

Supplementary Material

Plasma-Assisted Nitrogen Doping of Langmuir–Blodgett Self-Assembled Graphene Films

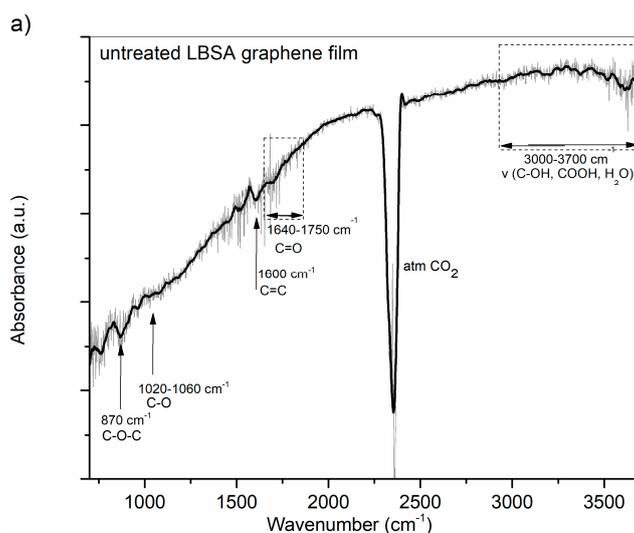
Tijana Tomašević-Ilić¹, Nikola Škoro¹, Đorđe Jovanović¹, Nevena Puač¹ and Marko Spasenović^{2,*}

¹ Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia; ttijana@ipb.ac.rs (T.T.-I.); nskoro@ipb.ac.rs (N.Š.); djordje@ipb.ac.rs (Đ.J.); nevena@ipb.ac.rs (N.P.);

² Center for Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

* Correspondence: spasenovic@nanosys.ihtm.bg.ac.rs

Figure S1 depicts FTIR spectra for untreated as well as 1 and 5 min nitrogen-plasma-treated LBSA graphene films. The FTIR spectra of the samples show bands near 880 cm^{-1} , in a spectral region associated with the formation of epoxides (C-O-C) at graphene edges [1], bands at 1285 cm^{-1} and $1020\text{--}1045\text{ cm}^{-1}$ associated with the C-O stretches of the hydroxyl and alkoxy groups [2], the peak at 1600 cm^{-1} due to vibrations of aromatic C=C bonds, and vibrational modes for carbonyl (C=O) and carboxyl groups (COOH) in the region at $1600\text{--}1750\text{ cm}^{-1}$ [3]. We also distinguish a broad band in the $3000\text{--}3700\text{ cm}^{-1}$ region before nitrogen exposure, corresponding to the presence of hydroxyl and carboxyl groups, as well as absorbed water. After exposure of graphene films to the nitrogen source, the intensity of peaks associated with these groups is reduced, and the peaks associated with nitrogen-containing groups appear. FTIR spectra of nitrogen-exposed samples (1 and 5 min) reveal a peak at 1134 cm^{-1} , an IR fingerprint of pyrrolic N [4]. The intensity of this peak increases with exposure. After 1 min of nitrogen plasma exposure, C-N stretching vibrations can be detected at 1430 cm^{-1} [5]. Also, in the spectra of 5 min treated film, a peak appears at 1187 cm^{-1} indicating the formation of nitrogen-containing groups [6].



