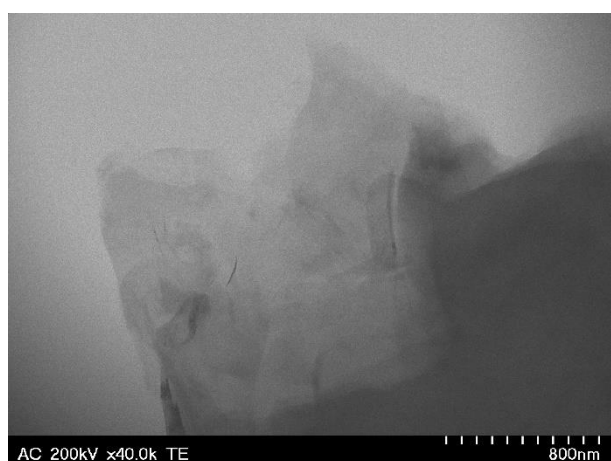*Supplementary Materials*

Eco-Friendly Nitrogen-Doped Graphene Preparation and Design for the Oxygen Reduction Reaction

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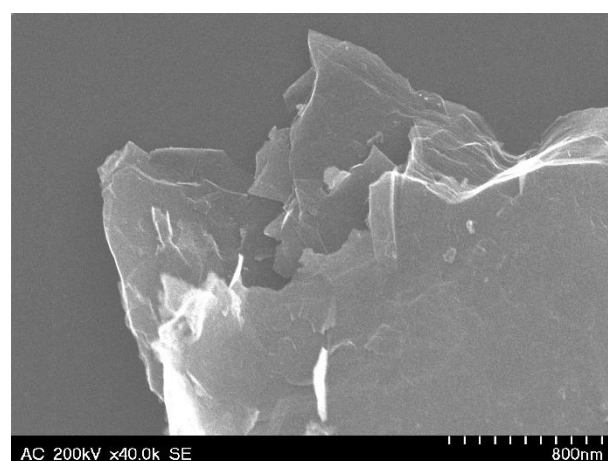
[1] National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat Street, 400293 Cluj-Napoca, Romania; monica.dan@itim-cj.ro (M.D.); sebastian.porav@itim-cj.ro (S.A.P.); cristian.leostean@itim-cj.ro (C.L.); gheorghe.borodi@itim-cj.ro (G.B.)

