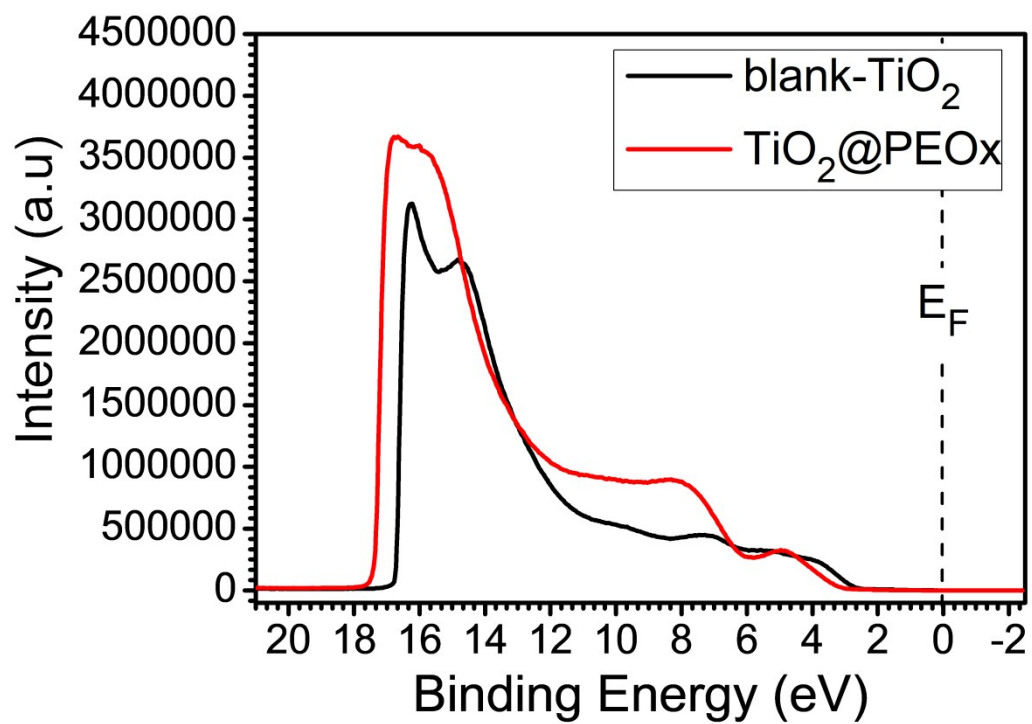


Fig. S5. Full-range UPS spectra of blank-TiO₂ and TiO₂@PEOx samples.

