Supplementary Materials

A Facile Synthesis of Noble-Metal-free Catalyst Based on Nitrogen Doped Graphene Oxide for Oxygen Reduction Reaction

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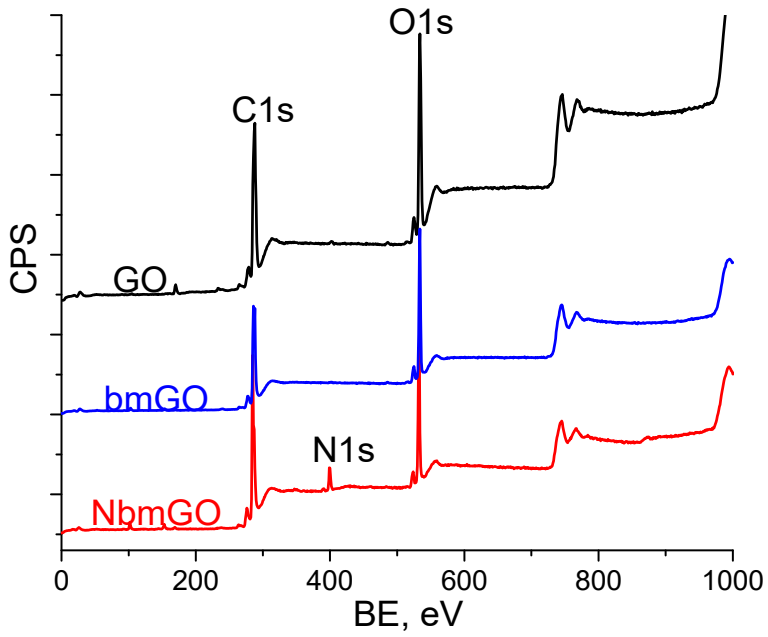

Figure S1. XPS survey spectra of the GO, bmGO, and NbmGO samples.

Table S1. Elemental composition (in at.%) of the samples under study.

Samples	Elements, %			
	C	N	O	S
GO	74.3	0.3	23.5	1.9
bmGO	76.8	0.0	23.0	0.2
NbmGO	76.7	5.5	17.4	0.4

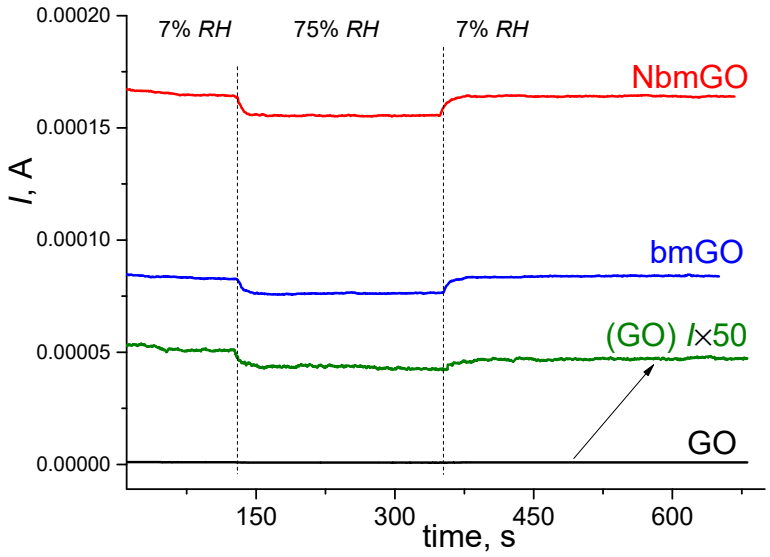

Figure S2. The conductivity of GO, bmGO, and NbmGO films at different *RH*%.

