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Nitrogen-enriched carbon powder prepared by ball-milling of graphene oxide with melamine: an efficient electrocatalyst for oxygen reduction reaction

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EXPERIMENTAL

Synthesis

Mechanochemical synthesis of nitrogen-doped carbon powder was carried out in the planetary ball mill Pulverisette 6 (Fritsch, Germany). We used the following conditions of synthesis. The material of milling chamber and balls is ZrO_2, volume of milling chamber is 85 ml, loading of the mill is 30 balls (5 mm in diameter). The graphene oxide/melamine weight ratio is 4:1, rotation speed is 400 rpm, and milling time is 6 min. Obtained powder was dispersed in a 10% ammonia aqueous solution and sonicated using an ultrasonic bath for 1 hour, then it was centrifuged and washed with water 5 times to remove melamine residues.

Characterization

The electron micrographs of the samples were acquired with a scanning electron microscope Zeiss SUPRA 25 (Carl Zeiss, Germany). Raman spectra were recorded using a SENTERRA Raman spectrometer (Bruker, USA). The excitation wavelength was 532 nm, and the laser power was ~1 mW at the sample point with the beam waist of ~1 μm. The IR spectra of N-bmGO were obtained with a FT-IR VERTEX 70v spectrometer (Bruker, USA), 50 scans in vacuum. XPS spectra were registered using a Specs PHOIBOS 150 MCD electron spectrometer with a Mg cathode ($h\nu$ = 1253.6 eV). The vacuum in the spectrometer chamber did not exceed 4×10^{-8} Pa. The survey spectra and individual lines were recorded in 1.00 eV and 0.05 eV increments, respectively.

Electrochemical measurements

The linear sweep voltammetry was performed in a three-electrode cell using the set-up with a RRDE-3A rotating disk electrode (ALS Co., Ltd, Japan) and an Autolab PGSTAT302N potentiostat (Metrohm Autolab, Netherlands) in an O_2-saturated solution of 0.1 M KOH (bulk concentration of dissolved oxygen c^0 = 1.2 mM)[S1] at potential scan rate v = 10 mV/s. The analysis of voltammograms obtained at various electrode rotation rates (ω = 360–6400 rpm) was carried out within the Koutecký-Levich equation as described in detail elsewhere.[S2] A 3 mm diameter glassy carbon (GC) disk pressed into polyether ether ketone (PEEK) polymer was used as a working electrode. The surface of the initial GC electrode was polished with 0.3 μm Al_2O_3 powder. Then, ca. 6 μl of the N-bmGO suspension (1 mg/ml) with ca. 0.01 wt% Nafion polymer added was drop-casted on the GC surface and dried at ambient temperature. Platinum coil with a 1 cm^2 surface area was an auxiliary electrode; a reference electrode was represented by an Ag/AgCl (saturated KCl) electrode, which the potential values (E) were referred to.

