Supporting Information

Supercritical fluid processing of nitric acid treated nitrogen doped graphene with enhanced electrochemical supercapacitance

S. Suresh Balaji and M. Sathish*
Functional Materials Division, CSIR-Central Electrochemical Research Institute,
Karaikudi -630 006, India.
E-mail: marappan.sathish@gmail.com; msathish@cecri.res.in

FT-IR Spectroscopy

In Figure S1, the FT-IR spectra of SCHGO, NGO and NA-NGO are compared and the bands around 1720, 1570 and 1020 cm^{-1} in SCHGO are attributed to carbonyl stretching of –COOH functional group, aromatic C=C stretching and alkoxy C-O stretching, respectively.[1] The carbonyl stretching frequency of NGO and NA-NGO is slightly budged to 1710 cm^{-1} which may be due to conversion of edge –COOH functional group into corresponding amides. While comparing the FT-IR spectra of NGO and NA-NGO with SCHGO, the alkoxy C-O stretching peaks are significantly decreased which clearly strengthen the incorporation of N-doping into graphene skeleton under supercritical treatment. The band around 1570 cm^{-1} in NGO and NA-NGO is attributed to C=N stretching and aromatic C=C stretching.[2, 3]The band around 1220 cm^{-1} observed in SCHGO is ascribed to the presence of epoxy C-O stretching.[2] But in NGO, there is no band around 1220 cm^{-1} instead a very small peak is observed around 1250 cm^{-1}. Thus, it is assumed that during the preparation of NGO under supercritical heat treatment epoxy C-O is predominantly reduced and very few epoxy C-O groups are retained. Thus, the small peak around 1250 cm^{-1} in the FT-IR spectrum of NGO is attributed of C-N and residual epoxy C-O group. The peak around 1210 cm^{-1} is found in NA-NGO is due to the presence of C-N stretching.[3] It is fascinating to signify that the C-N stretching peak is well distinctive in case of NA-NGO but not in NGO. In NA-NGO, the additional sharp band is appeared around 1400 cm^{-1} that may be attributed to N=O bending which suggest that some hydroxyl hydrogen is transformed into corresponding nitro group. However this is not found in FT-IR spectrum of NGO. These two vibration bands (1210 and 1400 cm^{-1}) strongly support the significance of nitric acid addition along with urea under supercritical treatment. The epoxy rings are preferentially opened by nitric acid treatment under supercritical condition that results the new band around 1210 cm^{-1} and absence of characteristic epoxy C-O bands in NA-NGO. However in NGO, the C-N stretching vibration bands are overlapped with epoxy C-O vibration band so that the C-N stretching peak is not clearly seen. The band observed around 1100 cm^{-1} for all these samples is assigned to C-C stretching.

FT-IR spectra of RSCHGO, RNGO and RNA-NGO are shown in Figure S1. The peak around 1555 cm^{-1} in RNGO and RNA-NGO is attributed to C=N stretching vibration band and the same is not observed in RSCHGO due to the absence of nitrogen.[3] A very negligible broad band around 1630 cm^{-1} in RSCHGO is due to C=C stretching. This may be due to the fact that the olefinic bonds are significantly reduced by hydrazine hydrate. The band around 1260, 1715 and 1020 cm^{-1} in RSCHGO may be ascribed to epoxy C-O stretching, carbonyl stretching of –COOH functional group and alkoxy C-O stretching, respectively.[2, 3] However both the alkoxy C-O stretching vibration band and the epoxy C-O stretching vibration band of RSCHGO are very small while compared with that of SCHGO suggesting that both the alkoxy C-O bonds and the epoxy C-O bonds are significantly reduced by hydrazine hydrate. The characteristic carbonyl stretching vibration band is also strongly minimized in case of both RNGO and RNA-NGO which clearly support the reduction of carbonyl groups by hydrazine hydrate. The band around 1205 cm^{-1} in RNGO is assigned to C-N stretching.[3] It is important to mention that in all the six samples the band around 800 cm^{-1} is attributed to **C=C** bending.[3] Interestingly, the band around 1400 cm^{-1} in RNA-NGO may be due to N=O bending. However this band is not sharp as observed in NA-NGO which clearly indicated that most of the nitro groups are reduced using hydrazine hydrate. Thus in all these samples (NGO, NA-NGO, RNGO and RNA-NGO) the peak around 1550 -1570 cm^{-1} is observed which clearly indicated the doping of nitrogen in graphene sheets.