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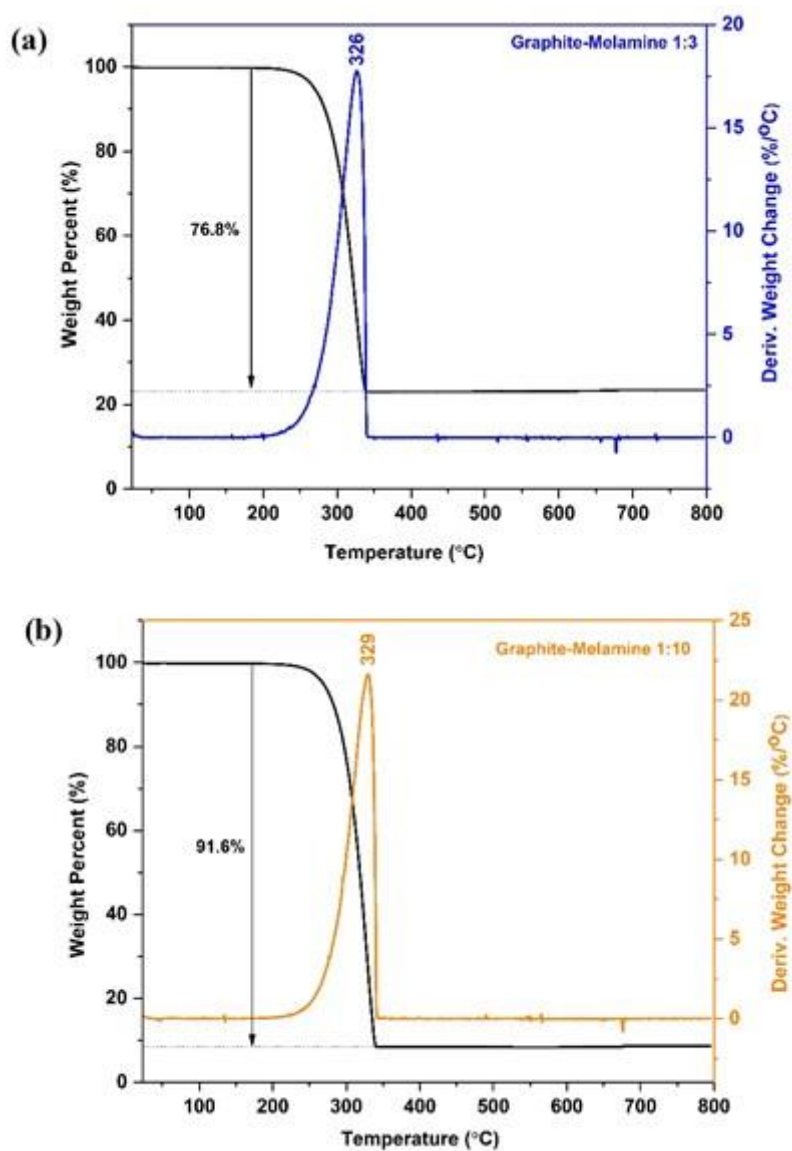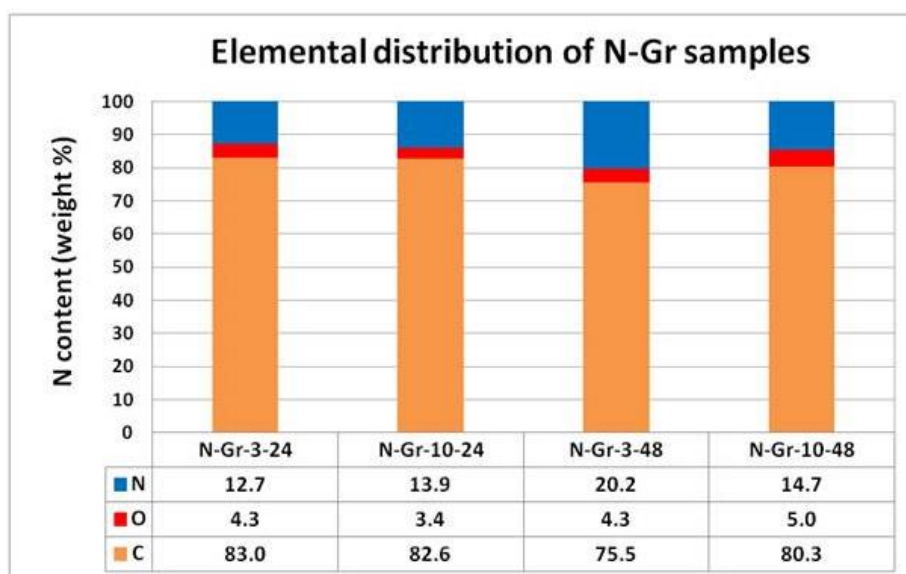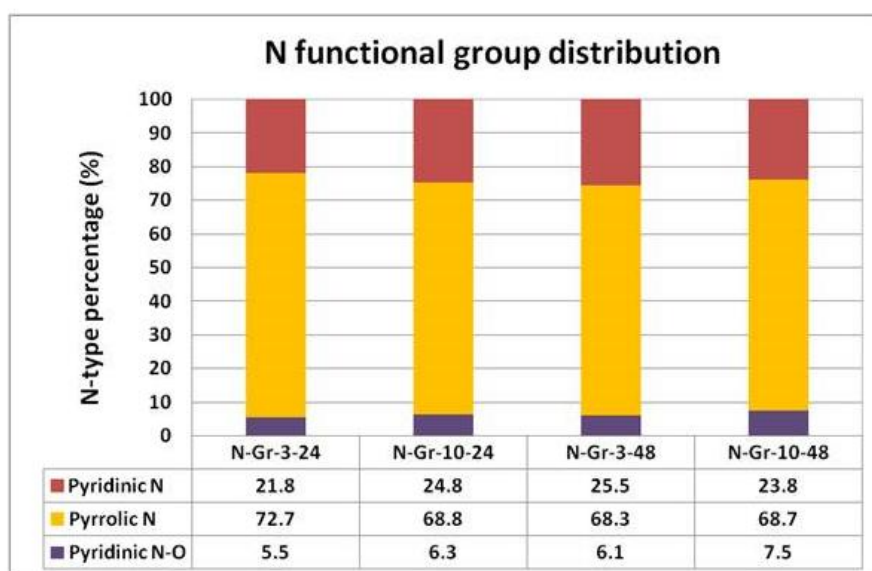**Figure S1. (a)** TEM and **(b)** SEM images for graphite.