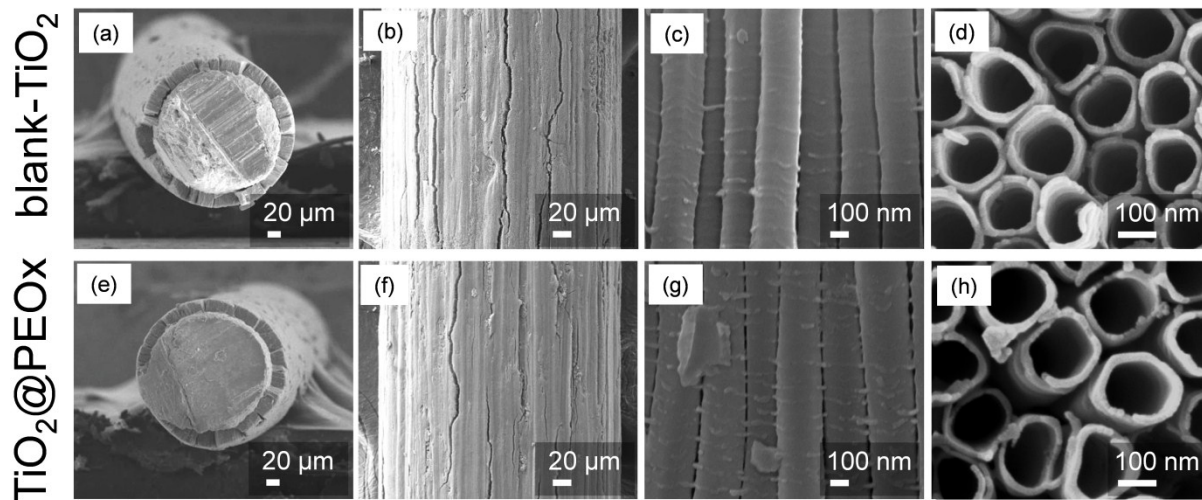


Fig. S6. (a, c, e, g) Cross-sectional and (b, d, f, h) surface SEM images of (a–d) blank-TiO₂ and (e–h) TiO₂@PEOx samples

