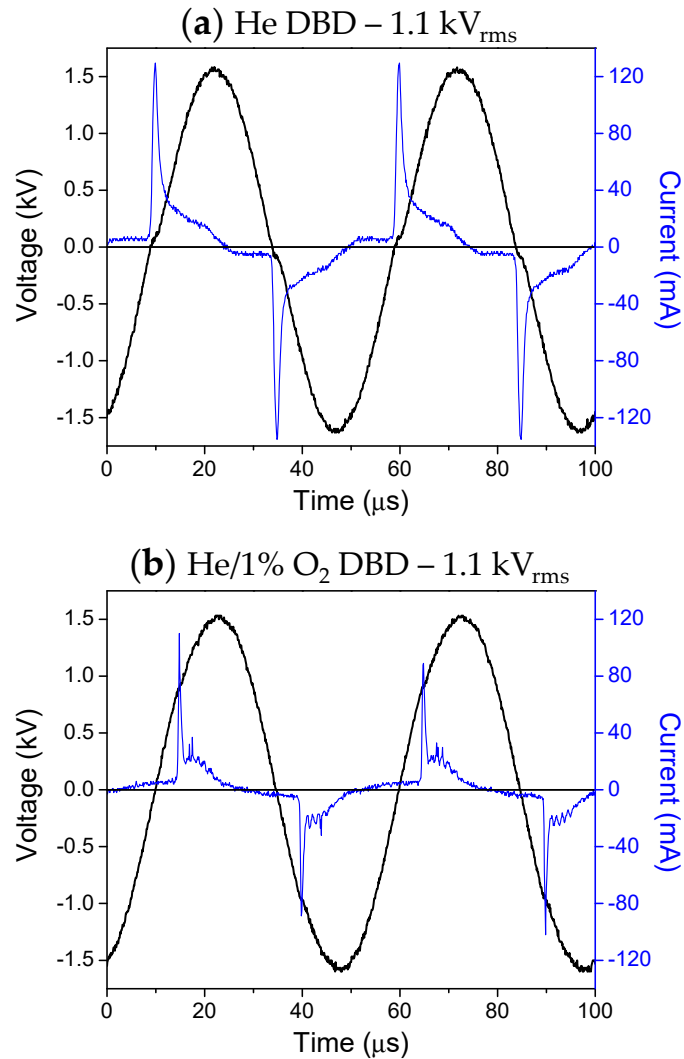
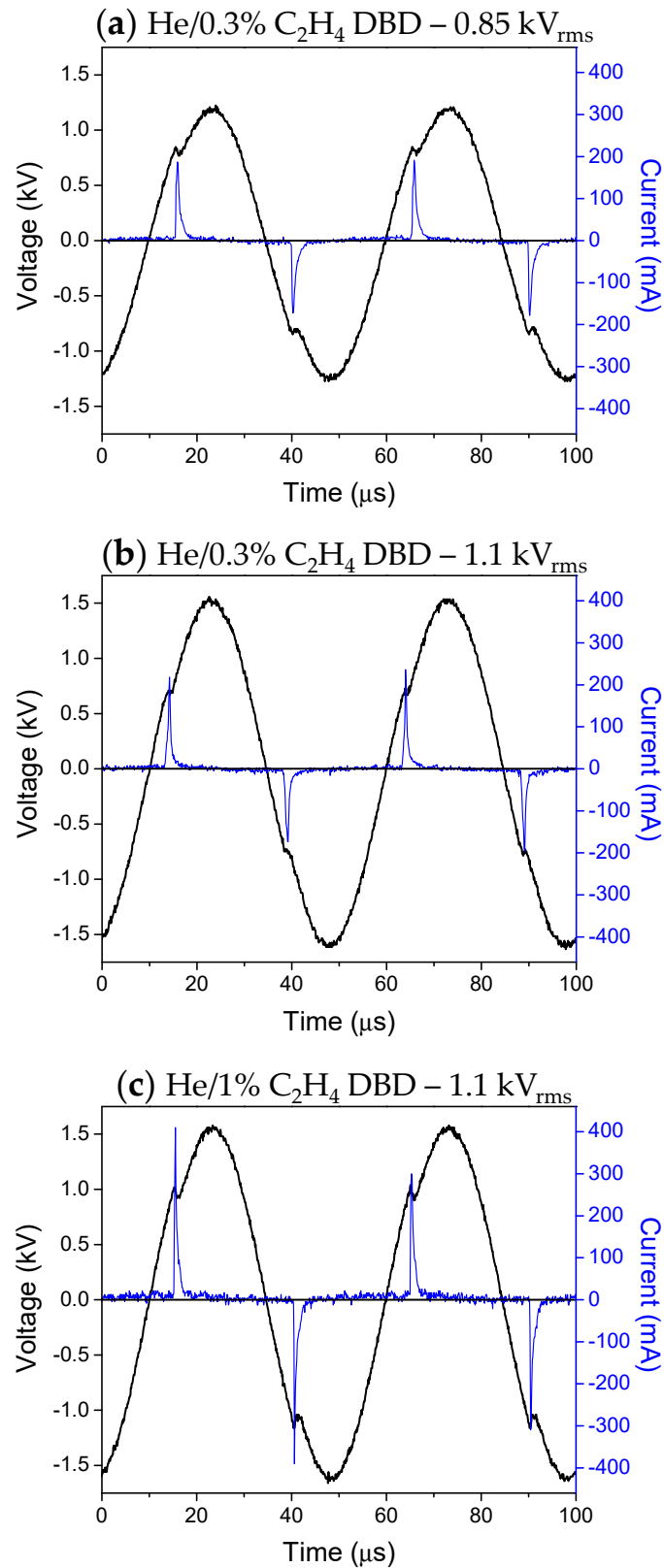