Figure S2. TGA data of **(a)** 1:3 and **(b)** 1:10 graphite–melamine mixtures obtained under the argon atmosphere.

Elemental distribution of N-Gr samples

N content (weight %)

	N-Gr-3-24	N-Gr-10-24	N-Gr-3-48	N-Gr-10-48
■ N	12.7	13.9	20.2	14.7
■ O	4.3	3.4	4.3	5.0
■ C	83.0	82.6	75.5	80.3

(a)

N functional group distribution

N-type percentage (%)

	N-Gr-3-24	N-Gr-10-24	N-Gr-3-48	N-Gr-10-48
■ Pyridinic N	21.8	24.8	25.5	23.8
■ Pyrrolic N	72.7	68.8	68.3	68.7
■ Pyridinic N-O	5.5	6.3	6.1	7.5

(b)

Figure S3. (a) Elemental (wt.%) and **(b)** N-functional groups' distribution in the four types of N-doped graphene hybrid materials.
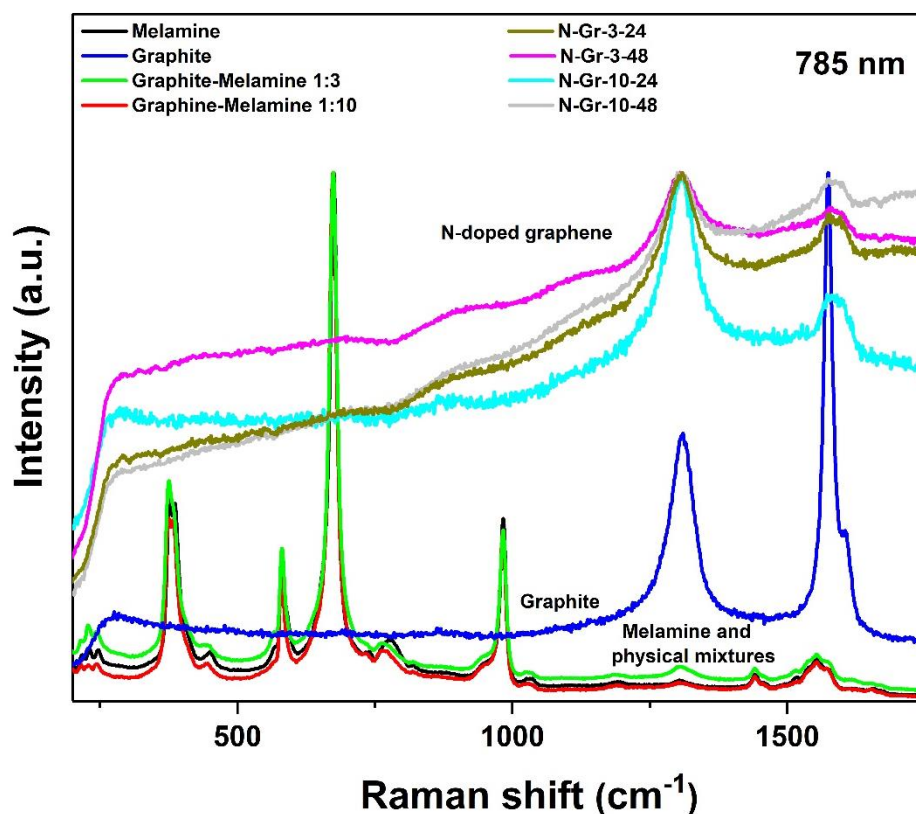
Table S1. Carbon types distribution (at%) obtained from XPS.