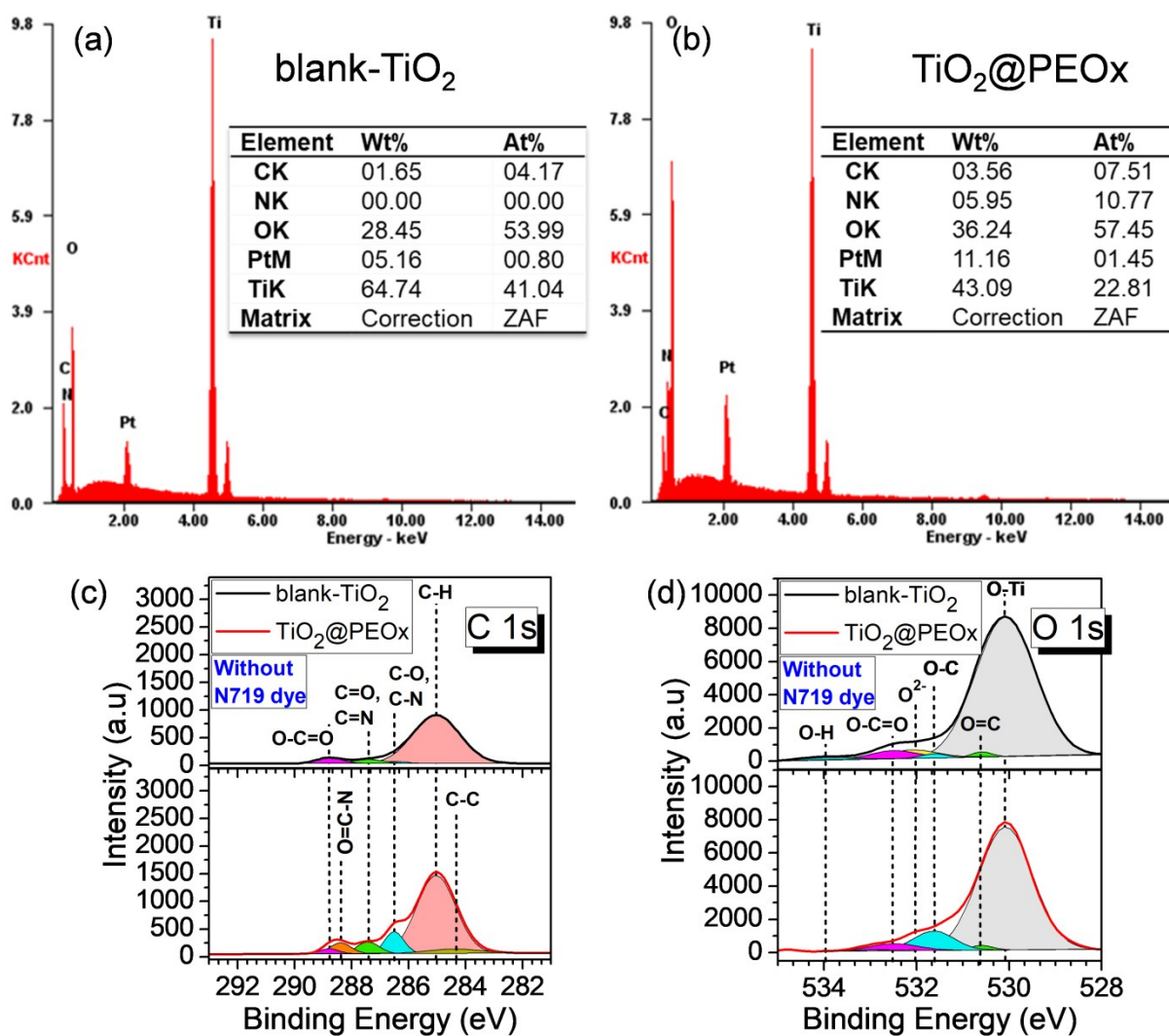


Fig. S7. Spectra for blank-TiO₂ and TiO₂@PEOx samples without dye immersion obtained by (a, b) EDS, (c) C 1s and (d) O 1s XPS.

