

Supplementary Information

Investigation of the Synergy between Atmospheric Plasma and Graphene-Oxide-Based Materials for Perfluorooctanoic Acid Degradation

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This file consists of 9 pages containing

- typical waveforms of voltage and current in M-SPD mode (Figure S1)
- the description of the characterization of the graphene-based materials including 1 table (Table S1) and 4 figures (Figure S2-S5).

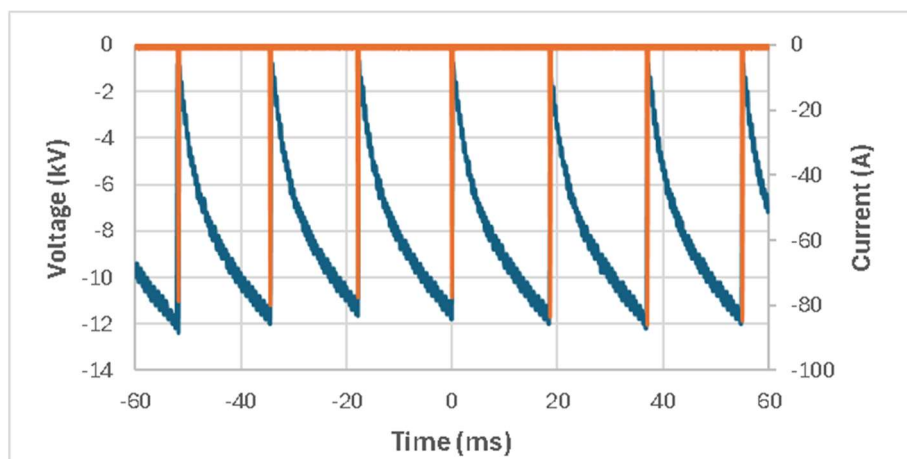


Figure S1. Waveforms of voltage and current in multipin self-pulsed discharge (M-SPD) discharge in argon at 6 W.

Characterization of Graphene-based materials

FT-IR spectroscopy was used to characterize the functional groups present in the synthesized catalysts. In Figure S2, a wide absorption band between ~ 3000 and $\sim 3500\text{ cm}^{-1}$ is observed in the spectrum of GO, which is attributed to the O-H stretching vibration of the carboxylic (-COOH) groups and, possibly, to adsorbed water molecules. The other absorption bands were attributed to C-O stretching ($\nu_{\text{C-O}} \sim 1050\text{ cm}^{-1}$), C-O-C stretching ($\nu_{\text{C-O-C}} \sim 1170\text{ cm}^{-1}$), C-O-H stretching ($\nu_{\text{C-O-H}} \sim 1350\text{ cm}^{-1}$), C=C stretching of unoxidized graphitic domain ($\nu_{\text{C=C}} \sim 1630\text{ cm}^{-1}$), and C=O stretching of carboxylic acid and carbonyl ($>\text{C=O}$) functionalities ($\nu_{\text{C=O}} \sim 1740\text{ cm}^{-1}$) [1]. The frequency values observed and assigned to the various groups are in good agreement with those published previously [2-5]. In the FT-IR spectra of reduced graphene oxide (rGO) (Figure S2), the wide peak observed at $\sim 3500\text{ cm}^{-1}$ in the GO spectrum corresponding to the O-H band has disappeared. Moreover, the intensity decrease of the C-O band at $\sim 1050\text{ cm}^{-1}$ and of the C-O-C band at $\sim 1170\text{ cm}^{-1}$ confirms the actual reduction of GO. The peaks at 1630 cm^{-1} and 1740 cm^{-1} in the GO spectrum shifted to 1570 cm^{-1} and 1720 cm^{-1} , respectively, after the reduction process. Thus, the disappearance of the characteristic peaks assigned to oxygen-containing groups and the shift of the peaks assigned to C=C and C=O bonds confirm the successful reduction of GO. The spectrum of B-rGO (Figure S2), provides evidence for the removal of functional groups on the surface of GO. These results are comparable to those of previous studies [2].

The synthesized GO, rGO, and B-rGO were examined for their structural morphology using SEM, and the EDS spectrum was acquired to calculate the C/O ratio (Table S1). Graphene oxide had an average C/O ratio of 2.0, which is within the typical C/O ratio range for GO of 1.5–2.5 [6] (Table S1). The SEM images show, in contrast with the flat sheet appearance of GO, irregular wrinkles at several places on the surface of B-rGO (Figure S3). Therefore, AFM

analysis of GO was also performed, where flat sheet-type images and the thickness of the particles were detected (Figure S4).