Supplementary Material

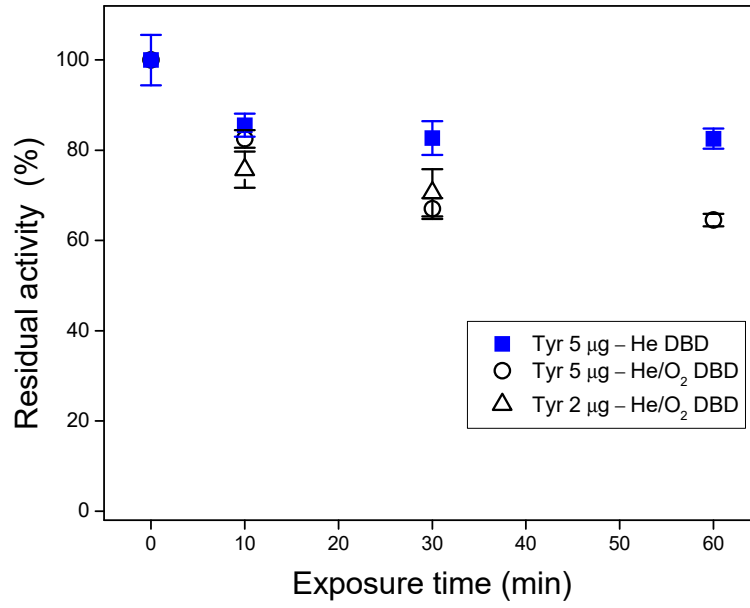
# Direct Exposure of Dry Enzymes to Atmospheric Pressure Non-Equilibrium Plasmas: The Case of Tyrosinase