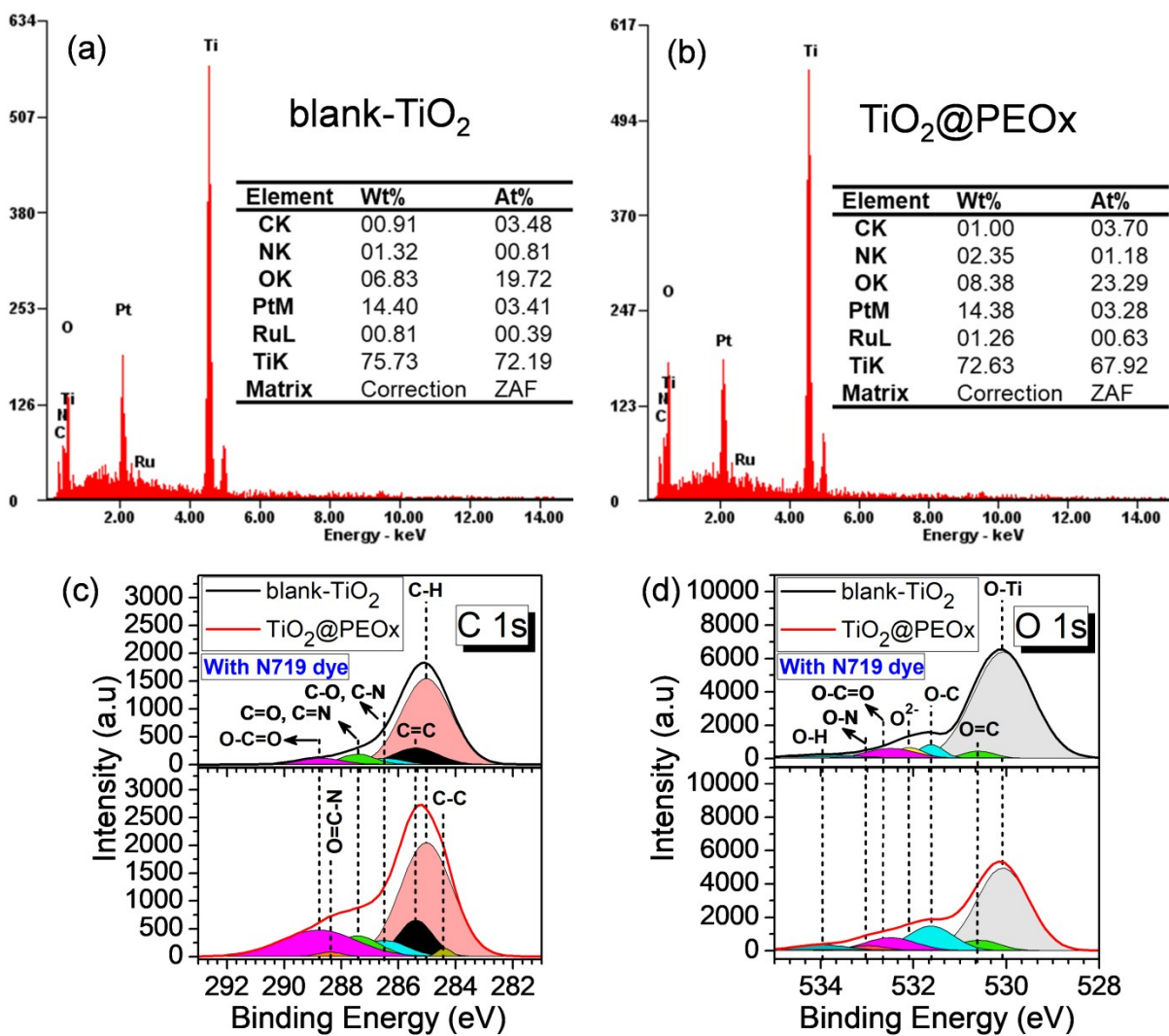


Fig. S8. Spectra for blank-TiO₂ and TiO₂@PEOx samples with dye immersion for 24 h obtained by (a, b) EDS, (c) C 1s and (d) O 1s XPS.