For reduced graphene oxide, a C/O ratio of 6.7 was found (Table S1), confirming the decrease in the amount of oxygen present in the particles and thus the actual reduction of GO. This result is in accordance with those reported by Araujo et al., who found that the C/O ratio increased up to 6.0–13.5 as a consequence of GO reduction. Figure S3b shows the SEM image and EDS spectrum of the rGO [6]. Several flat sheets with wrinkles were observed, which is a sign of GO reduction [2]. The B-rGO particles were also characterized via SEM imaging and EDS spectra (Figure S3c). The wrinkled flat sheet image can also be seen in B-rGO, which indicates GO reduction. As observed in rGO, the C/O ratio increased up to 7.0 by decreasing the amount of oxygen present in the particle (Table S1). Boron was not quantified due to overlapping of its peak with the carbon peak.

The AFM results for GO are presented in Figure S4a. By fitting all the heights of the surfaces with a Double Gaussian function, the height of the flake can be calculated as the distance between the two centers of the Gaussians, corresponding to the surface and flake heights. The average height of the GO flakes was 0.95 nm, illustrating the consistency of the GO monolayer. The rGO and B-rGO particles were sonicated using a microtip sonicator before AFM analysis, which facilitated the spin-coating of the particles. The layer thicknesses were approximately 1.6 nm and 1 nm for rGO (Figure S4b.) and B-rGO (Figure S4c.), respectively.

The XRD patterns of GO and B-rGO are presented in Figure S5. In accordance with Sahu et al. [7], GO spectra show a characteristic peak at approximately 10° , while this peak in B-rGO was shifted to around 25° , that indicates oxygen loss compared to GO [2,7]. While the peak at 15° can be assigned to B_2O_3 , the peaks at 34° can be attributed to the addition of boron atoms [2].

References

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Table S1. C/O ratio determined for the synthesized materials, GO, rGO and B-rGO

Particle	C (%)	O (%)	C/O ratio
Graphene Oxide	65.6	32.0	2.0
Reduced Graphene Oxide	85.2	12.7	6.7
Boron-doped Reduced Graphene Oxide	85.7	12.3	7.0

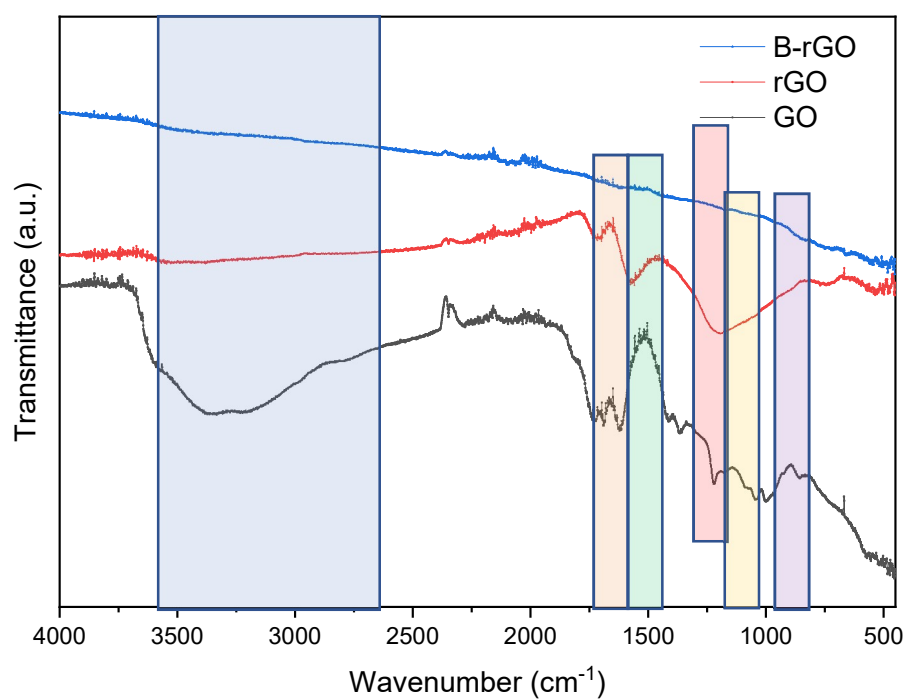


Figure S2. FT-IR spectrum of graphene oxide (GO), reduced graphene oxide (rGO), and boron-doped reduced graphene oxide (B-rGO)

