Supplementary Material (ESI) for Journal of Materials Chemistry

Nitrogen-doped graphene and its electrochemical applications

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Content

1. TEM images

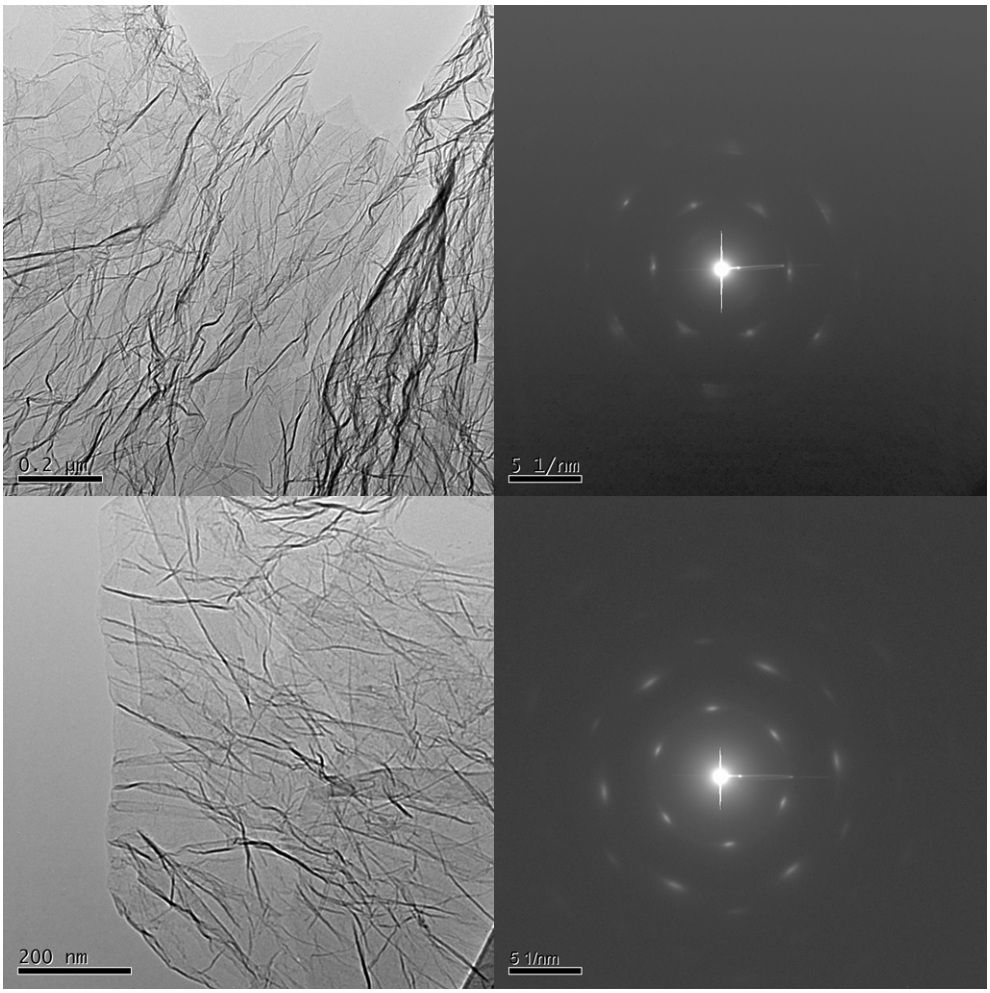

Fig. S1 TEM images and the SAED patterns of graphene (up) and N-graphene (bottom). (JEOL TEM 2010 microscope equipped with an Oxford ISIS system with an operating voltage of 200 keV).

Fig. S1 shows the TEM images and the selected area electron diffraction (SAED) patterns of graphene and N-graphene. Graphene exhibits typical wrinkled structure[1] with corrugation and scrolling which is intrinsic to graphene.[2] The well-defined diffraction spots in the SAED patterns confirm the crystalline structure of the graphene and N-graphene,[3] but the SAED spot patterns are slightly different from that expected for individual graphene sheets.[1] Therefore, graphene used in this work might contain one- to few-layer sheets.[4] We did not observe the difference in the morphology and structures (physical) between N-graphene and graphene, so the difference in their electorcatalytic acitivity is due to the different surface chemistry between N-graphene and graphene.

