Charge-Transfer Resistance in Nitrogen-Doped Graphene

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Abstract

Nitrogen-doped graphene samples were synthesized by the hydrothermal method at 160° C for 3, 8 and 12 hours. The samples were correspondingly denoted NGr-1, NGr-2 and NGr-3. Their morphology, structure and electrochemical properties were investigated by SEM/TEM, X-ray powder diffraction (XRD), elemental analysis, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). For NGr-1 and NGr-2 samples, the elemental analysis indicated a nitrogen concentration of around 6.36 wt% whereas in the case of NGr-3 sample the concentration was slightly higher (6.85 wt%). The electrochemical studies performed with NGr modified electrodes proved that the charge-transfer resistance (R_{ct}) depends not only on the nitrogen doping level but also on the type of nitrogen atoms found at the surface (pyrrolic-N, pyridinic-N, graphitic-N).

Morphological and structural characterization of NGr samples

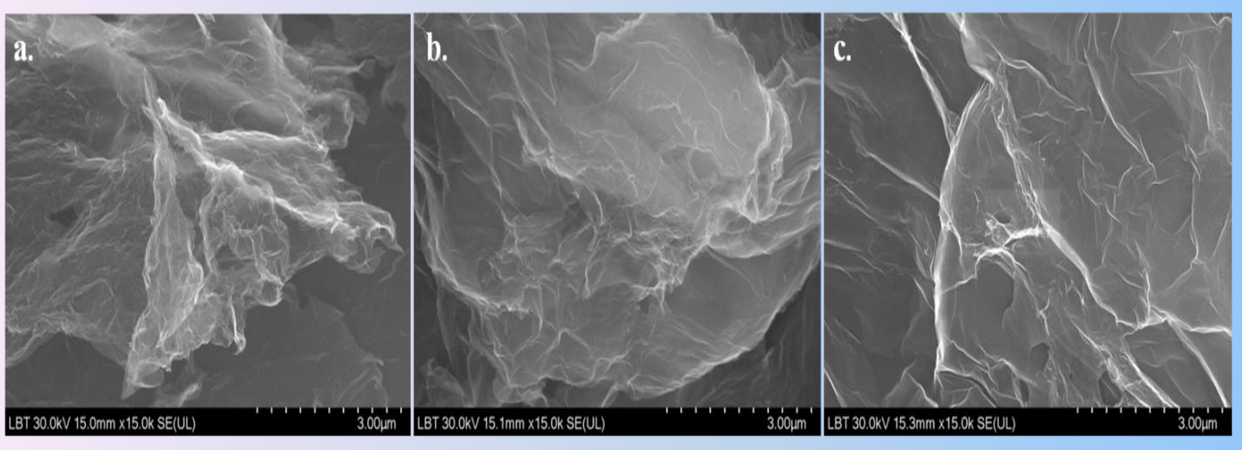

Figure 1. Representative SEM images of NGr-1 (a); NGr-2 (b) and NGr-3 (c)

Elemental analysis of NGr samples

Sample	Reaction Time (hours)	wt.%			
		C	N	H	O
NGr-1	3	80.57	6.36	1.39	11.68
NGr-2	8	80.27	6.37	1.09	12.27
NGr-3	12	80.45	6.85	1.34	11.36