RESULTS

Characterization of N-bmGO

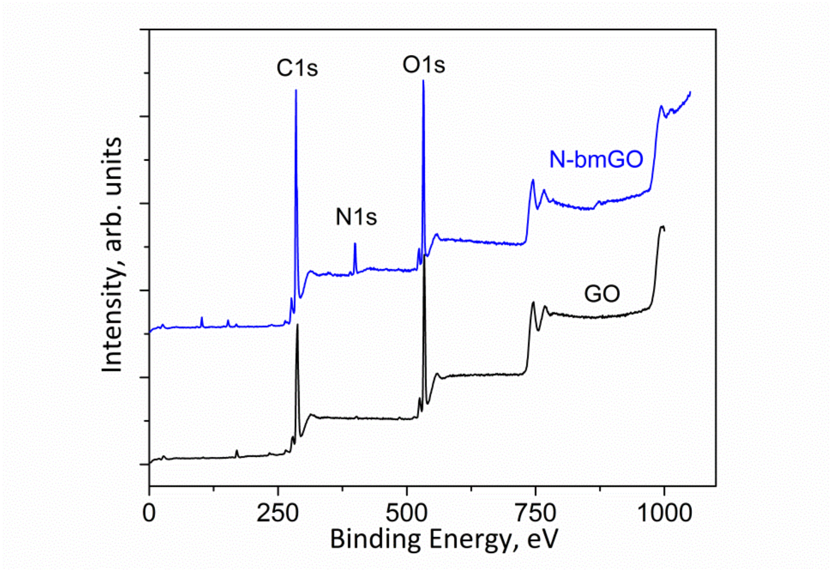


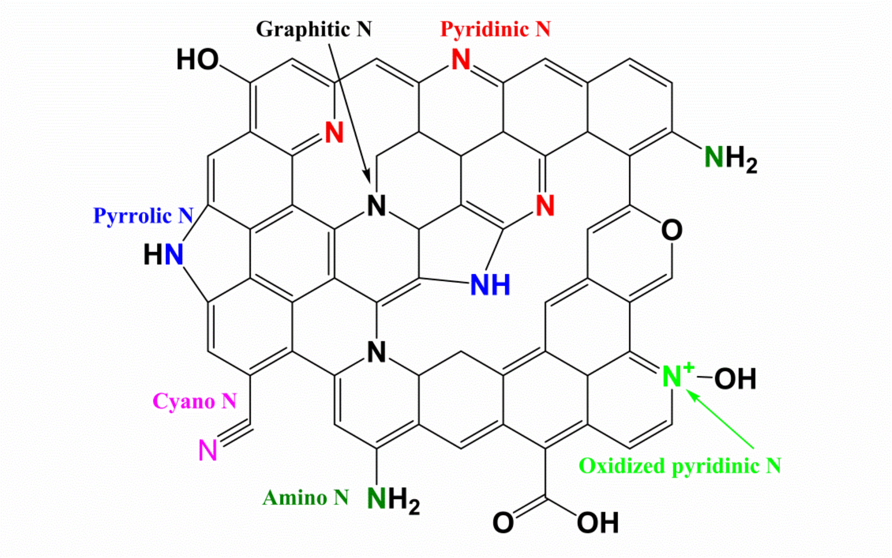
Figure S1 XPS survey spectra of GO and N-bmGO.

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

Sample	Element			
	C	N	O	S
GO	74.3	0.3	23.5	1.9
N-bmGO	76.7	5.5	17.4	0.4

Nitrogen in graphite-like matrix can exist in four-five configurations:[S3,S4] pyridinic N (N1, 6-membered cycle), pyrrolic N (N2, 5-membered cycle), graphitic N (N3/N4), and oxidized N (N5). The pyridinic N and pyrrolic N atoms are located at the edges of graphene layers or at the defect sites. The N3 and N4 atoms substitute carbon atoms in the graphene layer at the edges (N3) and in the center (N4). Nitrogen atoms can also be present in the form of cyano and amino groups (see Scheme S1).

Identification of nitrogen atoms can be performed based on the analysis of the structure of N1s high resolution XPS spectrum. The XPS peak positions for various nitrogen types are well known (see[S3,S4] and references therein). Pyridinic N (N1) corresponds to a peak at 398.0–399.3 eV, pyrrolic N (N2) corresponds to a peak around 399.8–401.2 eV, N3 corresponds to a peak close to 401 eV, and N4 corresponds to a peak at 402.3 eV. The highest energy of 402.8 eV has a peak corresponding to the oxidized pyridinic N (N5).[S3] Note peaks of amino and cayano groups at 399.1 and 399.3 eV, respectively,[S4] are overlapped with the peak of pyridic N and it is difficult to distinguish these types of nitrogen atoms. There also can be a peak of physisorbed N_2 at 404.7 eV.[S4]



Scheme S1 Schematic illustration of N-bmGO.

