Supplementary Information

Ultrasmooth and Thin Pheomelanin-like Film as a Metal-Free Electrocatalytic Enhancer

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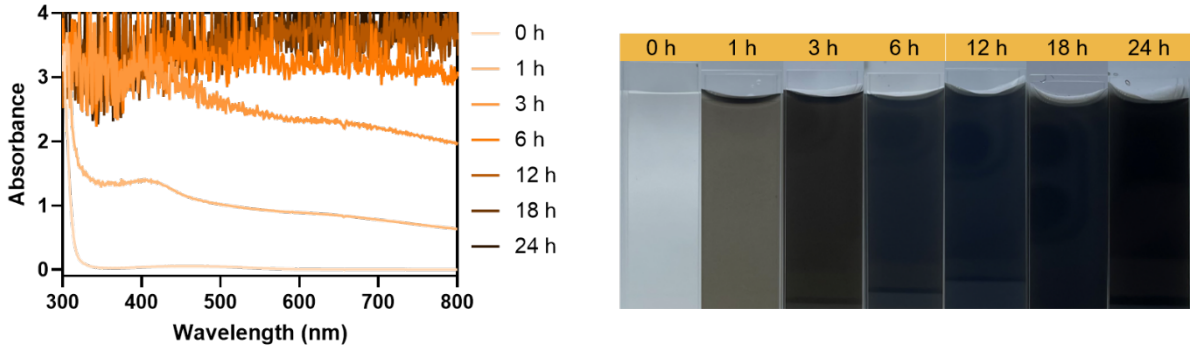

Figure S1. Rapid increase of light absorption in basic DA solution. (UV-Vis or photo).

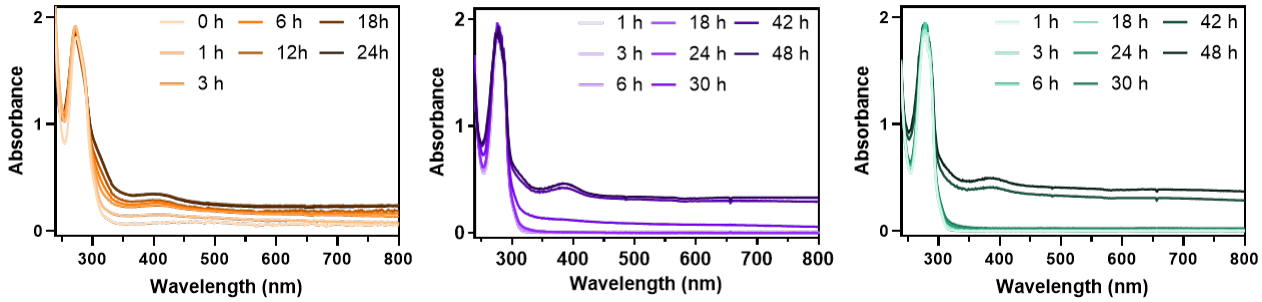

Figure S2. Time-dependent UV-vis spectra of solutions of DA (left), DA + CME (center) and DA + CEE (right; [DA]:[CXE] = 10:2 mM in the both cases). The solutions were diluted by 10 fold in order to better visualize the whole region.

Figure S3. Photos of a solution ([DA]:[CME] = 10:2 mM) before (left) and after (right) a burst.

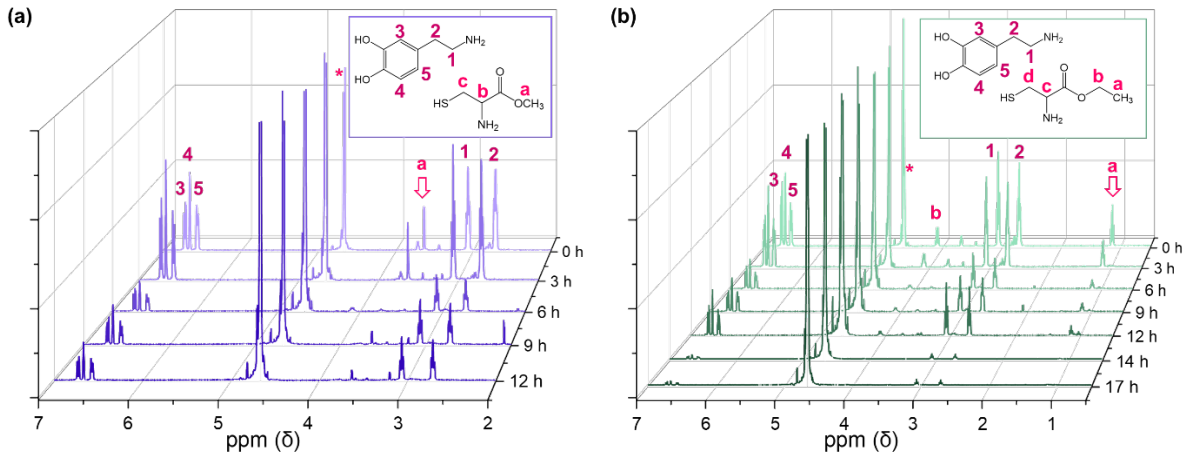

Figure S4. Time-dependent NMR spectra of solutions containing DA (10 mM) and (a) CME (2 mM) or (b) CEE (2 mM).

Table S1. Absorbances (405 nm) of solutions containing DA and CME (left) or CEE (right) at various concentrations in a 96-well plate at 52 h. Clear solutions (when observe by eyes) were marked green, blurred solutions were marked yellow, and dark brown solutions were marked red.