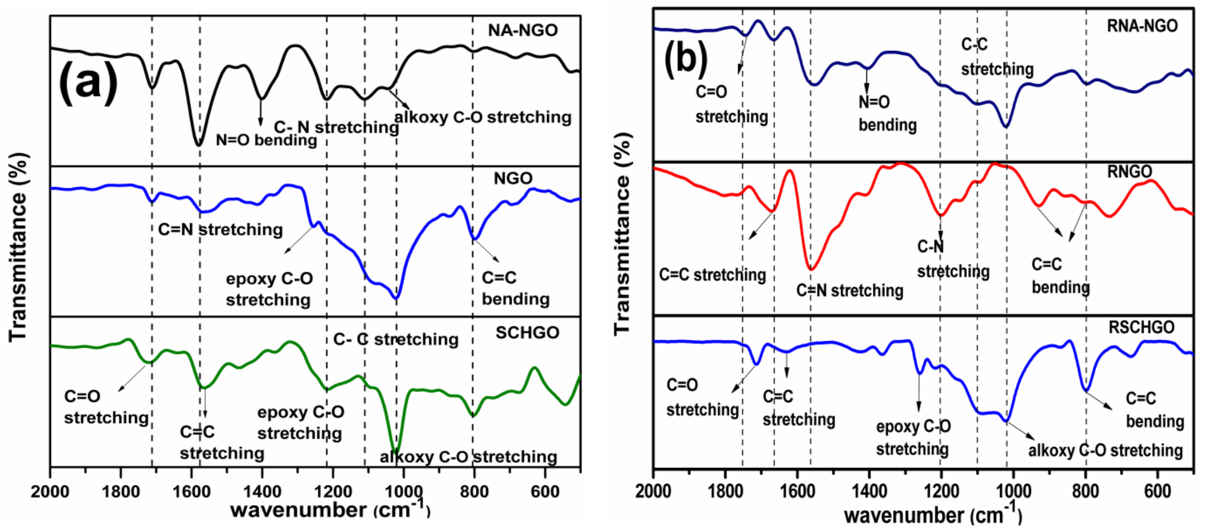

Fig S1. (a) FT-IR spectra of SCHGO, NGO & NA-NGO and (b) FT-IR spectra of RSCHGO, RNGO & RNA-NGO.

