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Mendeleev Commun., 2020, **30**, 472–473

Mendeleev Communications

Effect of graphene surface functionalization on the oxygen reduction reaction in alkaline media

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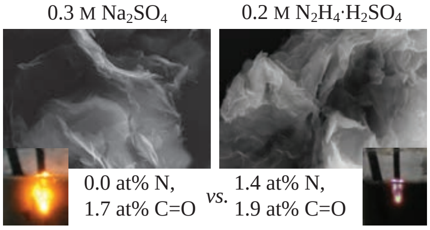
DOI: 10.1016/j.mencom.2020.07.021

Two types of few-layer graphene structures with different degrees of doping with nitrogen and with close surface concentrations of carbonyl groups were synthesized using the electrochemical exfoliation of graphite in the cathodic plasma mode. As for the concentrations of oxygen-containing functional groups and doping nitrogen atoms, pyridine N atoms make a dominating contribution to the electrocatalysis of oxygen reduction reaction on the synthesized structures.



Keywords: electrochemical exfoliation of graphite, electrolytic plasma, nitrogen-doped few-layer graphene structures, oxygen-containing functional groups, oxygen reduction reaction.

Various carbon nanoforms doped with nitrogen atoms demonstrate high catalytic activity toward the oxygen reduction reaction (ORR). As a rule, doping is an essential step in the production of promising electrode materials for fuel cell cathodes.[1,2] Note that, in addition to dopants, a significant amount of oxygen-containing functional groups (OFGs) is usually present on the surface of carbon nanostructures. At the same time, it is believed that high electrocatalytic characteristics can be achieved without dopants due to the presence of defects in few-layer graphene structures (FLGSs) and/or decoration of their surface with OFGs, which are active centers of ORR.[3,4] However, published data[2,5–9] on the role of doping atoms and oxygen-containing groups in the catalytic effect of modified carbon nanoforms are controversial. In this work, we used the plasma-assisted electrochemical exfoliation of graphite[10,11] to synthesize two types of few-layer graphene structures with different amounts of doping nitrogen atoms but similar degrees of surface functionalization with C–O–C and C=O groups. These structures were used as a model system for studying the contribution of dopants and oxygen-containing functional groups to the electrocatalytic performance of carbon nanomaterials in ORR.

Few-layer graphene structures were obtained by the electrochemical exfoliation of graphite with high voltage pulses ($U = 200$ V) in the cathodic plasma mode.[10,11] Nitrogen-free FLGSs and FLGSs doped with nitrogen (N-FLGS) were synthesized in 0.3 M Na_2SO_4 solution[11] and 0.2 M $N_2H_4 \cdot H_2SO_4$ solution, respectively. Figure 1 shows SEM images of FLGS and N-FLGS samples. The synthesized structures are graphene-like particles of similar morphology with rough edges and a wide distribution of lateral size: 0.07–0.7 μm for FLGS and 0.2–8 μm for N-FLGS.[†] Remarkable difference in lateral sizes is probably due to an increase in the hydrophobicity of carbon particles with injected nitrogen atoms, which leads to the coalescence of small flakes into large agglomerates (see Figure 1). According to elemental analysis,[‡] the bulk nitrogen content of FLGS and N-FLGS was 0.0 and 1.1 at%, respectively. X-ray photoelectron spectroscopy (XPS) data[†] demonstrate that the surface concentrations of oxygen and nitrogen were 18.8 and 0.0 at% (FLGS) and 20.7 and 1.4 at% (N-FLGS). A small amount of sulfur (1.3–2.5 at%) was due to C–SO_2 and C–SO_3 groups.[12] The deconvolution[13] of high-resolution O 1*s* spectra[†] indicated that epoxy (17.1–18.8 at%) and carbonyl (1.7–1.9 at%) groups were present on the FLGS and N-FLGS surfaces. According to the high-resolution N 1*s* spectra of N-doped structures (Figure 2), graphene planes contained pyridine

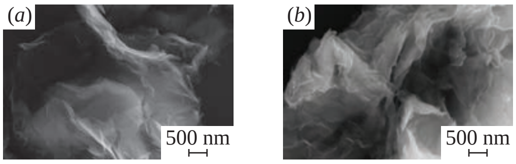


Figure 1 SEM images of (*a*) FLGS and (*b*) N-FLGS samples.

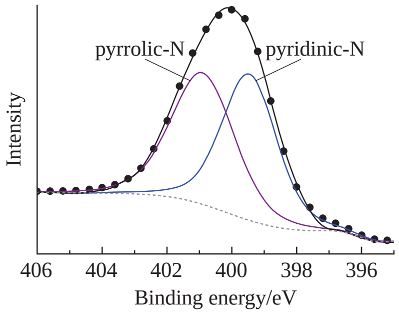


Figure 2 High-resolution N 1*s* XPS spectra of N-FLGS.