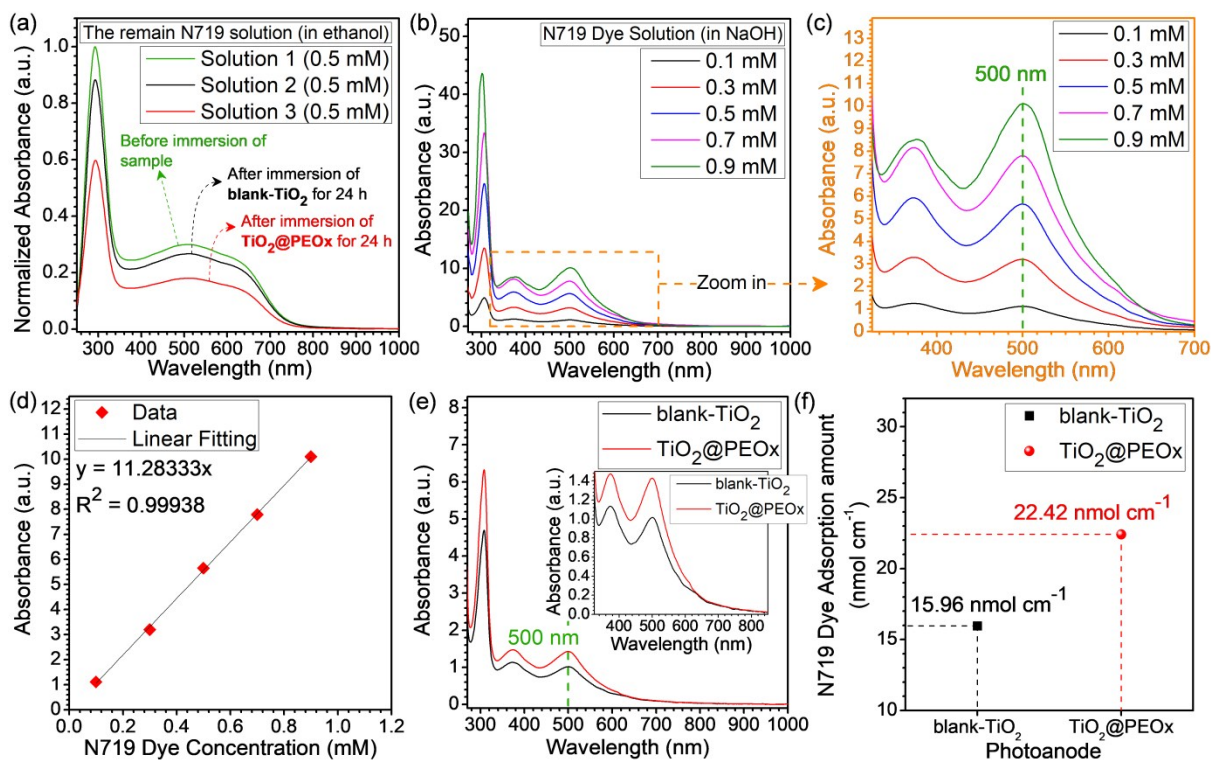


Fig. S9. (a) UV-vis spectra of 0.5 mM N719 dye-ethanol solutions, where Solution 1 has not undergone any photoanode immersion, Solution 2 has undergone blank-TiO₂ sample immersion for 24 h, and Solution 3 has undergone TiO₂@PEOx sample immersion for 24 h. (b) UV-vis spectra of N719 dye, at varied concentrations, in 0.1 M aqueous NaOH solutions. (c) The enlarged UV-Vis spectra from panel (b). (d) Calibration curve obtained from the UV-vis spectra depicted in panels (b) and (c). (e) UV-vis spectra of the desorbed N719 dye on blank-TiO₂ and TiO₂@PEOx surfaces. The N719 dye was desorbed by 0.1 M aqueous NaOH solution. The inset shows enlarged spectra from panel (e). (f) N719 dye loading adsorbed on blank-TiO₂ and TiO₂@PEOx samples calculated from the data in panels (d) and (e).

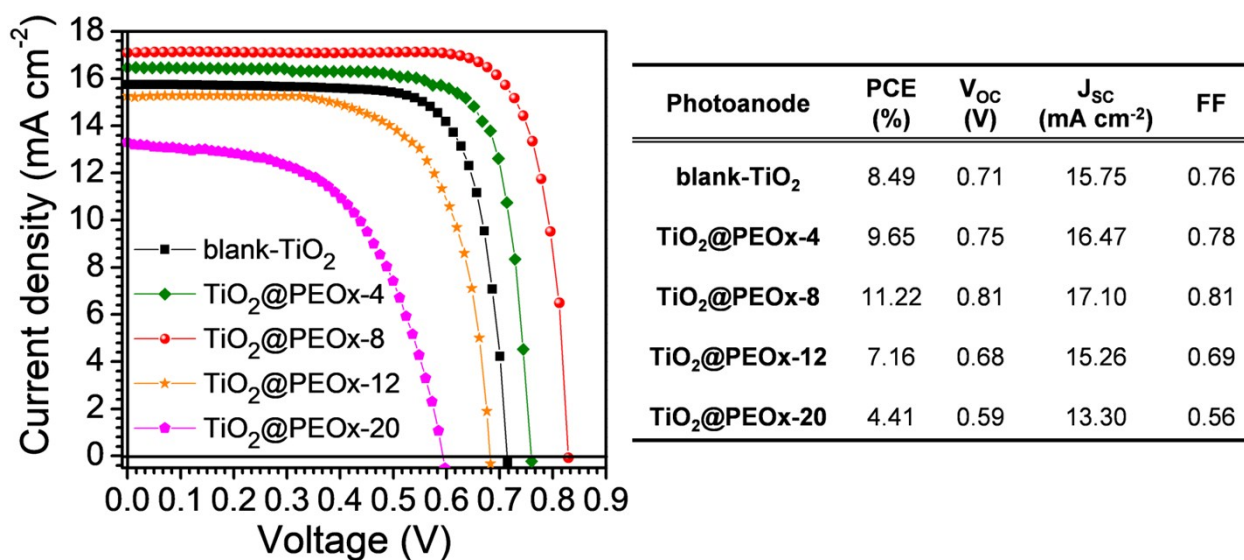


Fig. S10. J - V characteristics, under the 1 sun (1.5G) illumination condition, of blank-TiO₂-based and the TiO₂@PEOx-based FDSSCs with PEOx concentrations varied between 4-20 mg ml⁻¹.

Supporting Tables

Table S1. Summary of the full-range XPS spectra shown in **Fig. 2a, e**.