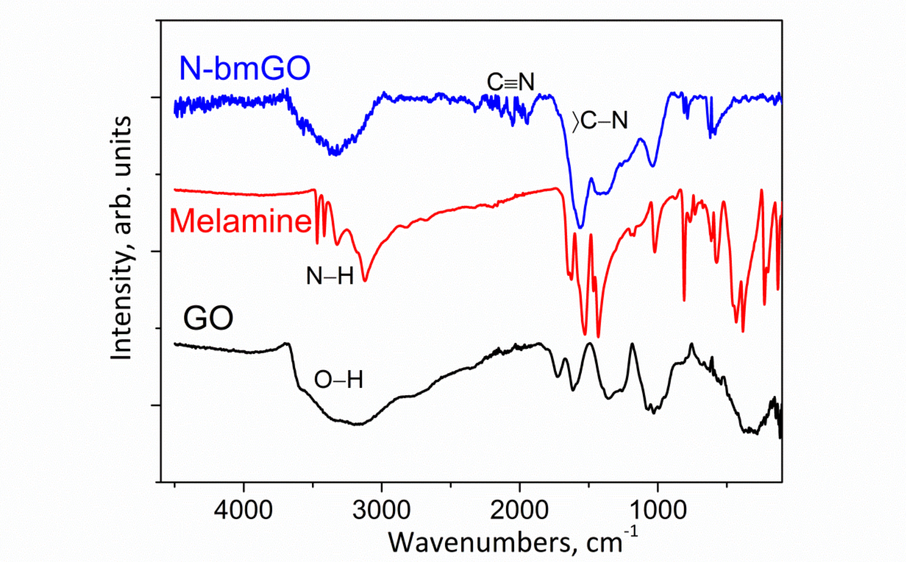


Figure S2 FTIR spectra of GO, melamine and N-bmGO.

FTIR spectra of melamine, graphene oxide and the product of their ball-milling (N-bmGO) are presented in the Figure S2. As is seen, the IR spectrum of N-bmGO differs from those of the initial reagents. N-bmGO spectrum shows no absorption bands of N–H valence vibrations which are present at 3468, 3417, 3324 and 3121 cm^{-1} in the spectrum of melamine. At the same time, a number of absorption bands in the region from 2350 to 1900 cm^{-1} of N-bmGO spectrum can be assigned to cyano groups. Note, IR spectra were acquired in vacuum; therefore, we do not consider any vibrations of CO_2 molecules from the gas phase in the discussed region.

At last, a broad absorption band in the region from 3670 to 3000 cm^{-1} of N-bmGO spectrum results from valence vibrations of O–H.

Raman spectrum of N-bmGO is presented in the Figure S3. The G mode is caused by tangential movement of carbon atoms and corresponds to the sp^2 carbon. The D peak is associated with the breathing modes and corresponds to structure defects and disorder at the edges of sp^2 domains. The ratio of D and G band intensities (I_D/I_G) allows one to estimate the degree of graphitization. The higher the ratio, the larger the structure disorder of the material. Position and shape of 2D band allows one to distinguish monolayer, two-layer and few-layer graphenes. If the material comprises more than 5 graphene sheets, the 2D band disappears.

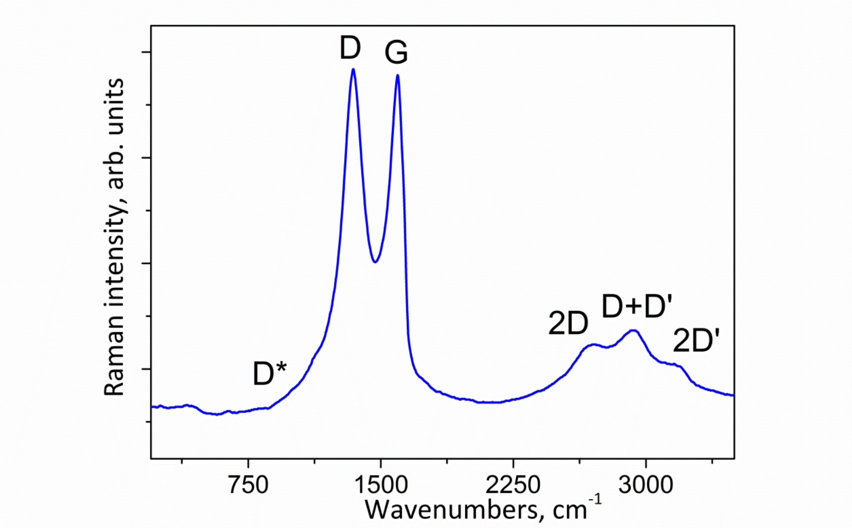


Figure S3 Raman spectra of N-bmGO.

The size of a crystallite is the inverse ratio I_D/I_G according to the equation:

$$L_a\ (\text{nm}) = (2.4\times10^{-10})\ \lambda^4\ (I_D/I_G)^{-1}, \qquad \text{(S1)}$$

where λ is the wavelength (in nm) of excitation laser.

Based on the ratio of peak intensities $I_D/I_G = 1.674$, the sp^2 domain size is ca. 11.5 nm. Higher content of defects in N-bmGO is associated with smaller crystallites.

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