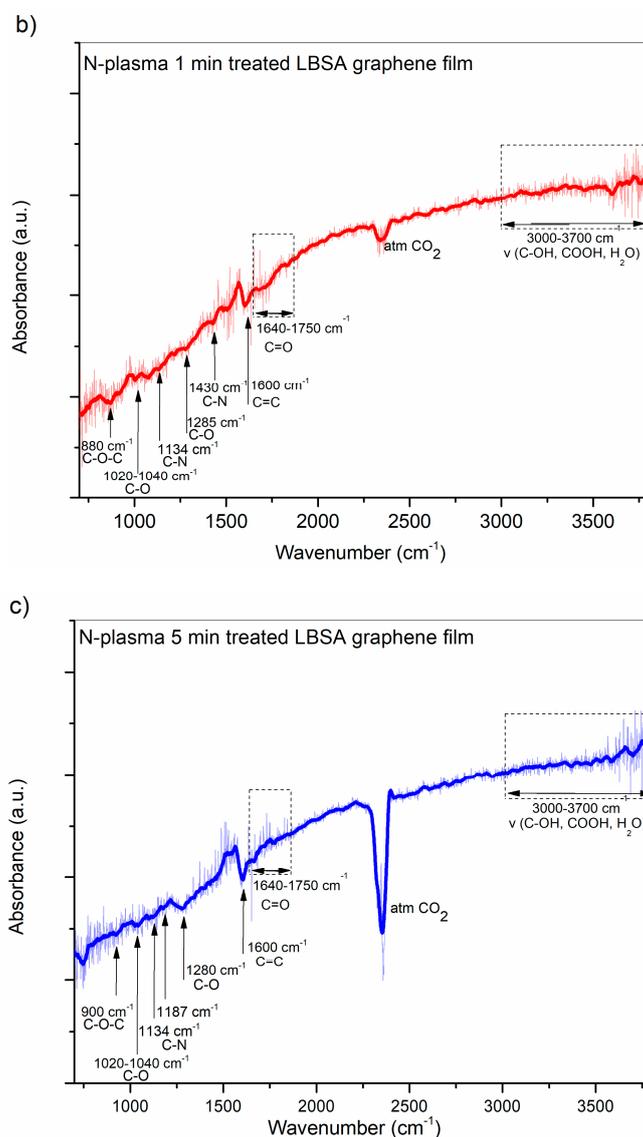


Figure S1. FTIR absorption spectra of (a) untreated (black), (b) 1 min (red), and (c) 5 min (blue) N-plasma-exposed LBSA graphene films. We indicate vibrational modes for hydroxyls (possible C-OH, COOH, and H₂O contributions) at 3000–3700 cm⁻¹, carbonyl (C=O) and carboxyl groups (COOH) at 1600–1750 cm⁻¹, sp²-hybridized (C=C) at 1600 cm⁻¹, the C–O stretches of the hydroxyl and alkoxy groups at 1285 cm⁻¹ and 1020–1045 cm⁻¹, respectively, C–N at 1430 and 1187 cm⁻¹, pyrrolic N at 1134 cm⁻¹, and epoxides (C–O–C) near 900 cm⁻¹.

References

- [1] Acik, M.; Lee, G.; Mattevi, C.; Pirkle, A.; Wallace, R.M.; Chhowalla, M.; Cho, K.; Chabal, Y. The role of oxygen during thermal reduction of graphene oxide studied by infrared absorption spectroscopy. *J. Phys. Chem. C* **2011**, *115*, 19761–19781.

- [2] Fedoseeva, Y.V.; Lobiak, E.V.; Shlyakhova, E.V.; Kovalenko, K.A.; Kuznetsova, V.R.; Vorfolomeeva, A.A.; Grebenkina, M.A.; Nishchakova, A.D.; Makarova, A.A.; Bulusheva, L.G.; Okotrub, A.V. Hydrothermal Activation of Porous Nitrogen-Doped Carbon Materials for Electrochemical Capacitors and Sodium-Ion Batteries. *Nanomaterials* **2020**, *10*, 2163.
- [3] Tomašević-Ilić, T.; Jovanović, Đ.; Popov, I.; Fandan, R.; Pedrós, J.; Spasenović, M.; Gajić, R. Reducing sheet resistance of self-assembled transparent graphene films by defect patching and doping with UV/ozone treatment. *Appl. Surf. Sci.* **2018**, *458*, 446–453.
- [4] Lazar, P.; Mach, R.; Otyepka, M. Spectroscopic Fingerprints of Graphitic, Pyrrolic, Pyridinic, and Chemisorbed Nitrogen in N-Doped Graphene. *J. Phys. Chem. C* **2019**, *123*, 10695–10702.
- [5] Sudhakar, S.; Jaiswal, K.K.; Peera, G.; Ramaswamy A.P. Green Synthesis of N-Graphene By Hydrothermal-Microwave Irradiation For Alkaline Fuel Cell Application. *Int. J. Recent Sci. Res.* **2017**, *8*, 19049–19053.
- [6] Kumar, M.P.; Kesavan, T.; Kalita, G.; Ragupathy, P.; Narayanan, T.N.; Pattanayak, D.K. On the large capacitance of nitrogen doped graphene derived by a facile route. *RSC Adv.* **2014**, *4*, 38689–38697.