CME (mM)								A405, 52h
100	0.026	0.013	0.013	-0.002	0.013	-0.002	-0.001	
50	0.075	0.055	0.058	0.065	0.065	0.063	0.036	
20	0.067	0.036	0.044	0.035	0.081	0.029	0.024	
10	0.086	0.164	0.112	0.109	0.118	0.118	0.109	
5	0.116	0.08	0.101	0.082	0.09	0.087	0.087	
2	0.094	0.114	0.094	0.15	**1.804**	**3.157**	**3.276**	
1	0.097	0.189	**1.968**	**2.203**	**3.276**	**3.601**	**4.078**	
	1	2	5	10	20	50	100	DA (mM)

CEE (mM)								A405, 52h
100	0.06	0.055	0.045	0.047	0.044	0.051	0.064	
50	0.071	0.08	0.092	0.098	0.091	0.131	0.138	
20	0.134	0.097	0.119	0.125	0.174	0.461	**0.795**	
10	0.161	0.186	0.199	0.211	0.22	0.468	**1.031**	
5	0.199	0.149	0.169	0.194	0.254	**1.296**	**2.739**	
2	0.116	0.188	0.293	**0.866**	**1.787**	**2.75**	**3.926**	
1	0.137	0.156	**0.878**	**2.265**	**2.877**	**3.303**	**3.926**	
	1	2	5	10	20	50	100	DA (mM)

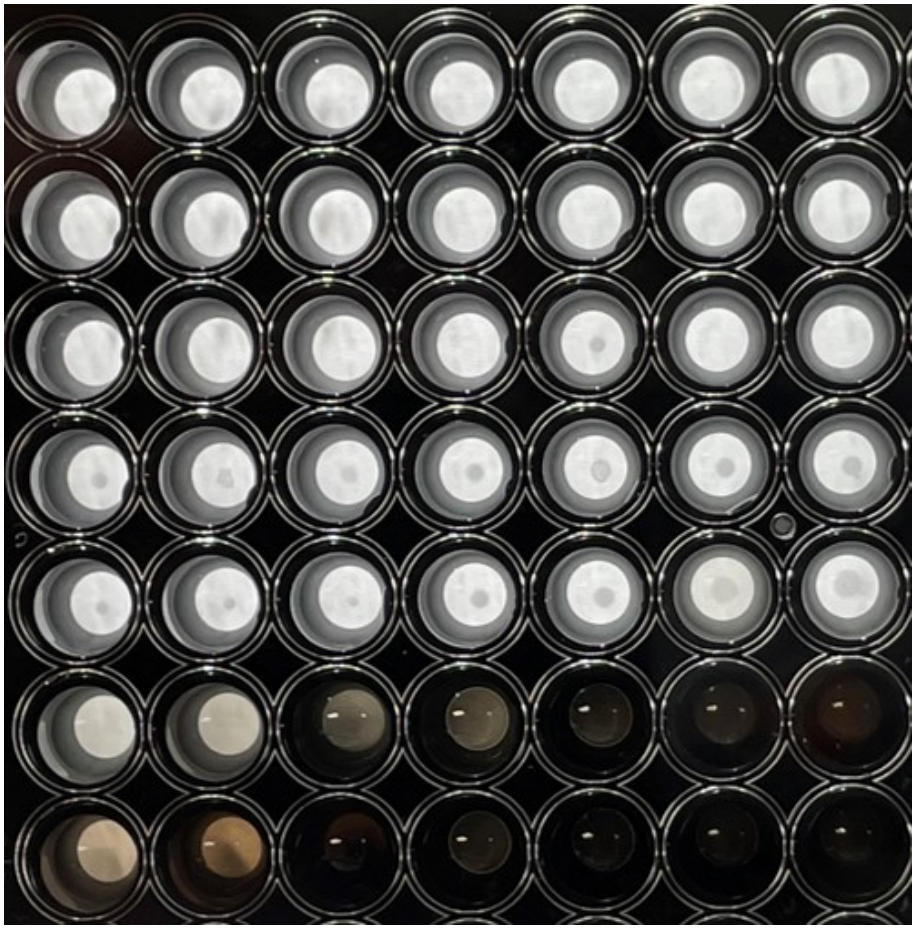

Figure S5. A representative photo of a 96-well plate containing the solutions of different conditions at 90 h (left to right direction: 1, 2, 5, 10, 20, 50 100 mM of [DA] and bottom to top direction: 1, 2, 5, 10, 20, 50, 100 mM of [CME]).