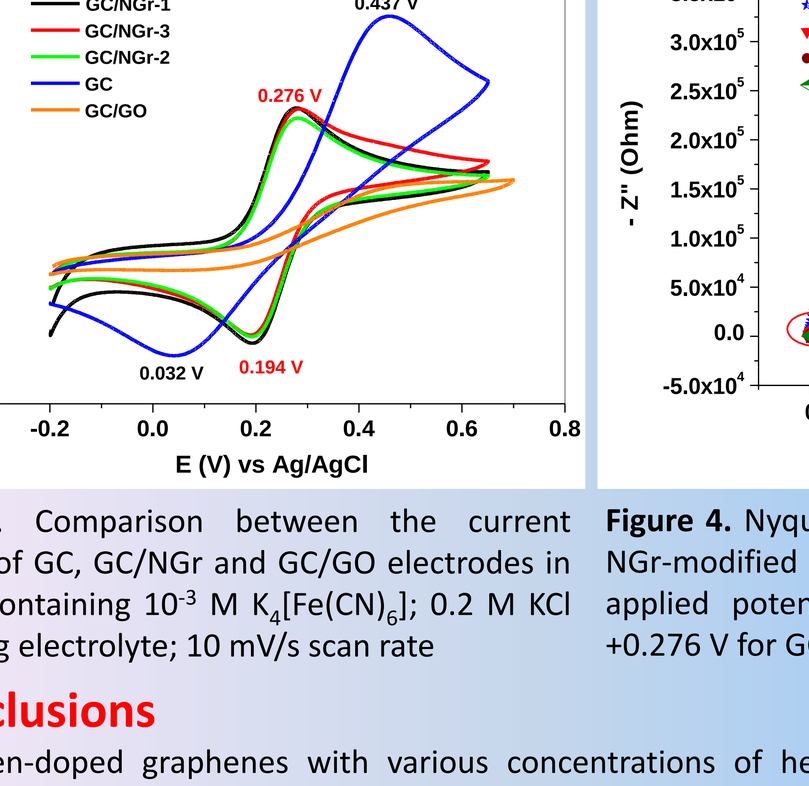

Figure 2. The XRD patterns of graphene-oxide (GO-black) and NGr samples

Structural parameters obtained from the XRD patterns of the samples

Sample	*2theta* (deg)	*D* (nm)	*d* (nm)	*n*	*%*
GO	11.56	6.78	0.77	9	92
	15.65	2.85	0.56	5	8
NGr-1	20.23	3.09	0.44	7	11
	23.16	2.88	0.38	8	45
	25.52	2.53	0.35	7	44
NGr-2	16.05	4.02	0.55	7	4
	19.99	2.35	0.44	5	16
	23.76	1.82	0.37	5	80
NGr-3	20.39	1.66	0.43	4	28
	23.35	4.07	0.38	11	29
	25.47	2.89	0.35	8	43

Electrochemical studies

Figure 3. Comparison between the current densities of GC, GC/NGr and GC/GO electrodes in solution containing 10^{-3} M $K_4[Fe(CN)_6]$; 0.2 M KCl supporting electrolyte; 10 mV/s scan rate

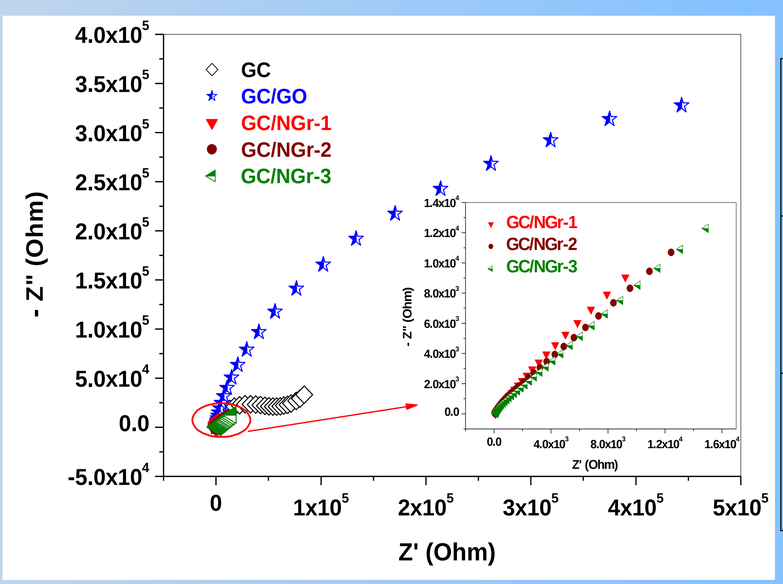

Figure 4. Nyquist plots obtained for GC, GC/GO and NGr-modified electrodes in 10^{-3} M $K_4[Fe(CN)_6]$; applied potential: +0.437 V for GC and GC/GO; +0.276 V for GC/NGr;

The values of R_{ct} and K_{app} for bare and GC modified electrodes

Electrode	GC/ NGr-1	GC/ NGr-2	GC/ NGr-3	GC	GC/ GO
R_{ct} (Ohm)	38.3	257	112	50.9 x 10^3	145 x 10^3
K_{app} (cm/s)	13.9 x 10^{-2}	2.39 x 10^{-2}	6.55 x 10^{-2}	2.6 x 10^{-4}	2.1 x 10^{-4}

Conclusions

Nitrogen-doped graphenes with various concentrations of heteroatom (6.36; 6.37 and 6.85 wt.%) were prepared by hydrothermal method using urea as reducing/doping source for graphene oxide. The structural characterization of the synthesized materials revealed that after doping, significant changes were observed in the XRD, Raman and XPS spectra, confirming the presence of heteroatom. For exemplification, the largest value for the in-plane crystallite size *(L_a)* was obtained for GO (17.11 nm) followed by NGr-1 sample (16.24 nm) and NGr-2 (16.16 nm) samples which according to elemental analysis had similar amounts of nitrogen (6.36 wt%). For NGr-3 sample, the L_a value is slightly lower (16.12 nm) being in good agreement with the higher doping level (6.85 wt%). In addition, the EIS studies conducted with NGr modified electrodes indicated that sample with the lowest doping level and the highest concentration of pyrrolic-N among all nitrogen-doped graphene (NGr-1) exhibits the best electrochemical parameters: a very small R_{ct} (38.3 Ω) and a large K_{app} (13.9 x 10^{-2} cm/s).

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