Photoanode	Atomic Percent (%)						Total
	C 1s	O 1s	Ti 2p	N 1s	Ru 3d	S 2p	
Before the N719 dye immersion							
blank-TiO ₂	25.62	51.43	22.95	—	—	—	100.00
TiO ₂ @PEOx	28.94	47.06	21.38	2.62	—	—	100.00
After the N719 dye immersion							
blank-TiO ₂	39.50	34.47	13.37	9.52	2.75	0.38	100.00
TiO ₂ @PEOx	52.13	22.41	7.03	12.93	4.54	0.96	100.00

Table S2. Summary of de-convoluted XPS results for blank-TiO₂ and TiO₂@PEOx photoanode samples without dye immersion, corresponding to **Fig. 2b, 2c, S7c, and S7d.**

Photoanode	Bonding species	Peak position (eV)	Peak Area	Bond content (%)	Peak FWHM (eV)
XPS peak region = N 1s					
blank-TiO ₂	—	—	—	—	—
	—	—	—	—	—
	Total		—	—	—
TiO ₂ @PEOx	N=C	398.53	172.49	27.85	1.29
	N-C=O (Amide)	400.05	372.34	60.12	1.30
	N-C	401.90	74.49	12.03	1.39
	Total		619.32	100.00	—
XPS peak region = Ti 2p					
blank-TiO ₂	Ti ³⁺	457.10	662.44	3.51	1.39
	Ti ⁴⁺	458.85	11628.25	61.63	1.30
	Ti ³⁺	463.35	1914.97	10.15	5.00
	Ti ⁴⁺	464.60	4660.92	24.70	1.94
	Total		18866.58	100.00	—
TiO ₂ @PEOx	Ti ³⁺	456.85	125.25	1.15	0.75
	Ti ⁴⁺	458.60	7551.93	69.42	1.36
	Ti ³⁺	463.05	118.00	1.08	1.39
	Ti ⁴⁺	464.23	3084.07	28.35	1.99
	Total		10879.25	100.00	—
XPS peak region = C 1s					
blank-TiO ₂	C-C (sp ²)	284.40	0.10	0.00	0.50
	C-H	285.03	1802.49	87.41	1.94
	C-O, C-N	286.50	40.01	1.94	1.00
	C=O, C=N	287.42	96.19	4.66	1.23
	O=C-N (Amide)	288.40	0.10	0.00	0.10
	O-C=O	288.78	123.23	5.98	1.09
	Total		2062.12	100.00	—
TiO ₂ @PEOx	C-C (sp ²)	284.40	173.84	5.17	2.18
	C-H	285.03	2401.87	71.37	1.60
	C-O, C-N	286.50	332.24	9.87	0.78
	C=O, C=N	287.42	201.45	5.99	0.89
	O=C-N (Amide)	288.40	182.00	5.41	0.87
	O-C=O	288.78	74.21	2.20	0.75
	Total		3365.61	100.00	—
XPS peak region = O 1s					
blank-TiO ₂	O-Ti	530.08	13620.71	87.22	1.52
	O=C	530.60	174.82	1.12	0.50
	O-C	531.63	187.29	1.20	0.65
	O ²⁻ (oxygen vacancy)	532.09	709.85	4.55	1.28
	O-C=O	532.50	644.72	4.13	1.20
	O-H	534.00	278.50	1.78	1.22
	Total		15615.89	100.00	—
TiO ₂ @PEOx	O-Ti	530.08	10892.82	83.64	1.38
	O=C	530.60	174.08	1.34	0.57
	O-C	531.63	1297.15	9.96	1.04
	O ²⁻	532.09	10.92	0.08	0.18
	O-C=O	532.50	560.24	4.30	1.21
	O-H	533.00	87.65	0.67	1.27
	Total		13022.86	100.00	—

Table S3. Summary of de-convoluted XPS results of blank-TiO₂ and TiO₂@PEOx photoanode samples with dye immersion for 24 h corresponding to Fig. 2f, S8c, and S8d.