N-doped Graphene	Csp²	Csp³	C-N	C-O	C=O	Csp²/Csp³
N-Gr-3-24	36.8	39.2	8.5	5.8	9.8	0.94
N-Gr-10-24	37.7	38.8	6.8	6.2	10.5	0.97
N-Gr-3-48	31.5	41.1	7.3	4.3	15.8	0.77
N-Gr-10-48	37.7	41.2	4.8	3.1	13.3	0.92

Table S2. XRD parameters obtained for the graphite and the N-doped graphene materials.

Carbon-Based Materials	2θ (°)	FWHM (°)	D (nm)	d (nm)	~n
Graphite	26.39	0.255	44.2	0.337	131
N-Gr-3-24	26.134	2.599	3.23	0.341	10 (9.5)
N-Gr-10-24	26.181	1.886	4.5	0.340	13
N-Gr-3-48	23.24	2.794	3.0	0.339	9 (8.8)
N-Gr-10-48	26.142	2.713	3.09	0.341	9 (9.1)

Where: θ—angle of diffraction; FWHM—full width of peaks at half maxima; D—crystallite size; d—interlayer spacing; n—number of graphene sheets.

Figure S4. Raman spectra (excitation 785 nm) of the graphite, melamine, 1:3 and 1:10 graphite–melamine mixtures and N-doped graphene materials obtained by ball milling procedure.

Table S3. Raman parameters obtained for the N-doped graphene materials.

N-Doped Graphene	I_D/I_G	$I_{D'}/I_G$	I_{2D}/I_G	$I_D/I_{D'}$	N wt%
Graphite	0.15	*0.03*	*0.54*	5.83	–
N-Gr-3-24	2.02	*0.51*	*0.38*	3.94	9.61
N-Gr-10-24	1.58	*0.41*	*0.46*	3.90	8.34
N-Gr-3-48	2.00	*0.56*	*0.32*	3.54	13.1
N-Gr-10-48	1.95	*0.53*	*0.37*	3.70	11.4

