## Supporting Information

## Engineered biochar derived from pyrolyzed waste tea as a carbon support for

## Fe-N-C electrocatalysts for the oxygen reduction reaction

Stefano Zago<sup>1</sup>, Mattia Bartoli<sup>2,3</sup>, Mohsin Muhyuddin<sup>4</sup>, Giovanni M. Vanacore<sup>4</sup>, Pravin Jagdale<sup>2</sup>,

Alberto Tagliaferro<sup>1,3</sup>, Carlo Santoro<sup>4</sup>, Stefania Specchia<sup>1\*</sup>



Figure S1. XPS survey spectra of Fe-N-C<sub>pyro-tea</sub> (a); Fe-N-C<sub>CO2-tea</sub> (b), and Fe-N-C<sub>urea-tea</sub> (c).

**Table S1.** Main elements peak binding energies (b.e.) and relative areas (r.a.) for the three Fe-N-C electrocatalysts synthesized, from the deconvolution of the high-resolution peaks from XPS analysis

		Fe-N-Cpyro-tea		Fe-N-Cco2-tea		Fe-N-Curea-tea	
		b.e. [eV]	r.a. [%]	b.e. [eV]	r.a. [%]	b.e. [eV]	r.a. [%]
C 1s	C-sp <sup>3</sup>	284.4	12.0	n.d.	n.d.	284.3	11.2
	C-sp <sup>2</sup>	284.9	51.2	284.6	50.2	284.9	45.4
	C–OH	285.4	26.6	285.7	25.6	285.6	33.9
	C=O	288.4	5.5	288.9	21.8	288.7	6.7
	COOH	292.9	3.6	292.7	1.7	292.8	1.8
	$\pi$ – $\pi$ *	295.8	1.1	295.8	0.7	295.5	1.0
N 1s	N1	398.6	40.6	398.5	25.2	398.6	52.4
	N2	400.0	59.4	400.2	74.8	400.0	47.6
O 1s	C–OH	529.9	24.5	530.9	23.6	530.9	31.5
	С=О	531.5	61.1	531.9	67.1	531.9	38.2
	СООН	533.1	14.5	533.6	9.3	533.4	30.3
Fe 2p3	Fe(II)	710.6	55.1	710.6	78.1	710.9	68.1
	Fe(III)	712.5	44.9	712.5	21.9	712.5	31.9

(N1: pyridinic-N; N2: pyrrolic-N; n.d.: not determined).



Figure S2. Raman spectra of C<sub>pyro-tea</sub> (A), Fe-N-C<sub>pyro-tea</sub> (B), Fe-N-C<sub>CO2-tea</sub> (C) and Fe-N-C<sub>urea-tea</sub>

(D).



Figure S3. Cumulative pore volume (A) and dV/dw pore volume (B) for the three Fe-N-C electrocatalysts according to the N<sub>2</sub> @ 77 K on Carbon Slit Pores NL-DFT model by Micromeritics software.



Figure S4. SCV curves of the starting materials:  $C_{pyro-tea}$ , (pyrolized tea leaves without further activation treatment) and Fe-Pc recorded in RDE at room temperature, in N<sub>2</sub>-saturated 0.1 M KOH solution, scan rate 10 mV s<sup>-1</sup>, electrode loading 400 µg cm<sup>-2</sup>.



**Figure S5.** SCV curves of different amounts (150 and 200 mg) of  $C_{pyro-tea}$  and Fe-Pc in the translational mixer for ball milling: recorded in RDE at room temperature, in N<sub>2</sub>-saturated 0.1 M KOH solution, scan rate 10 mV s<sup>-1</sup>, electrode loading 400 µg cm<sup>-2</sup>.  $C_{pyro-tea}$  : Fe-Pc ratio = 2:1.

Milling time: 99 min.



Figure S6. SCV curves of different  $C_{pyro-tea}$ : Fe-Pc ratios (2:1 / 3:1 / 4:1) in the translational mixer for ball milling: recorded in RDE at room temperature, in N<sub>2</sub>-saturated 0.1 M KOH solution, scan rate 10 mV s<sup>-1</sup>, electrode loading 400 µg cm<sup>-2</sup>.  $C_{pyro-tea}$  + Fe-Pc amount = 200 mg. Milling time: 99

min.



Figure S7. LSV curves of Fe-N-C<sub>pyro-tea</sub> (A), Fe-N-C<sub>CO2-tea</sub> (B), and Fe-N-C<sub>urea-tea</sub> (C) at different rotation speeds of the RDE, recorded at room temperature, in O<sub>2</sub>-saturated 0.1 M KOH solution (scan rate 1 mV s<sup>-1</sup>, electrode loading 400  $\mu$ g cm<sup>-2</sup>).



**Figure S8.** Chronoamperometric curves performed at 0.6 V vs RHE for 5,000 s, on Fe-N-C<sub>CO2-tea</sub>, Fe-N-C<sub>urea-tea</sub>, and Pt/C, in 0.1 KOH solution, saturated with O<sub>2</sub>, rotation speed 900 rpm (electrode loading 400  $\mu$ g cm<sup>-2</sup>, 30  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup> for Pt/C).



Figure S9. XRD spectra of Fe-N-C<sub>CO2-tea</sub> (A) and Fe-N-C<sub>urea-tea</sub> (B) from 15 up to 85 2 $\theta$ . Peaks attributed to Fe<sub>3</sub>O<sub>4</sub> are marked with \*.