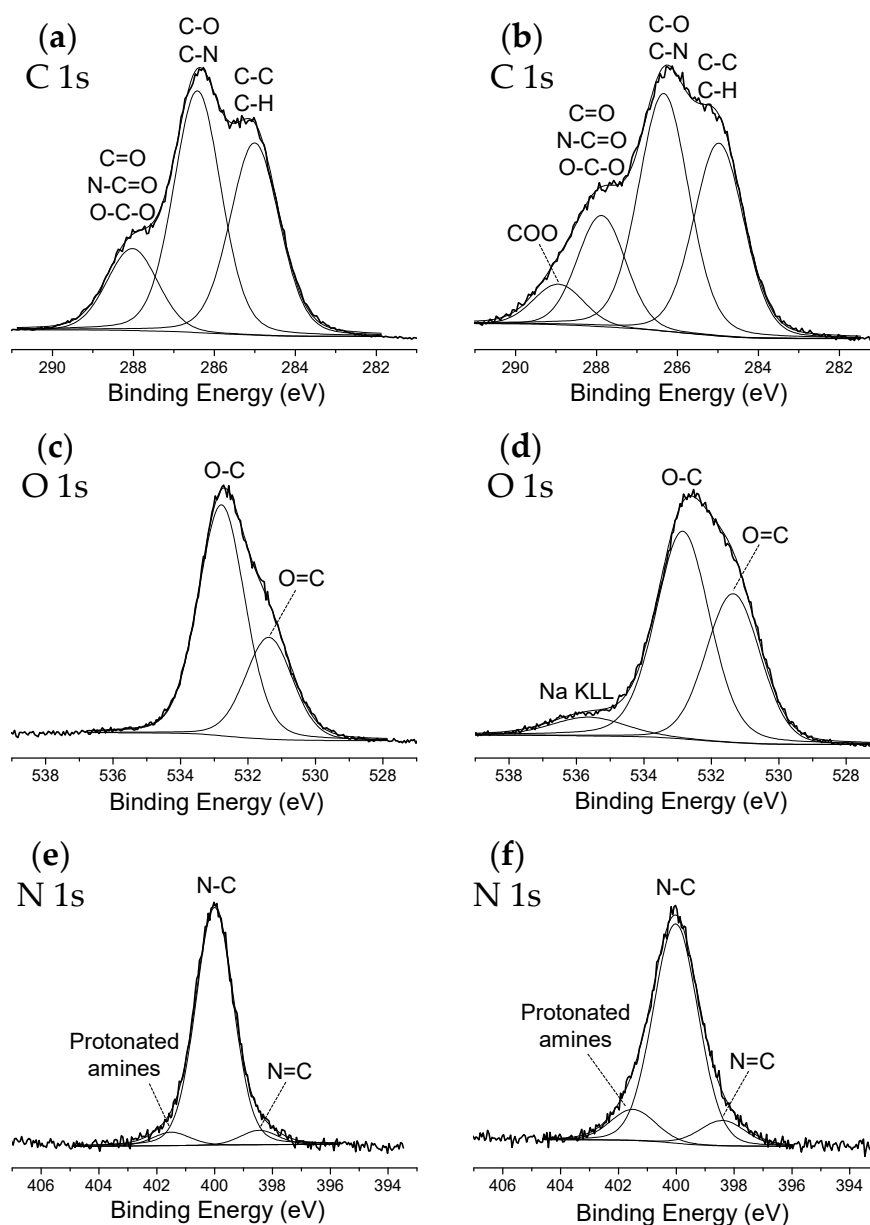
**Figure S1.** Voltage and current signals of (a) a pure He DBD and (b) a He/1% O<sub>2</sub> fed DBD ( $f = 20$  kHz,  $V_a = 1.1$  kV<sub>rms</sub>).



**Figure S2.** Voltage and current signals of He/C<sub>2</sub>H<sub>4</sub> fed DBDs generated at 20 kHz under different experimental conditions (Table 1): (a) [C<sub>2</sub>H<sub>4</sub>] = 0.3%, V<sub>a</sub> = 0.85 kV<sub>rms</sub>; (b) [C<sub>2</sub>H<sub>4</sub>] = 0.3%, V<sub>a</sub> = 1.1 kV<sub>rms</sub>; (c) [C<sub>2</sub>H<sub>4</sub>] = 1%, V<sub>a</sub> = 1.1 kV<sub>rms</sub>.



**Figure S3.** Residual activity of tyrosinase (2 and 5 µg) exposed to DBDs fed with He and He/1% O<sub>2</sub> mixture as a function of the exposure time ( $f = 20$  kHz,  $V_a = 1.1$  kV<sub>rms</sub>).