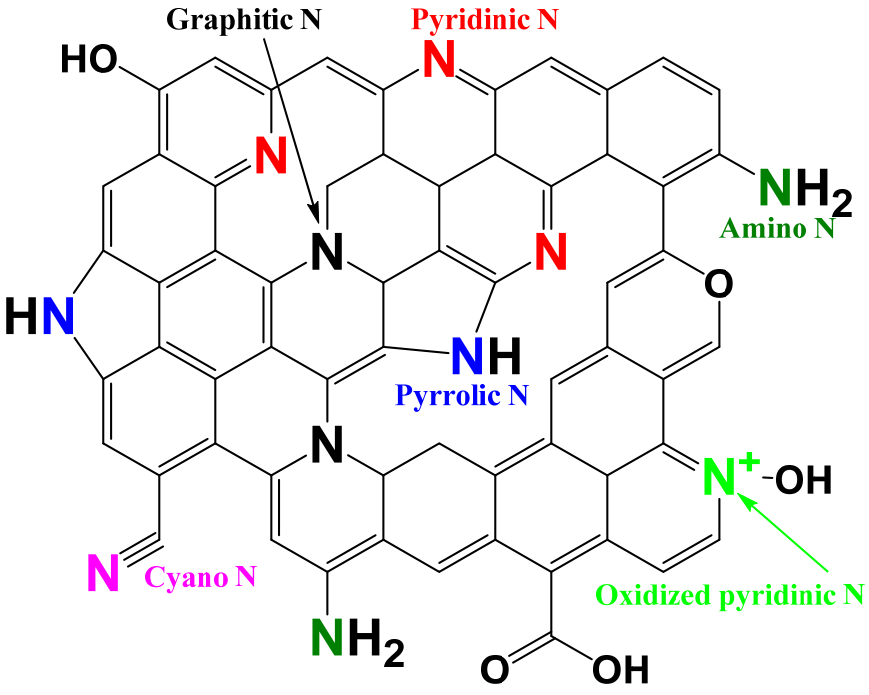

Figure S3. A model structure of NbmGO.

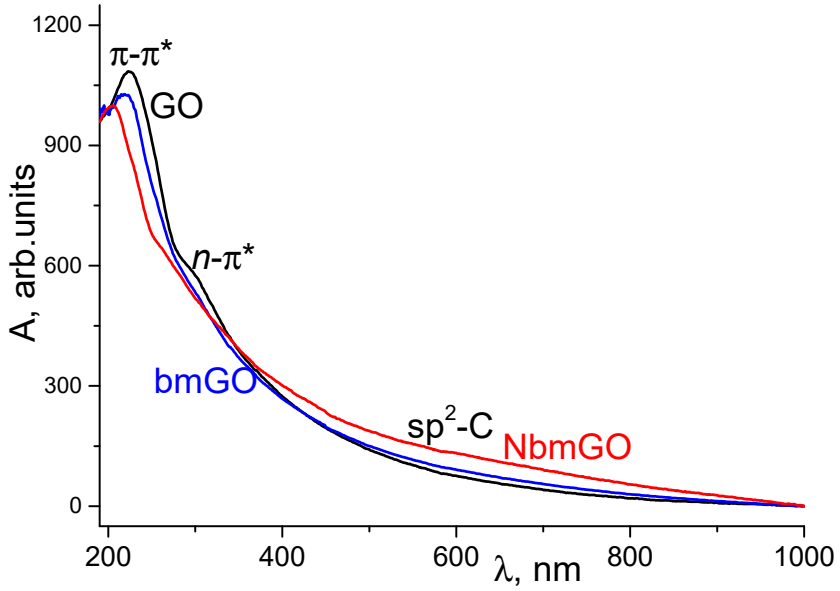

Figure S4. Electronic absorption spectra of GO, bmGO and NbmGO films (quartz glass). The maximum of the electronic absorption spectrum shifts to shorter wavelengths (224 nm → 205 nm) for the samples of GO, bmGO and NbmGO and there is an increase in absorption observed in the range 400-800 nm, which is typical for sp^2-carbon.

Table S2. Positions (Eb), full widths at half maximum (FWHM), and intensities (Int) of the peaks in the XPS spectra of the GO, bmGO and NbmGO samples

Samples	Line (Peak)	E_b, eV	*FWHM*, eV	*Int*, %	*Assignment*
GO	C1*s*(C1)	284.6	1.70	40.7	C=C/C–C
	C1*s*(C2)	286.6	1.65	41.6	C–O/C–OH
	C1*s*(C3)	288.1	2.00	15.2	C=O
	C1*s*(C4)	289.7	1.90	2.5	O–C=O
	O1*s*	533.5	2.10	100	
bmGO	C1*s*(C1)	284.6	1.45	46.2	C=C/C–C
	C1*s*(C2)	286.7	1.40	43.1	C–O/C–OH
	C1*s*(C3)	288.4	1.80	9.5	C=O
	C1*s*(C4)	290.1	1.65	1.2	O–C=O
	O1*s*	533.8	2.00	100	
NbmGO	C1*s*(C1)	284.7	1.40	57.1	C=C/C–C
	C1*s*(C2)	286.7	1.65	31.1	C–O/C–OH
	C1*s*(C3)	288.6	1.95	10.2	C=O
	C1*s*(C4)	290.6	1.90	1.6	O–C=O
	O1*s*	533.9	2.00	100	
	N1*s*(N1)	398.5	1.50	19.4	Pyridinic N
	N1*s*(N2)	399.6	2.00	67.6	Pyrrolic N
	N1*s*(N3)	401.0	2.60	13.0	Graphitic

Table S3. Peak positions and the band intensity ratios (ID/IG) in the Raman spectra of graphite, GO, bmGO, and NbmGO.