2. Oxygen reduction activity and durability

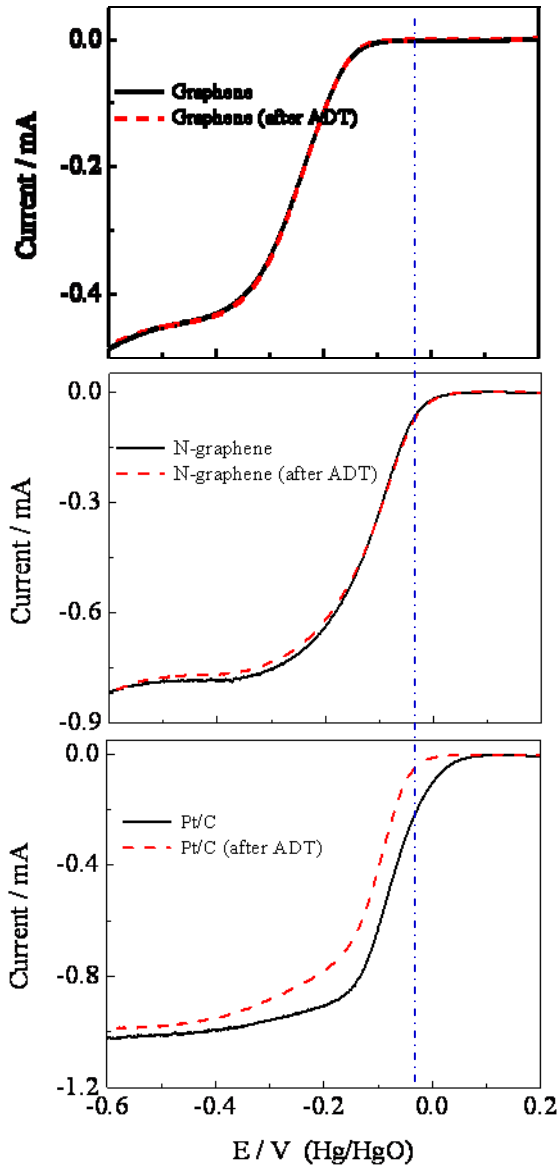

Fig. S2 Oxygen reduction polarization curves (background-subtracted, 10 mV/s, 1600 rpm) in O_2-saturated 0.1 M KOH on graphene, N-graphene and Pt/C (ETek, 20wt% Pt) electrodes before and after accelerated degradation test (ADT) (carbon loading: 20 μg; Pt/C loading 15 μg). ADT condition: 1000 cyclic voltammograms (-0.3~0.3 V vs. Hg/HgO) in N_2-saturated 0.1 M KOH (50 mV/s). The ORR kinetic currents (i_k, Figure 1a) are calculated using mass-transport correction Koutecky–Levich equation (S1).