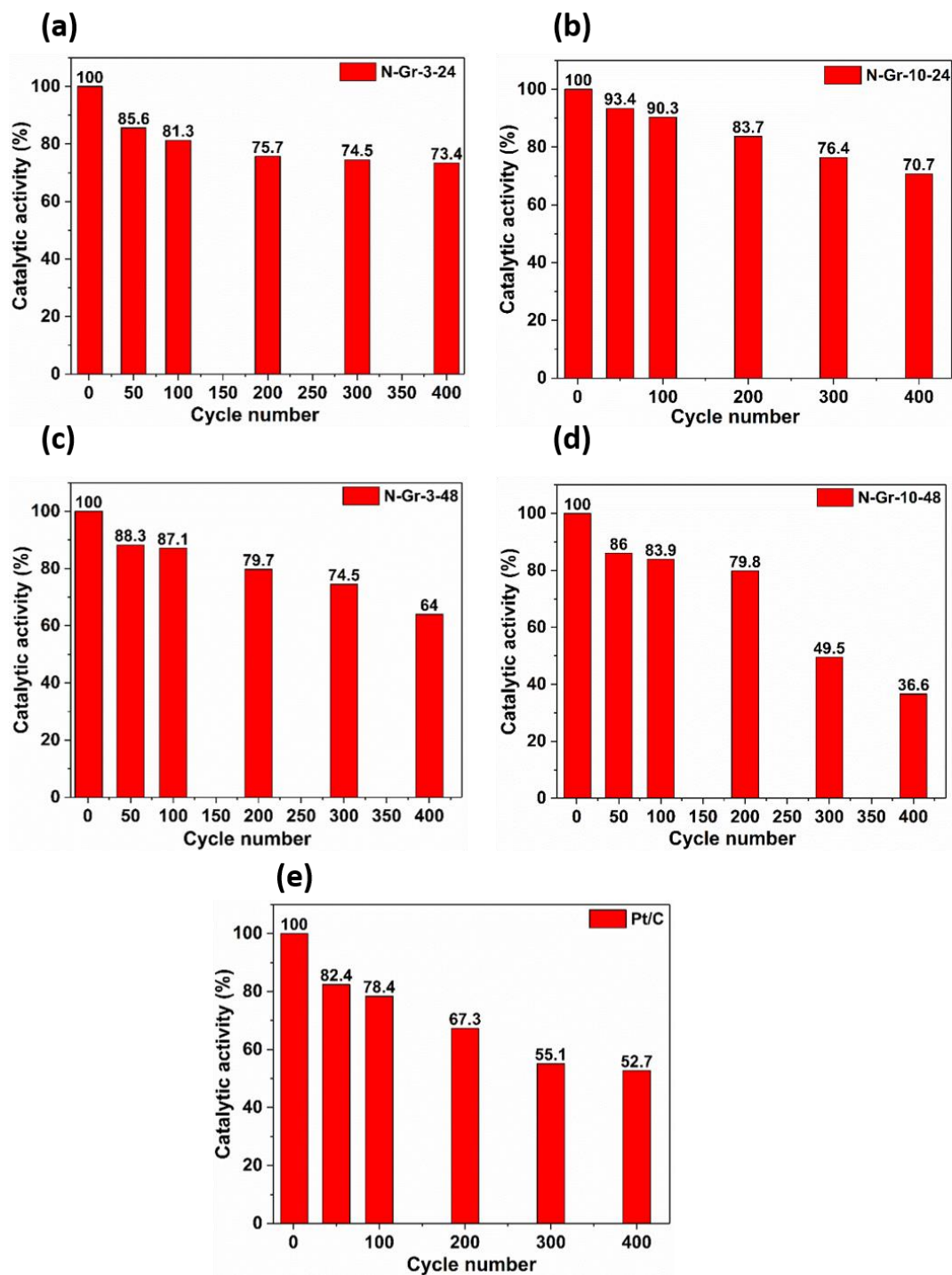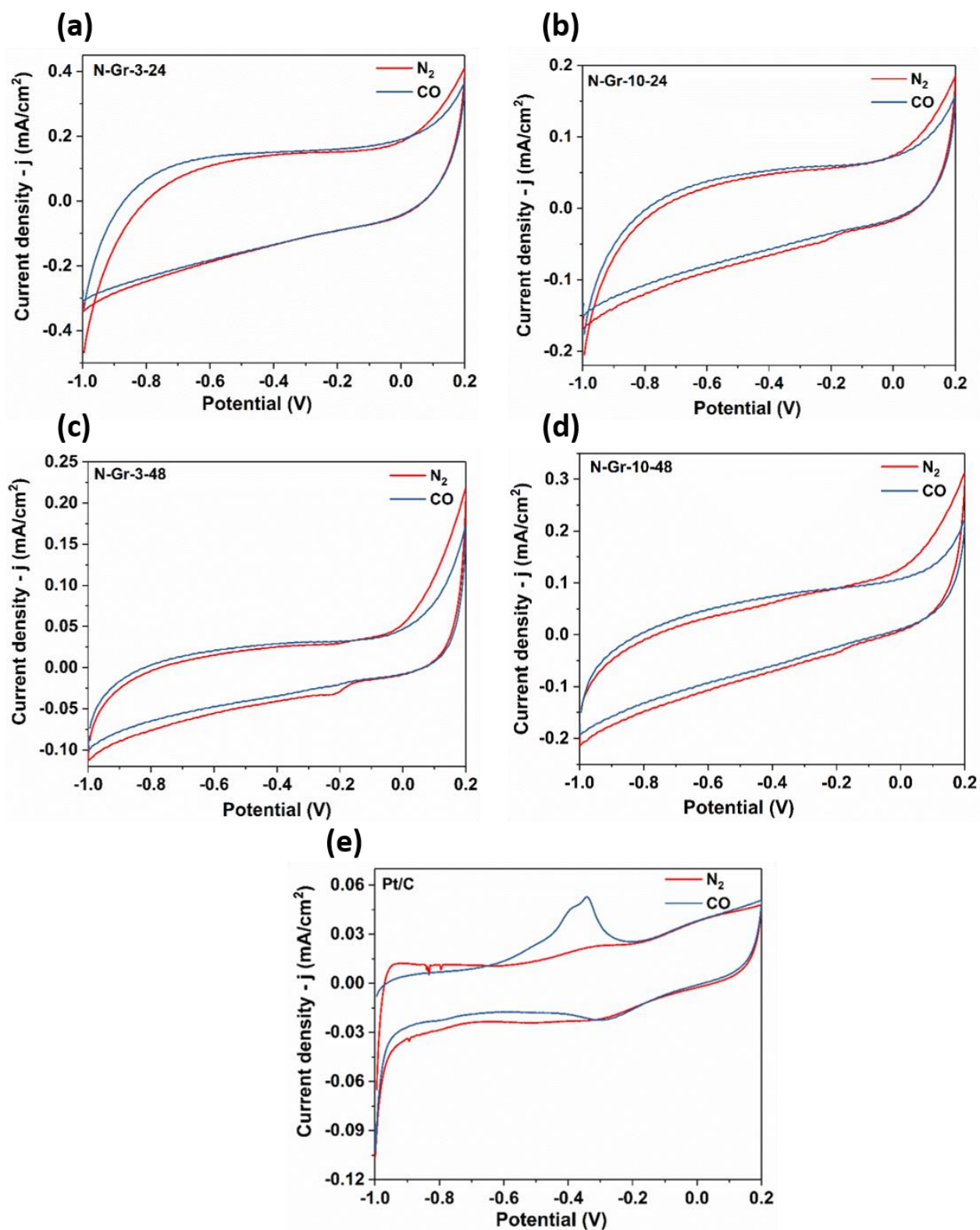**Figure S5.** Evaluation of the catalytic activity retention (%) over 400 cycles of the **(a–d)** N-doped graphene/GC electrodes, respectively **(e)** Pt/C/GC electrode in O_2-saturated 1M NaOH solutions at a scan rate of 50 mV/s.