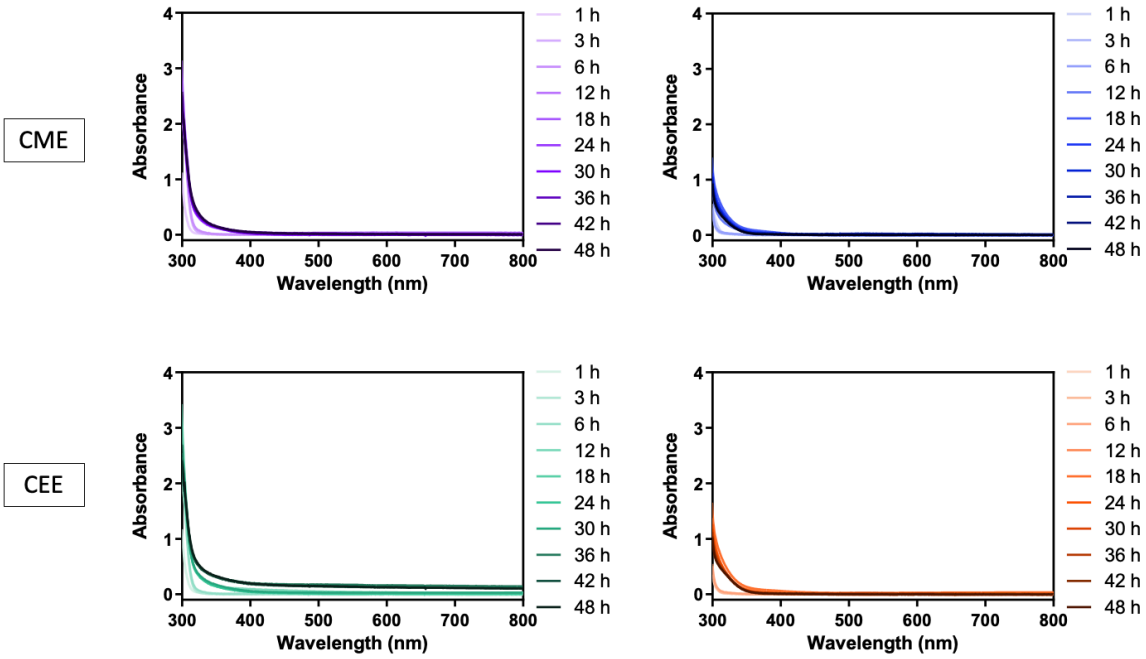

Figure S6. Time-dependent UV-vis spectra of solutions of DA and CME (top) or DA and CEE (bottom) in a glass vial. The concentrations of DA and CXE were 20 and 10 mM (left), or 10, and 20 mM (right), respectively.

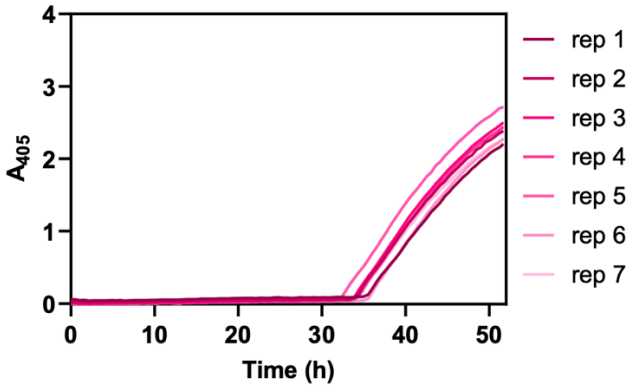

Figure S7. Repetitive measurement of temporal changes of A_{405} values at the same condition ([DA]:[CME] = 10:1 mM).

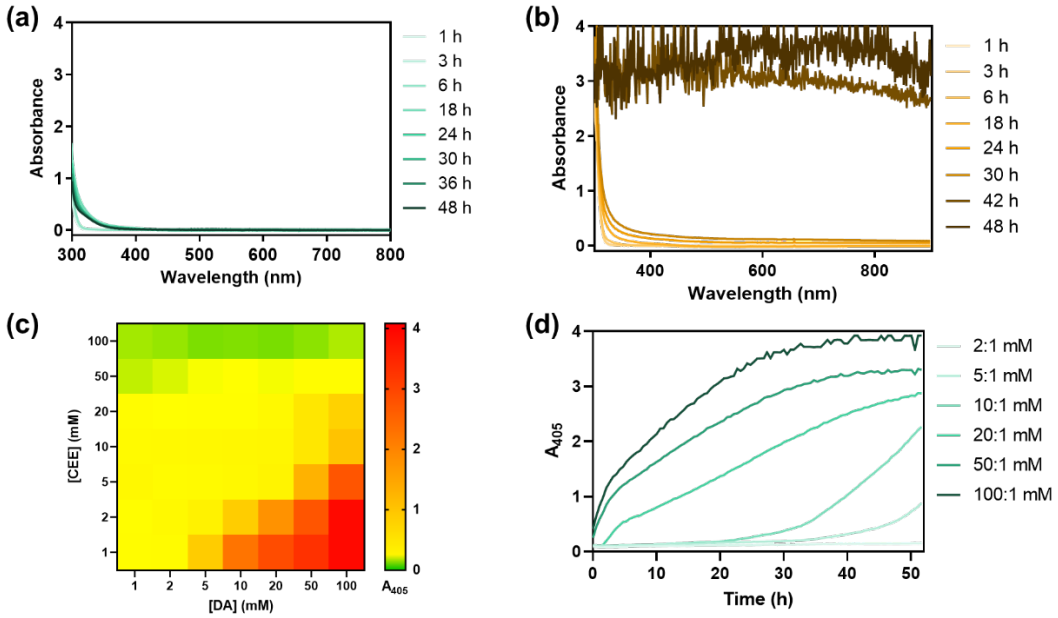

Figure S8. (a,b) Time-dependent UV-vis spectra of solutions of DA and CEE at (a) a non-bursting condition ([DA]:[CEE] = 10:10 mM) and (b) a bursting condition ([DA]:[CEE] = 10:2 mM). (c) Heat map presentation of A_{405} values of solution with various ratios of DA and CME at 52 h. (d) Temporal changes of A_{405} values for different ratios of [DA] and [CEE].

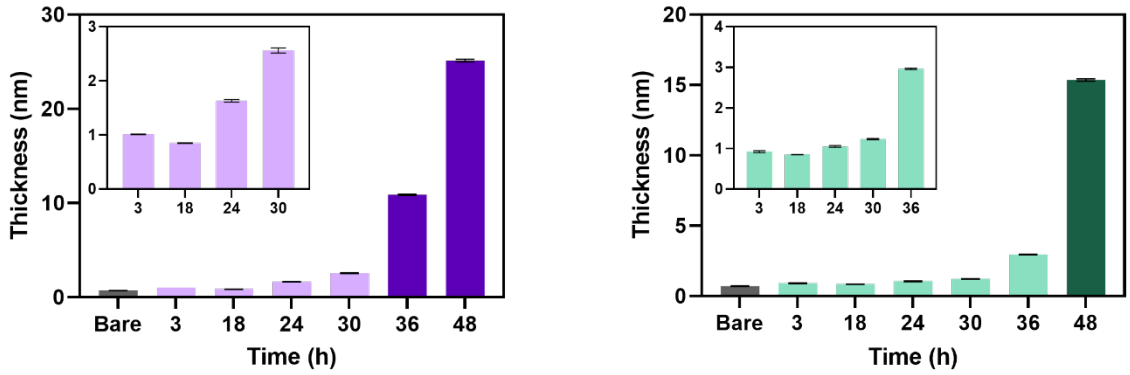

Figure S9. Time-dependent thickness of films coated on Si wafers with concentrations of DA and CXE (left: CME, right: CEE) of 10 and 2 mM, respectively. The burst occurred at around 36 h.