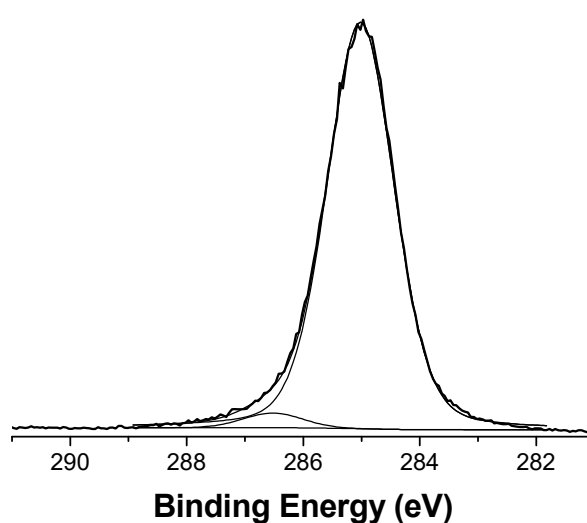
**Figure S4.** High-resolution XPS C 1s, O 1s and N 1s spectra of a 5 µg Tyr deposit (a)-(c)-(e) before and (b)-(d)-(f) after exposure to a DBD fed with He/1% O<sub>2</sub> mixture for 30 min ( $f = 20$  kHz,  $V_a = 1.1$  kV<sub>rms</sub>).

**Table S1.** Curve fitting results of high-resolution C 1s, O 1s and N 1s XPS spectra of the a 5 µg Tyr deposit before and after 30 min exposure to a DBD fed with He/1% O<sub>2</sub> mixture ( $f = 20$  kHz,  $V_a = 1.1$  kV<sub>rms</sub>).

Component Assignment	Position (eV)	Pristine Tyr - Control	Tyr - He/1% O <sub>2</sub> DBD
		Component Peak Area %	Component Peak Area %
C-C/C-H	284.8 ± 0.2	37	32
C-N/C-O	286.3 ± 0.2	46	41
C=O/N-C=O/O-C-O	288.1 ± 0.2	17	20
COO	289.0 ± 0.2	-	7
O=C	531.4 ± 0.2	31	45
O-C	532.8 ± 0.2	69	55
N=C	398.4 ± 0.2	5	9
N-C	400.0 ± 0.2	90	79
Protonated amine groups	401.5 ± 0.2	5	12

**Table S2.** Deposition rate (DR) of the polyethylene-like coating under the PECVD conditions investigated in the present work.

Feed Mixture	f (kHz)	V <sub>a</sub> (kV <sub>rms</sub> )	P <sub>s</sub> (W·cm <sup>-2</sup> )	Φ <sub>He</sub> (slm)	[C <sub>2</sub> H <sub>4</sub> ] (%)	DBD Regime	DR (nm·min <sup>-1</sup> )
He/C <sub>2</sub> H <sub>4</sub>	20	0.85	0.25 ± 0.05	8	0.1	Homogeneous	23.0 ± 1.0
He/C <sub>2</sub> H <sub>4</sub>	20	0.85	0.25 ± 0.05	8	0.3	Homogeneous	27 ± 2
He-C <sub>2</sub> H <sub>4</sub>	20	0.85	0.25 ± 0.05	8	0.5	Homogeneous	31 ± 2
He/C <sub>2</sub> H <sub>4</sub>	20	1.10	0.40 ± 0.04	8	0.3	Homogeneous	30 ± 3
He/C <sub>2</sub> H <sub>4</sub>	20	1.10	0.40 ± 0.04	8	0.5	Homogeneous	34 ± 3
He-C <sub>2</sub> H <sub>4</sub>	20	1.10	0.40 ± 0.04	8	1.0	Filamentary	43 ± 2



**Figure S5.** High-resolution XPS C 1s spectrum of the polyethylene-like coating deposited on Tyr (5 μg) by using a He/0.1% C<sub>2</sub>H<sub>4</sub> fed DBD (f = 20 kHz, V<sub>a</sub> = 0.85 kV<sub>rms</sub>, t = 10 min, thickness of the coating = 230 ± 10 nm).



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