Figure S6. CO stripping voltammograms of (**a–d**) N-doped graphene/GC electrodes, respectively (**e**) Pt/C/GC electrode in 1M NaOH.

Table S4. Input and output variables used for ML investigations and the obtained prediction for a number of 4 electrons transferred during the ORR process.

Variables	N-Gr-3-24	N-Gr-10-24	N-Gr-3-48	N-Gr-10-48	Prediction
Melamine (g)	3	10	3	10	–
Reaction time (h)	24	24	48	48	*25*
N-composition (weight%)	9.61	8.34	13.1	11.4	*8.64*
C-composition (weight%)	80	81.3	72.5	80.2	–
O-composition (weight%)	9.31	9.43	12.98	7.34	–
Pyridinic N (%)	21.8	24.8	25.5	23.8	*19*
Pyrrolic N (%)	72.7	68.8	68.3	68.7	*72.9*
Pyridinic N-O (%)	5.5	6.3	6.1	7.5	–
Csp2/Csp3	0.94	0.97	0.77	0.92	*1.04*
C-O (at%)	5.8	6.2	4.3	3.1	*5.9*
C=O (at%)	9.8	10.5	15.8	13.3	*9.6*
FWHM (º)	2.599	1.886	2.794	2.713	–
D (nm)	3.23	4.5	3	3.09	–
d (nm)	0.341	0.34	0.339	0.341	–
n	9.5	13	8.8	9.1	–
I_D/I_G	2.02	1.58	2	1.95	–
$I_{D'}/I_G$	0.51	0.41	0.56	0.53	*0.44*
I_{2D}/I_G	0.38	0.46	0.32	0.37	*0.45*
$I_D/I_{D'}$	3.94	3.9	3.54	3.7	–
G-band (cm^{-1})	1593	1590	1596	1594	*1591*
Output (number of electrons)	*3.96*	*4.1*	*3.41*	*3.08*	