Photoanode	Bonding species	Peak position (eV)	Peak area	Bond content (%)	Peak FWHM (eV)
XPS peak region = N 1s					
blank-TiO ₂	N=C=S (NCS)	397.85	19.30	6.26	1.60
	N=C	398.62	73.88	23.95	2.22
	Pyridine ring	399.87	196.86	63.81	1.70
	N-C=O (Amide)	400.36	0.00	0.00	0.00
	N-O	400.94	0.00	0.00	0.00
	N-C	401.62	12.36	4.06	1.16
	TBA	402.67	5.92	1.92	1.56
Total			308.32	100.00	—
TiO ₂ @PEOx	N=C=S (NCS)	397.85	108.58	6.72	1.19
	N=C	398.62	501.57	31.03	1.68
	Pyridine ring	399.87	676.44	41.85	1.16
	N-C=O (Amide)	400.36	35.90	2.22	1.15
	N-O	400.94	187.28	11.59	1.53
	N-C	401.62	37.60	2.33	1.31
	TBA	402.67	68.88	4.26	1.36
Total			1616.25	100.00	—
XPS peak region = C 1s					
blank-TiO ₂	C-C (sp ²)	284.40	0.00	0.00	0.00
	C-H	285.03	3372.21	72.37	2.05
	C=C (sp ³)	285.40	582.78	12.51	1.85
	C-O, C-N	286.50	190.43	4.09	1.63
	C=O, C=N	287.42	282.25	6.06	1.42
	N-C=O (Amide)	288.39	0.00	0.00	0.00
	O-C=O	288.78	231.74	4.97	1.92
Total			4659.41	100.00	—
TiO ₂ @PEOx	C-C (sp ²)	284.40	93.58	1.08	0.57
	C-H	285.03	4645.82	53.49	2.13
	C=C (sp ³)	285.40	977.59	11.26	1.40
	C-O, C-N	286.50	586.88	6.76	1.89
	C=O, C=N	287.42	714.93	8.23	1.80
	N-C=O (Amide)	288.39	84.58	0.97	1.01
	O-C=O	288.78	1581.61	18.21	3.13
Total			8684.99	100.00	—
XPS peak region = O 1s					
blank-TiO ₂	O-Ti	530.08	10187.39	78.93	1.50
	O=C	530.60	370.16	2.87	0.79
	O-C	531.63	555.55	4.30	0.61
	O ²⁻ (oxygen vacancy)	532.09	504.14	3.91	0.72
	O-C=O	532.50	823.04	6.38	1.29
	O-N	533.00	0.10	0.00	0.10
	O-H	534.00	467.17	3.62	1.87
Total			12907.55	100.00	—
TiO ₂ @PEOx	O-Ti	530.08	7022.60	60.79	1.33
	O=C	530.60	721.76	6.25	1.07
	O-C	531.63	1852.75	16.04	1.17
	O ²⁻ (oxygen vacancy)	532.09	1.52	0.01	0.67
	O-C=O	532.50	1090.19	9.44	1.30
	O-N	533.00	325.65	2.82	1.00
	O-H	534.00	537.73	4.65	1.39
Total			11552.20	100.00	—

Table S4. Comparison of the performance of TiO₂@PEOx-based FDSSC and other FDSSC examples reported in the literature.