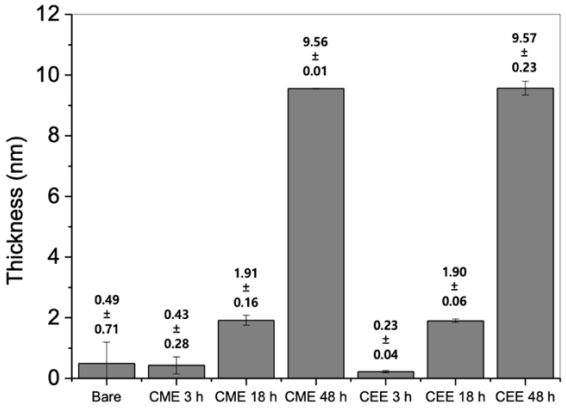

Figure S10. Growth of thin films on Au substrates ([DA]:[CXE] = 10:10 mM). A burst occurred around 36 h for both cases. The experiment was performed using the same reaction batch as the Si wafer coating experiment in Fig S9.

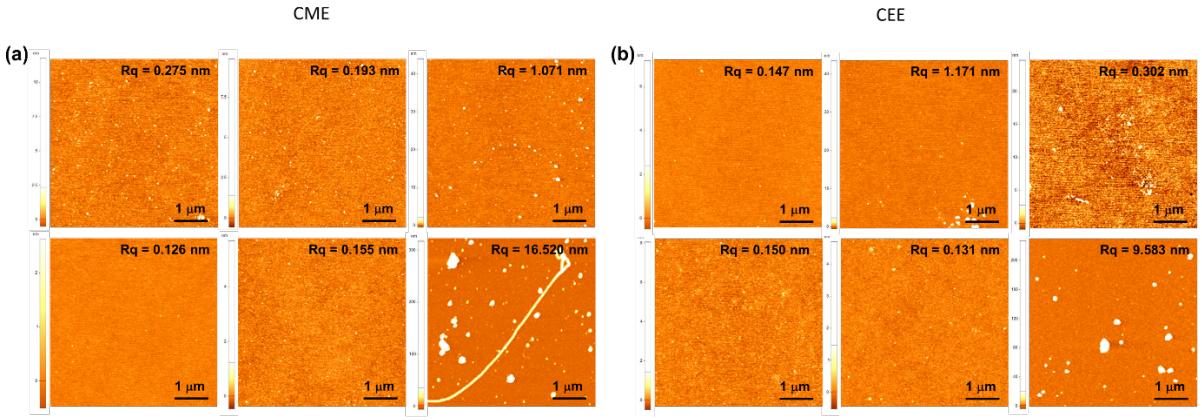

Figure S11. AFM images of (a) DA + CME and (b) DA + CEE films on Si wafers. The top three images of each group were obtained from a non-bursting condition ([DA]:[CXE] = 10:10 mM) and the bottom three images of each group were obtained from a bursting condition([DA]:[CXE] = 10:2 mM), respectively.

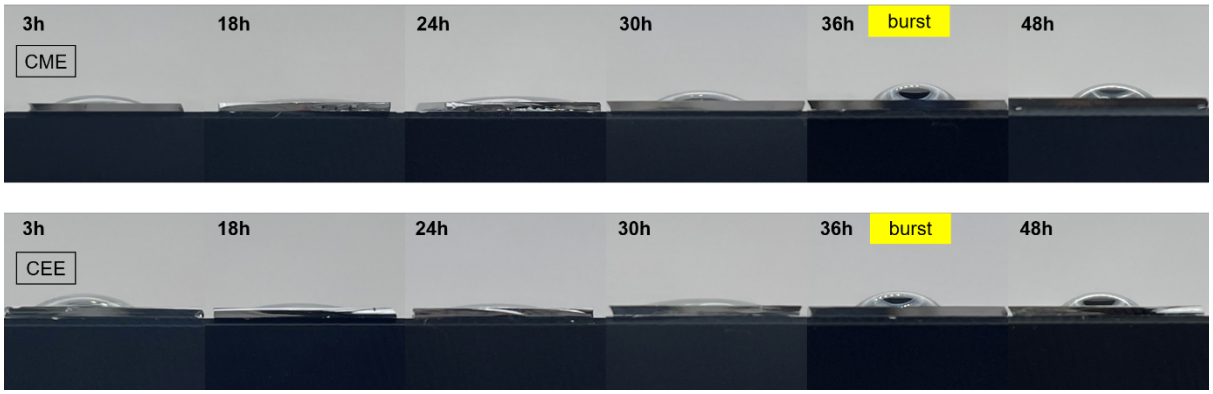

Figure S12. Photos of water drops on pheomelanin-like films on Si wafers coated with various conditions. All films were coated in solutions containing [DA]:[CXE] = 10:2 mM.