3. Oxygen plasma-treated graphene (O-graphene)

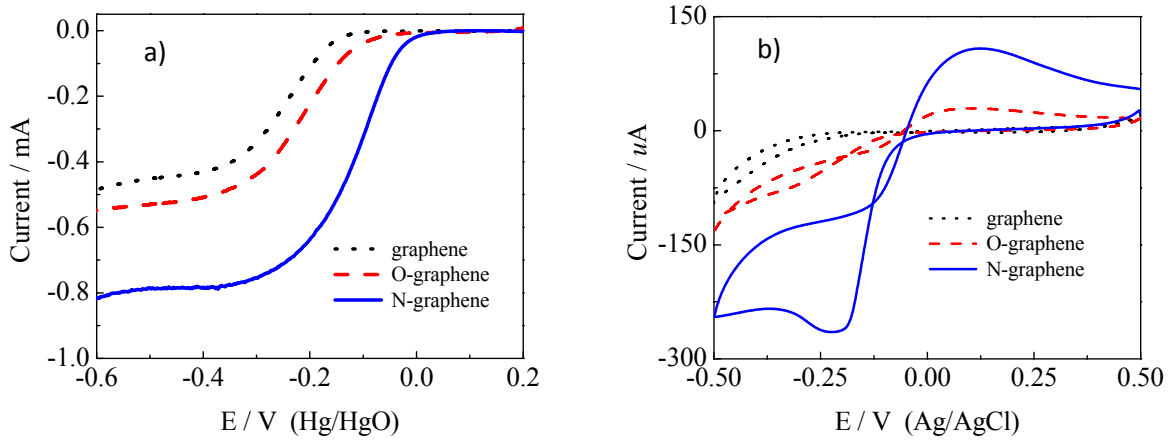

Fig. S3 a) Oxygen reduction polarization curves (background-subtracted, 10 mV/s, 1600 rpm) on graphene, O-graphene and N-graphene in O_2-saturated 0.1 M KOH; b) Cyclic voltammograms (50 mV/s, background-subtracted) of H_2O_2 reduction on graphene, O-graphene and N-graphene electrodes in N_2-saturated 5 mM H_2O_2 +10 mM PBS +100 mM KCl (pH=7.4).

Fig S3 shows that the onset reduction potentials and the reduction currents at a certain potential (for example, H_2O_2 reduction at -0.2 V vs Ag/AgCl and O_2 reduction at -0.1V vs Hg/HgO) for both O_2 and H_2O_2 are in the order of N-graphene >> O-graphene > graphene, which indicate that N-graphene exhibits much higher activity than both O-graphene and graphene. As shown in Table S1, oxygen-containing functional groups are similar for N-graphene and O-graphene (and there is trace nitrogen on O-graphene, which might be due to trace air leakage of plasma chamber during the synthesis of O-graphene or the adsorption of nitrogen on O-graphene). So the enhanced electrocatalytic activity of N-graphene is mainly due to nitrogen doping. This is consistent with the results in the literatures:[5, 6] when both nitrogen and oxygen functional groups exist on carbon, nitrogen functional groups control the electrocatalytic activity.

4. XPS spectra

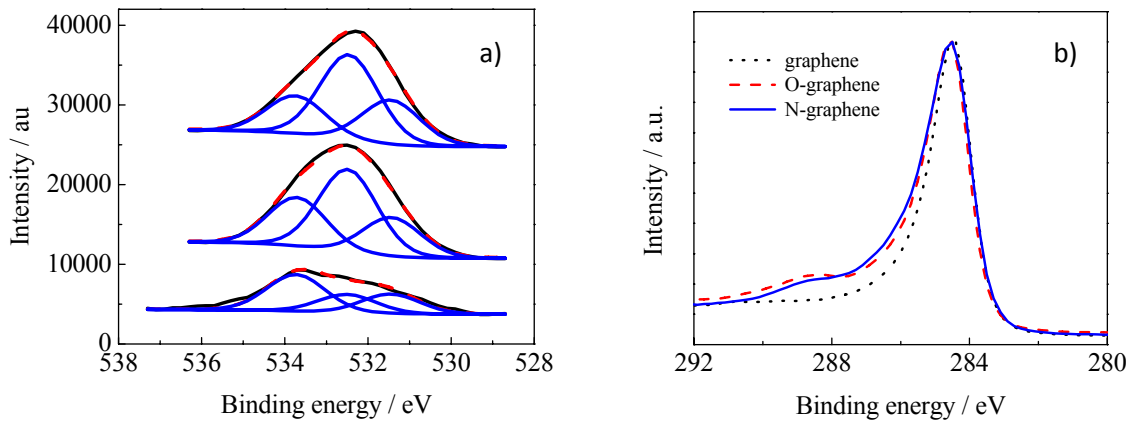

Fig. S4 a) O1s core level high-resolution XPS spectra of graphene, O-graphene and N-graphene (from bottom to up); b) C1s XPS spectra of graphene, O-graphene and N-graphene.

Fig. S4 shows the core level high-resolution XPS spectra of graphene, O-graphene and N-graphene. The fitted data of O1s XPS spectra are shown in Table S1. It is too difficult to deconvolve the C1s spectra into different peaks like that in N1s and O1s spectra because the C-N and C-O bond peaks are mixed together in the binding energy (BE) range of 285.0 -287.5 eV.[7] But it can still be seen from the enhanced shoulder (BE=285.0-290.0 eV) in C1s spectra that, after plasma treatment, new bonds of C-N, C-O, and carbon structure defects are produced.

References:

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