Year	Photoanode	Photoanode current collector	Counter electrode	N719 dye concentration (mM)	PCE (%)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	Reference number	
									Main article	Supporting information
2019	TiO₂@PEOx	Ti wire	Pt wire	0.50	11.21	0.80	17.04	0.82	This work	
2019	TiO ₂ nanotube	Ti wire	CF@PANI@CoSe Pt wire	0.50	10.28 8.34	0.73 0.76	17.65 16.33	0.80 0.68	38	(S1)
2019	TiO ₂ -rGO	Stainless steel wire	Pt wire	0.30	5.36	0.79	12.94	0.52	39	S2
2018	TiO ₂ microridge/nanorods	Ti wire	Pt wire	0.50	8.13	0.70	14.79	0.78	8	S3
2018	TiO ₂ nanowire	Ti wire	Pt wire	0.50	3.13	0.69	7.58	0.60	9	S4
2018	TiO ₂ nanotube	Ti wire	Pt-modified CS-CNT fibre Pt wire	0.30	10.00 6.11	0.73 0.74	19.43 14.59	0.71 0.56	40	S5
2017	TiO ₂ nanotube	Ti wire	CF@TiO ₂ @MoS ₂	0.30	9.50	0.74	16.95	0.75	41	S6
2016	TiO ₂ micron-cone-nanowire	Ti wire	Pt wire	0.50	4.75	0.67	10.44	0.68	6	S7
2016	TiO ₂ nanotube	Ti wire	Pt-coated carbon fibre	0.30	5.64	0.74	11.92	0.64	30	S8
2015	TiO ₂ micron-cone	Ti wire	Pt wire	0.50	8.07	0.70	16.04	0.72	42	S9
2015	TiO ₂ nanotube	Ti wire	RACNTs fibre Pt wire	0.50	6.80 2.74	0.70 0.67	14.50 12.01	0.67 0.34	43	S10
2015	TiO ₂ nanotube	Ti wire	Graphene fibre Pt wire	0.30	3.25 2.14	0.58 —	14.10 —	0.40 —	44	S11
2014	TiO ₂ nanotube	Ti wire	MWCNT fibre	0.30	7.13	0.71	16.28	0.61	45	S12
2014	TiO ₂ nanotube	Ti wire	CNT/GNRPt Fibre	0.30	6.83	0.69	13.55	0.73	46	S13
2012	TiO ₂ NRs-coated CFs	CFs (carbon fibres)	Pt-coated optical fibre	0.30	1.28	0.61	4.58	0.46	47	S14
2011	TiO ₂ nanotube	Ti wire	Pt wire	0.30	5.84	0.64	13.62	0.67	48	S15
2010	TiO ₂ nanotube	Ti wire	Pt wire	0.50	2.78	0.52	10.90	0.48	49	S16
2010	TiO ₂ nanotube	Ti wire	Pt wire	0.50	4.10	0.69	11.65	0.51	50	S17

Table S5. EIS parameters of **Fig. 6c, 6d, 6f** and **6g**, simulated by the equivalent circuit depicted in **Fig. 6a, 6b**.

Photoanode	Applied Voltage (V)	R_{Ti} (Ω cm)	R_{Pt} (Ω cm)	R_{TT} (Ω cm)	C_{Ti} (F cm $^{-1}$)	C_{Pt} (F cm $^{-1}$)	C_{TT} (F cm $^{-1}$)
blank-TiO ₂	0.20	56.79	105.07	123.20	2.65×10^{-6}	6.10×10^{-4}	5.39×10^{-11}
	0.40	46.07	72.43	79.19	1.73×10^{-6}	2.95×10^{-4}	2.43×10^{-11}
	0.60	42.69	58.42	66.23	1.66×10^{-6}	2.62×10^{-4}	1.40×10^{-11}
	0.80	18.01	45.08	50.35	1.53×10^{-6}	2.20×10^{-4}	1.24×10^{-11}
	1.00	17.66	31.24	35.34	1.24×10^{-6}	2.08×10^{-4}	1.14×10^{-11}
TiO ₂ @PEOx	0.20	56.48	102.40	122.50	2.63×10^{-6}	5.93×10^{-4}	5.19×10^{-11}
	0.40	36.58	67.00	76.50	1.70×10^{-6}	2.92×10^{-4}	2.41×10^{-11}
	0.60	34.81	55.70	65.30	1.64×10^{-6}	2.54×10^{-4}	1.35×10^{-11}
	0.80	15.49	43.08	46.10	1.50×10^{-6}	2.13×10^{-4}	1.16×10^{-11}
	1.00	13.30	29.33	34.30	1.23×10^{-6}	1.97×10^{-4}	1.08×10^{-11}

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