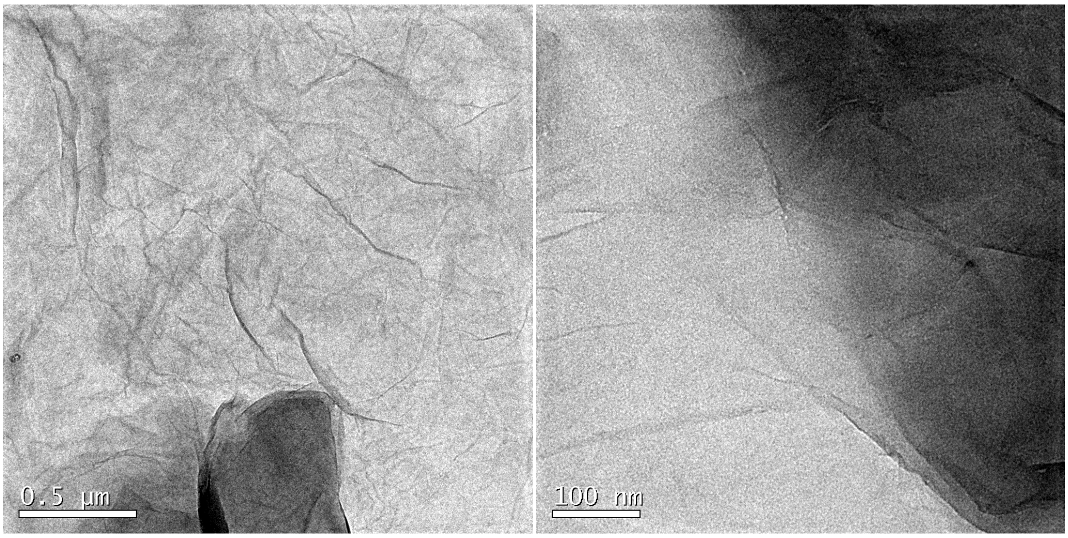

Fig S2. TEM images of GO (without supercritical treatment) at different magnification

Electrochemical Impedance spectroscopy (EIS)

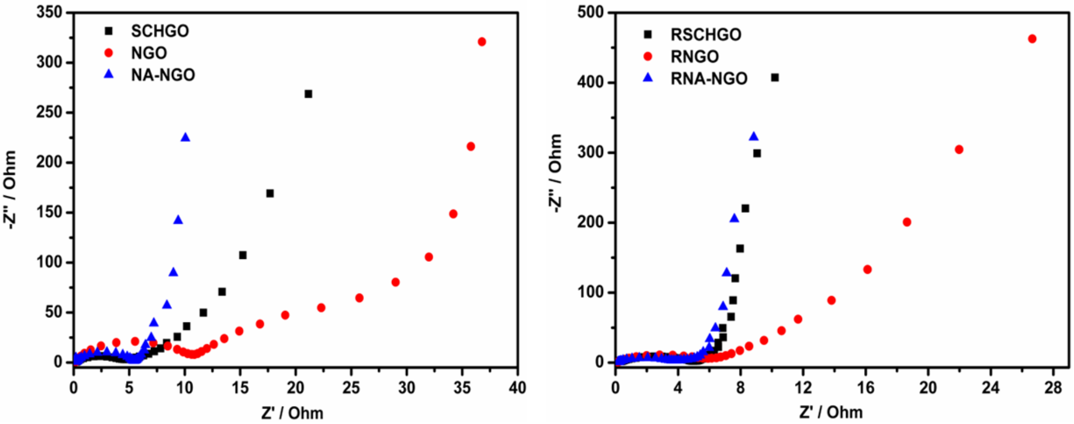

Fig S3. Nyquist plot of SCHGO, NGO, NA-NGO , RSCHGO, RNGO & RNA-NGO in 1 M H_2SO_4 aqueous electrolyte.

The electrochemical impedance spectroscopy was recorded for all the samples and the characteristic impedance curves are shown in Figure S2. In the high frequency region, the radius of semicircle plotted is symptomatic of electrode conductivity and the charge-transfer resistance in the electrode materials. Among the six electrode materials, RNA-NGO possesses low charge transfer resistance and good conductivity. In the middle-frequency region, the 45° sloped curve known as the Warburg portion which is closely associated with the transport of electrolyte ions in the electrodes. The very short Warburg curve observed for RNA-NGO indicated that ions of the electrolyte are significantly diffused through electrode surface in a shorter path in such a manner that there will be easier access of ions of the electrolyte to the electrode surface. In the low-frequency region, the slope of the plot for RNA-NGO is steeper among the six electrode materials emphasizing that RNA-NGO exhibits a more ideal capacitive behaviour.

Table S1. Charge transfer resistance values of SCHGO, RSCHGO, NGO, RNGO, NA-NGO & RNA- NGO samples.

Samples	**R_{ct} (Ω)**
SCHGO	4.23
RSCHGO	4.70
NGO	10.68
RNGO	5.87
NA-NGO	5.22
RNA-NGO	3.71

References

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