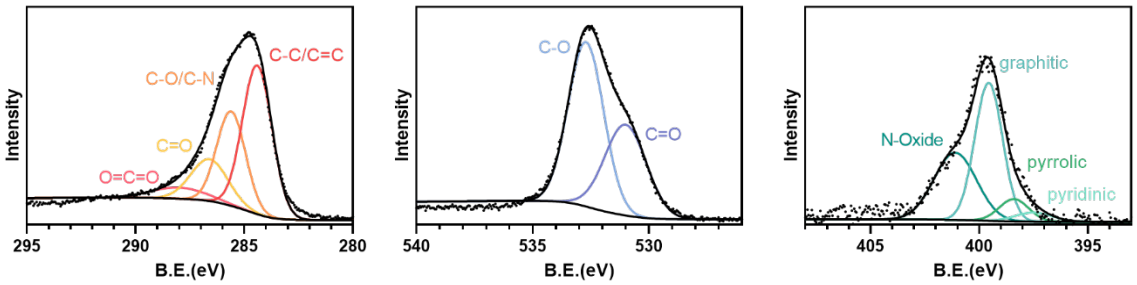

Figure S13. XPS data of DA + CME film after burst (48 h).

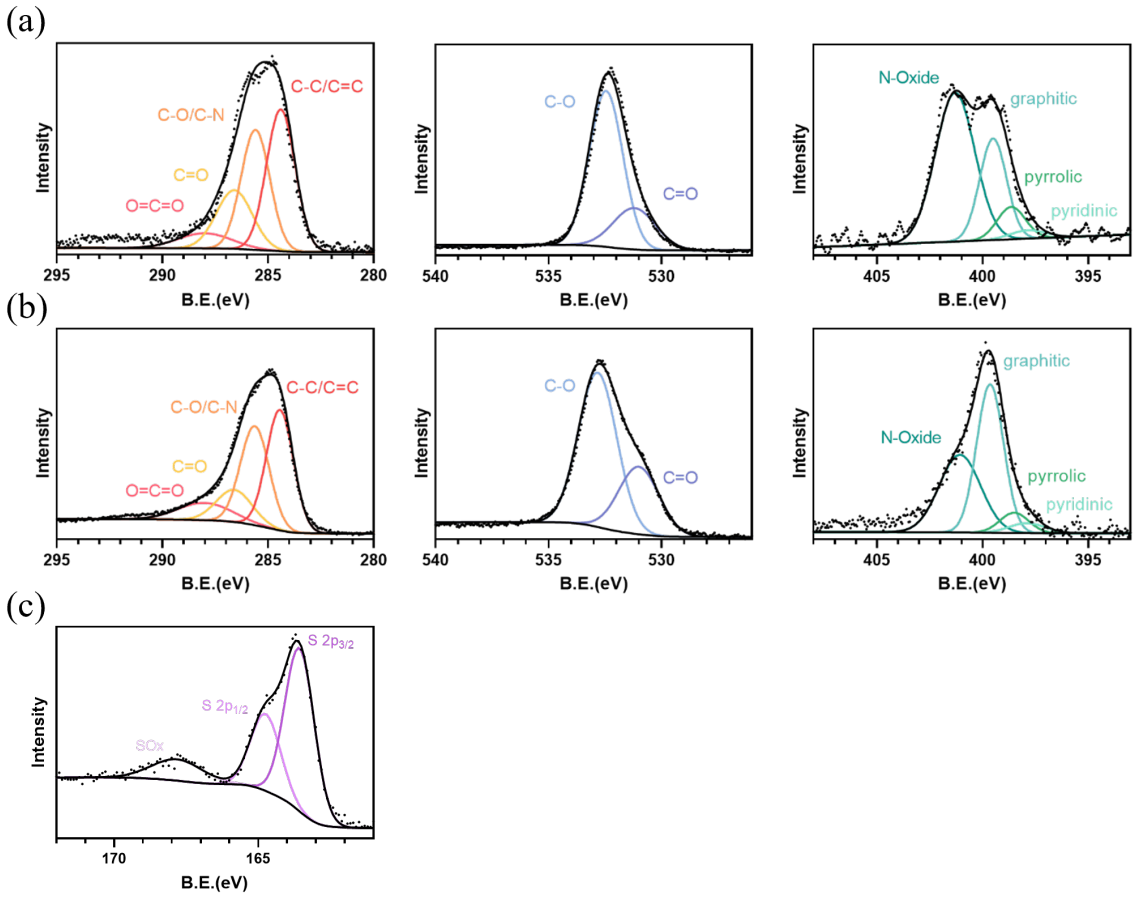

Figure S14. XPS data of DA + CEE films (a) before (18 h), and (b) after burst (48 h). (c) S 2p XPS high resolution spectra of DA+CEE film at the time the burst occurred (36 h). Concentration ratio [DA]:[CXE] = 10:2 mM.

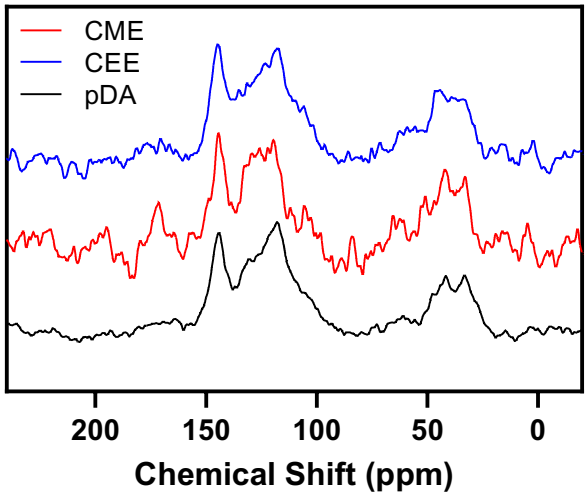

Figure S15. Solid-state ^{13}C CP-TOSS NMR spectra of DA + CME (Red), DA + CEE (Blue) and pDA (Black).