[†] See Online Supplementary Materials.
[‡] The experimental error was no greater than 10%.

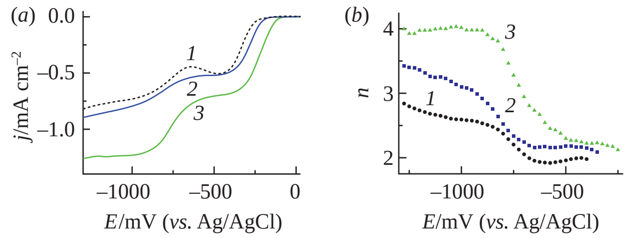


Figure 3 (*a*) Oxygen reduction in an air-saturated 0.1 M KOH solution at 2000 rpm and $v = 10$ mV s^{-1} and (*b*) *n*–*E* plots on (*1*) GC, (*2*) FLGS, and (*3*) N-FLGS.

(0.7 at%) and pyrrole (0.7 at%) N atoms. At sufficiently low concentrations of carbonyl groups and doping nitrogen atoms, their synergetic effect was minimal. Thus, our samples differ from those studied by Zhang *et al.*,[14] in which the nitrogen concentration was significantly higher (5.5–6.2 at%), and the amount of oxygen varied from 6.2 to 20.5 at%.

Figure 3(*a*) shows the *j*–*E* curves for a pristine glassy carbon (GC) electrode and GC electrodes covered with FLGS and N-FLGS measured in an air-saturated 0.1 M KOH solution at the potential scan rate $v = 10$ mV s^{-1} and an electrode rotation rate of 2000 rpm. The preparation of the electrodes was described in detail elsewhere.[11] The oxygen reduction reaction overpotential for FLGS and N-FLGS decreased, as compared to that of the pristine GC. Namely, the half-wave potentials of the first wave of oxygen reduction for GC, FLGS[§] and N-FLGS were −325, −280 and −210 mV (*vs.* Ag/AgCl), respectively. The limiting diffusion current density calculated from the Levich equation at an electrode rotation rate of 2000 rpm was 0.64 or 1.27 mA cm^{-2} for a two- or four-electron process, respectively, which are in good agreement with experimental values [see Figure 3(*a*)] for the first (curves *2* and *3*) and second (curve *3*) oxygen reduction waves.

Figure 3(*b*) shows the values of *n* derived from the slopes of the *j*–*ω* curves plotted in the Koutecký–Levich coordinates at various *E*. For FLGS and N-FLGS, *n* is ~2.2 at $E > -500$ mV, which is somewhat higher than *n* values for the pristine GC. The *n*–*E* curves in a range of *E* between −600 and −900 mV correspond to two-electron oxygen reduction to hydrogen peroxide and four-electron oxygen reduction to water,[15] and the latter process significantly contributes to the total current for N-FLGS. In accordance with published data,[16–18] the catalytic activity in ORR is mainly caused by pyridine N atoms on which oxygen molecules are adsorbed. Moreover, these active centers lead to the prevalence of direct four-electron oxygen reduction. As for OFGs, carbonyl (quinone) groups[11,19] are the active centers of four-electron oxygen reduction at $E < -700$ mV. However, the surface concentration of these groups in the cited publications was significantly higher than that used in this study. The influence of sulfur-containing groups on the decrease of ORR overpotential is highly unlikely,[8,20] and it is possible to correctly estimate the comparative catalytic activity of pyridine N atoms and quinone groups in our case. It follows from Figure 3 that the presence of active centers in the vicinity of pyridine N atoms results in (i) a decrease in the overpotential of two-electron oxygen reduction and (ii) a direct oxygen reduction to water at $E < -900$ mV. At the same time, at $E < -900$ mV, the four-electron pathway of ORR[11,15,19] contributes to a lesser extent in the overall process for FLGS (*n* is much lower than 4) than in the case of N-FLGS. Note that, for few-layer graphene structures obtained in the anodic plasma mode,[11] the limiting *n* value of about 4 at $E < -900$ mV also corresponds to the complete reduction of oxygen to water, whose active centers are carbonyl groups (7.1 at%). Obviously, the doping of few-layer graphene structures with nitrogen atoms results in a catalytic effect similar to that observed for FLGS with a higher surface concentration of carbonyl groups, but the ORR overpotential of the former is lower than that of the latter.[11]

Thus, at sufficiently low dopant and carbonyl group concentrations, the doping of few-layer graphene structures with N atoms is a more efficient way to produce ORR electrocatalysts.

This work was supported by the Russian Science Foundation (grant no. 17-73-20236) and performed using the equipment of the Multi-User Analytical Center of IPCP RAS and the equipment of the Multi-User Center of Scientific Center in Chernogolovka RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.021.

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Received: 31st January 2020; Com. 20/6125

[§] Curves *1* and *2* measured in the present study are close to those obtained earlier.[11]