Samples	Peak position, cm^{-1}		I_D/I_G
	D	*G*	
Graphite [1]	1350	1583	–
GO	1350	1599	0.864
bmGO	1348	1598	0.962
NbmGO	1344	1595	1.011

Table S4. ESR data obtained for samples of GO, bmGO, and NbmGO at room temperature.

Samples	g-factor	Line widths ΔH, mT (G)	Form-factor FF	The number of paramagnetic centers *N*, spin/g
GO	2.0048	0.17 (1.7 G)	3.4	5.4×10^{17}
bmGO	2.0027	0.25 (2.5 G)	3.4	5.5×10^{18}
NbmGO	2.0034	0.39 (3.92 G)	3.6	6.2×10^{18}

Table S5. The characteristic features in the FTIR spectra of GO and melamine

Absorption bands (cm^{-1})	Description
	GO (see Ref. S2–S8)
3000–3700	stretching vibrations of O–H
1720–1730	stretching vibrations of C=O carbonyl groups and/or ketones
1620–1630	vibrations of double C=C bonds and bending vibrations of the water molecules
1220–1230	C–OH stretching
1040–1060	vibrations epoxy and alkoxy groups
	Melamine (see Ref. S9–S10)
3468	stretching vibrations of N–H
3417	stretching vibrations of N–H
3324	stretching vibrations of N–H
3121	stretching vibrations of N–H
1630–1660	NH_2 deformation

Table S6. Electrochemical properties of N-doped carbon materials.

No	Catalyst	Half-wave potential/Onset potential (V vs. Ag/AgCl)	Ref. SI
1	NbmGO	–0.175/–0.09	This work
2	bmGO	–0.215/–0.105	This work
3	rGOA-MS	–0.295/–0.15	[11]
4	NG5	–0.25/–0.1	[12]
5	NG-C	–0.2/–0.06	[13]
6	PDI-900	–0.215/–0.14	[14]
7	NrGO800	–0.205/–0.08	[15]

The chronoamperometry test of NbmGO catalyst was carried out at 2000 rpm in O_2-saturated 0.1 M KOH solution (Fig. SI5). The high current retention of 93 % after continuous polarization at –250 mV during 720 min clearly demonstrates the excellent long-term stability of NbmGO, which can be attributed to the quite little loss of active sites during the test.

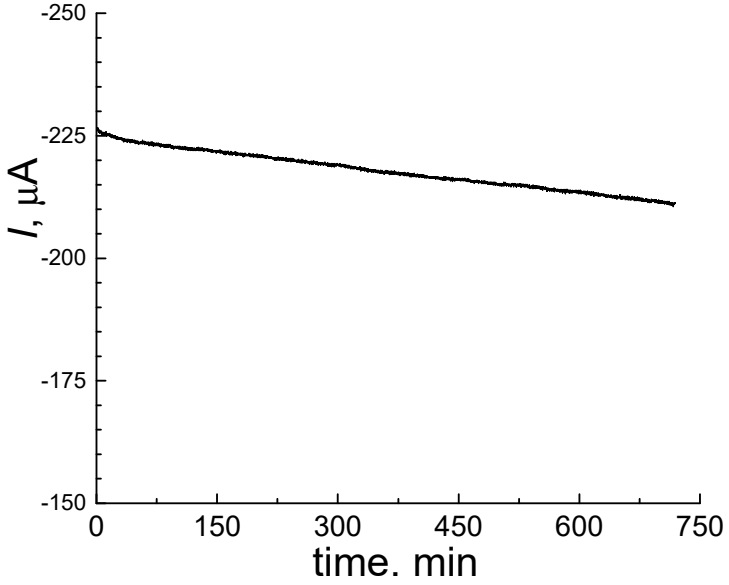

Figure S5. Long-term stability of NbmGO *via* chronoamperometry test at –300 mV in 0.1 M KOH and at room temperature, ω = 2000 rpm.

Materials and Synthesis of GO

All the materials were used without further purification. Graphite powder (<50 μm, Merck (Germany), 98+%), potassium permanganate ($KMnO_4$, Rushim (Russia), 98%), concentrated sulfuric acid (H_2SO_4, Rushim (Russia), 99%), nitric acid (HNO_3,Rushim (Russia), 99%), 30% hydrogen peroxide (H_2O_2, Chimmed (Russia), 98%), 37% hydrochloric acid (HCl, Rushim (Russia), 99%). Melamine ($C_3N_6H_6$, BASFSE (Germany), 99.9%).Graphite oxide was prepared by Hammers [16], with some modification [17].The elemental composition of the product corresponded to a formula $C_8O_{4.6}H_{1.8}(H_2O)_{0.58}$. According to X-ray diffraction study, the interplanar distance is 0.81 nm in our sample.

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