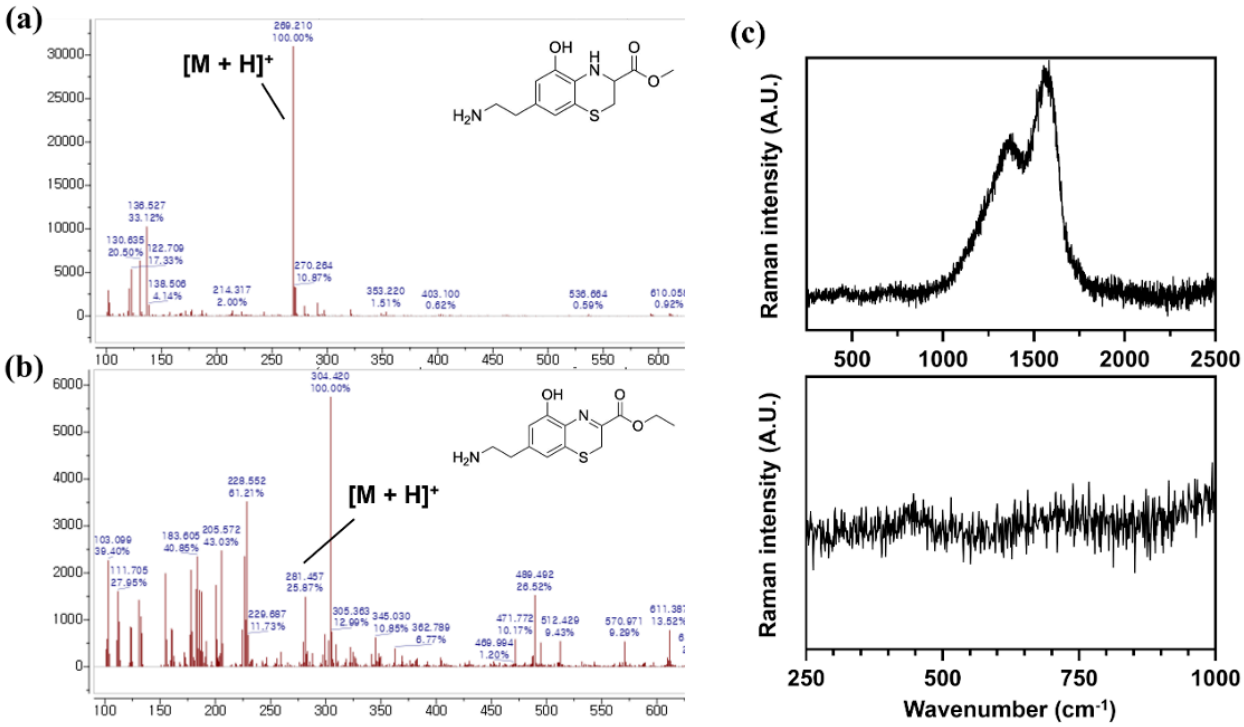

Figure S16. LC–MS and Raman characterization of products formed from dopamine (DA) with cysteine ester derivatives. (a,b) ESI+/MS spectra obtained from LC–MS analysis of aliquots collected after 23 h of reaction: (a) CME + DA and (b) CEE + DA. (c) Raman spectrum of the powder sample obtained from the CEE + DA reaction after 36 h. (d) Enlarged view of the pheomelanin fingerprint region from the Raman spectrum in (c), highlighting bands at 500–550 cm^{-1} and 700–750 cm^{-1}. Concentration ratio [DA]:[CXE] = 10:2 mM.

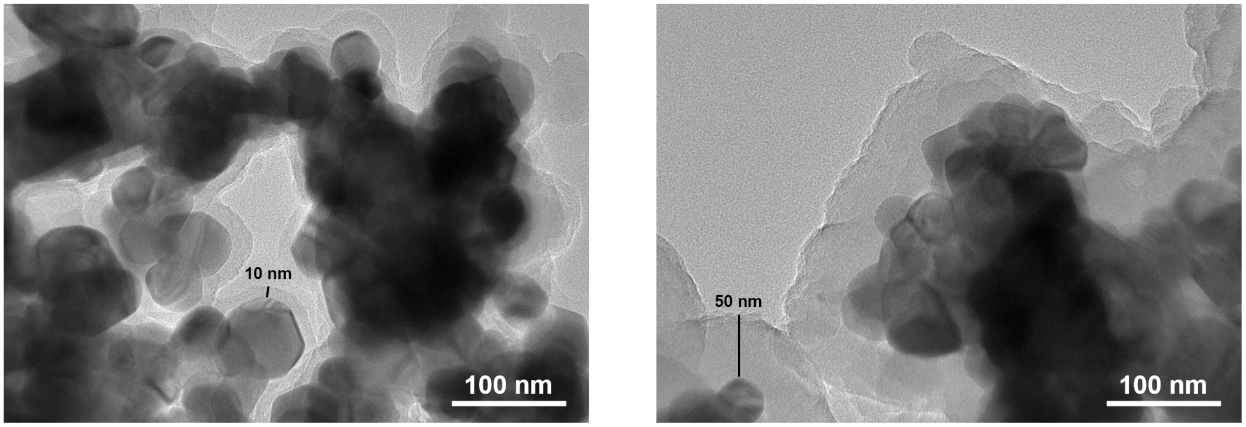

Figure S17. TEM image of RuO_2@pDA deposited for 1 h (left) and 48 h (right), with the corresponding film thickness values indicated in each image.

Table S2. Overview of pDA thin film studies via various methods.

Ref.	Substrates	Methods	Conditions	Time (hour)	Thickness (nm)	Comments
39	Glass	AFM	2 mg/mL DA in 10 mM pH 8.5 Tris buffer	1	4–6	
				2	9–10	
				6	18–22	
40	TiO_2	Ellipsometry	0.25 mg/mL DA in 10 mM pH 8.5 Tris buffer	12	< 5	
			0.5 mg/mL DA in 10 mM pH 8.5 Tris buffer	12	~ 15	
41	Au	AFM, SEM	1 mg/mL of DA in 100 mM pH 7.0 phosphate buffer	-	~ 11	5 CV cycles (±0.5 V)
					< 14	10 CV cycles (±0.5 V)
					~ 10	100 pulses (pulse cycles:+0.5 V/2 s; 0 V/2 s; −0.3 V/2 s; and 0 V/3 s)
					< 14	150 pulses (pulse cycles:+0.5 V/2 s; 0 V/2 s; −0.3 V/2 s; and 0 V/3 s)
42	Si wafer	AFM	2 mg/mL DA in 50 mM pH 8.5 Tris buffer	2	7.5	AFM scratch height
		Ellipsometry			5.88–6.50	5.88 ± 0.107 nm (Cauchy model), 6.50 ± 0.021 nm (Cauchy with Urbach absorption model)
43	Mica	AFM	2 mg/mL DA in 10 mM pH 8.5 Tris buffer	60–540 sec	0.5–1.1	Complete pDA layer formed at 300 sec.
44	Template stripped gold (TSG)	XPS	1 mg/mL DA in 100 mM pH 8.5 Carbonate/bicarbonate buffer	1	~ 8	Thickness of polydopamine films determined from attenuation of Au 4f XPS signal intensity as a function of deposition time.

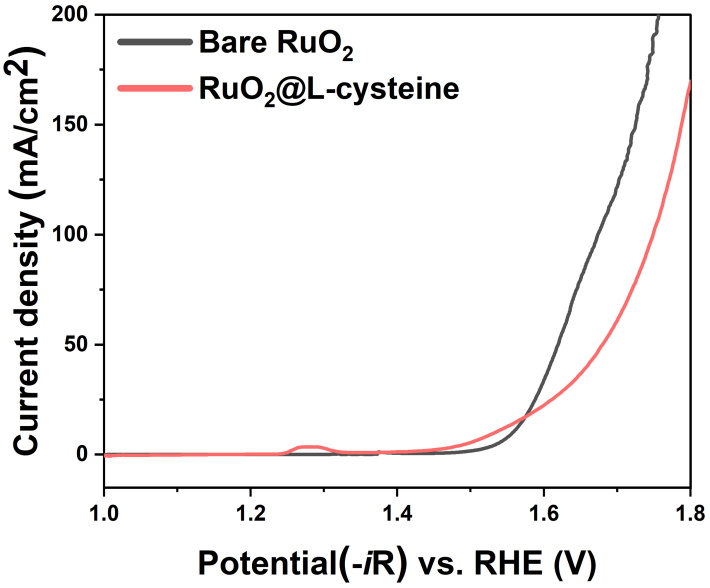

Figure S18. A linear sweep voltammetry (LSV) curves of Bare RuO_2 and RuO_2@*L*-cysteine measured in 1M KOH. RuO_2@L-cysteine denotes RuO_2 particles coated by immersion in an aqueous solution containing dopamine and *L*-cysteine.

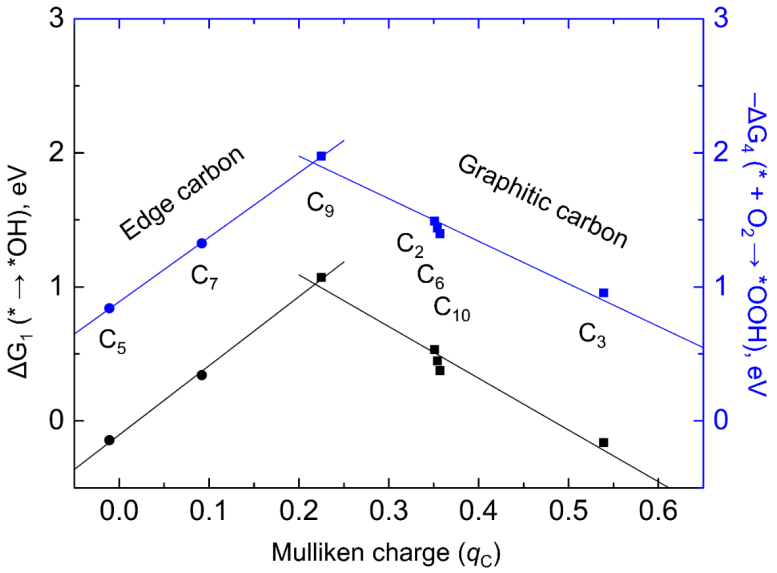

Figure S19. Gibbs free energy changes of *OH adsorption, ΔG_1 ($* + OH^- \rightarrow *OH + e^-$, black, left y axis), and *OOH adsorption, $-\Delta G_4$ ($* + O_2 + H_2O + e^- \rightarrow *OOH + OH^-$, blue, right y axis) according to Mulliken charge of carbon atoms (x axis). Round and square marks indicate edge and graphitic carbon atoms, respectively.

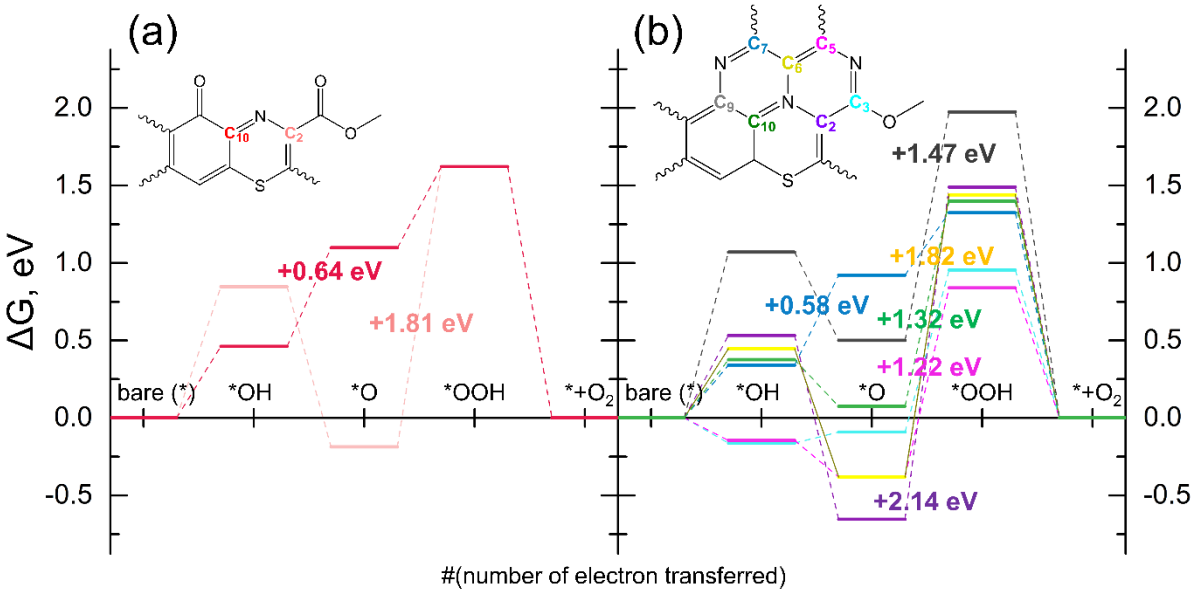

Figure S20. Gibbs free energy changes of oxygen evolution reaction at diverse carbon sites in the structure (a) without graphitic nitrogen and (b) with graphitic nitrogen. The numbers are the thermodynamic barriers at the potential determining steps.

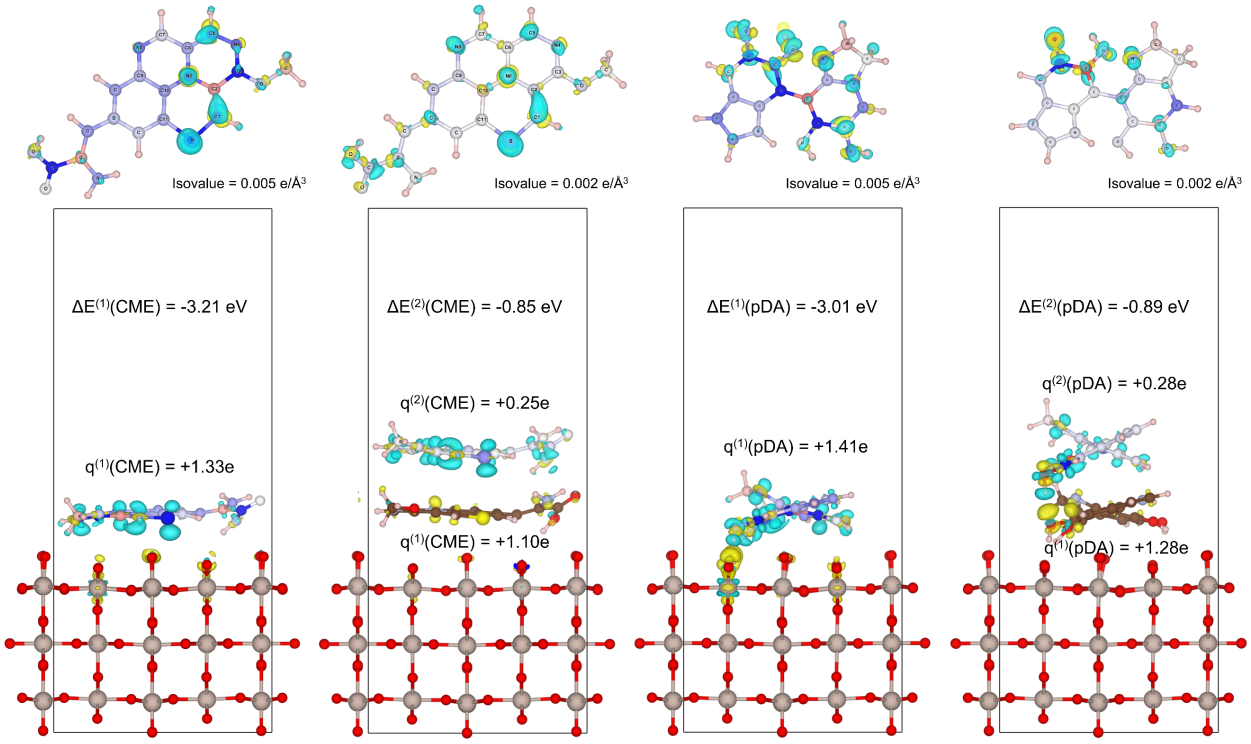

Figure S21. Theoretically estimated adsorption affinity and charge transfer efficiency of organic films on RuO_2 (110) surface. Bader charge differences by adsorption of the primary and secondary molecules, $q^{(1)}$ and $q^{(2)}$ (atom-decomposed Bader charges are coloured as red for -0.1e to blue for +0.1e, respectively), and the corresponding adsorption energies, $\Delta E^{(1)}$ and $\Delta E^{(2)}$, respectively. Charge density differences by adsorption of the first and second molecules are shown as isosurfaces, coloured by cyan and yellow for electron depletion and accumulation, respectively.