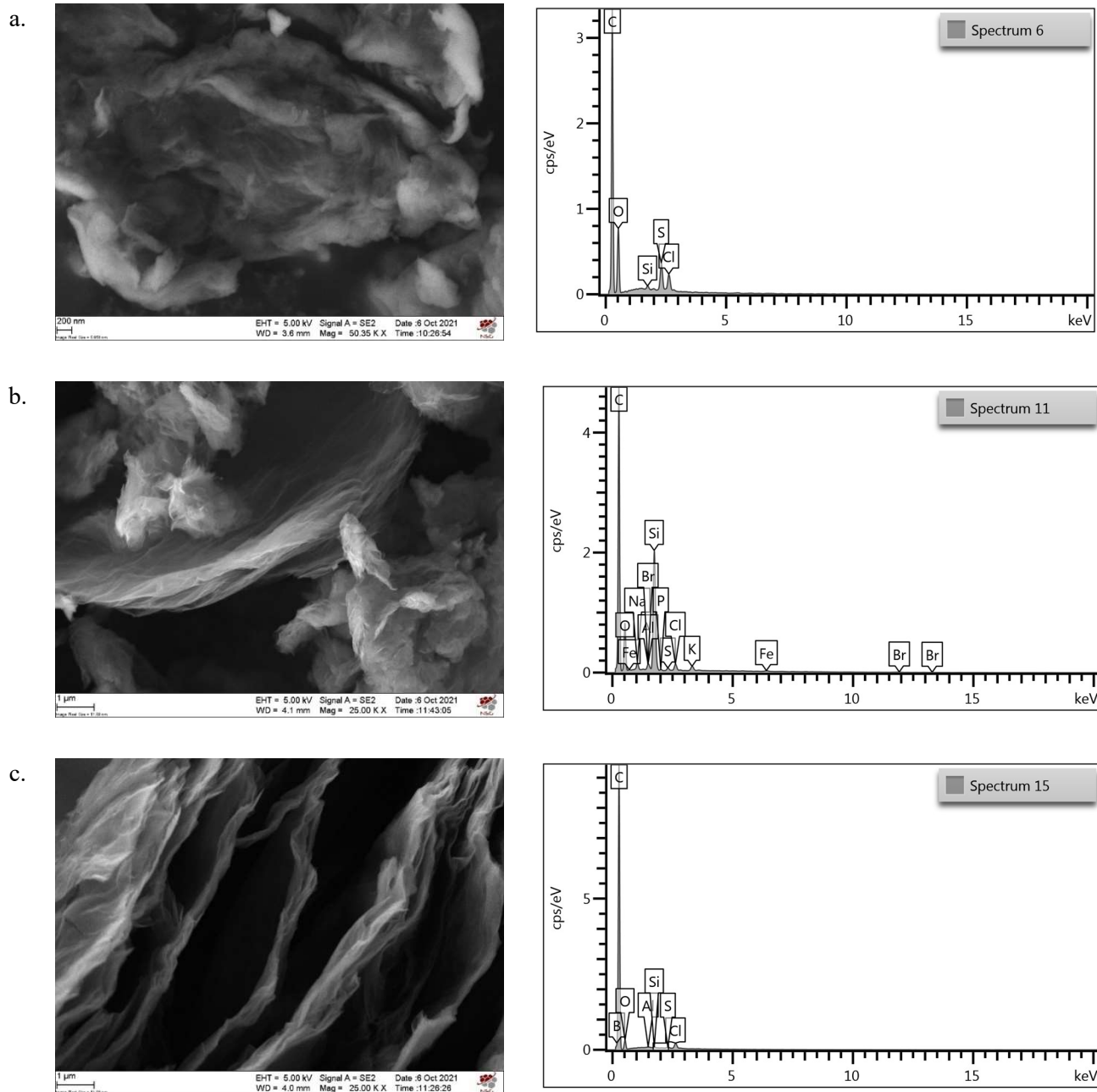


Figure S3. SEM image and relative EDS spectrum of (a) GO, (b) rGO, and (c) B-rGO

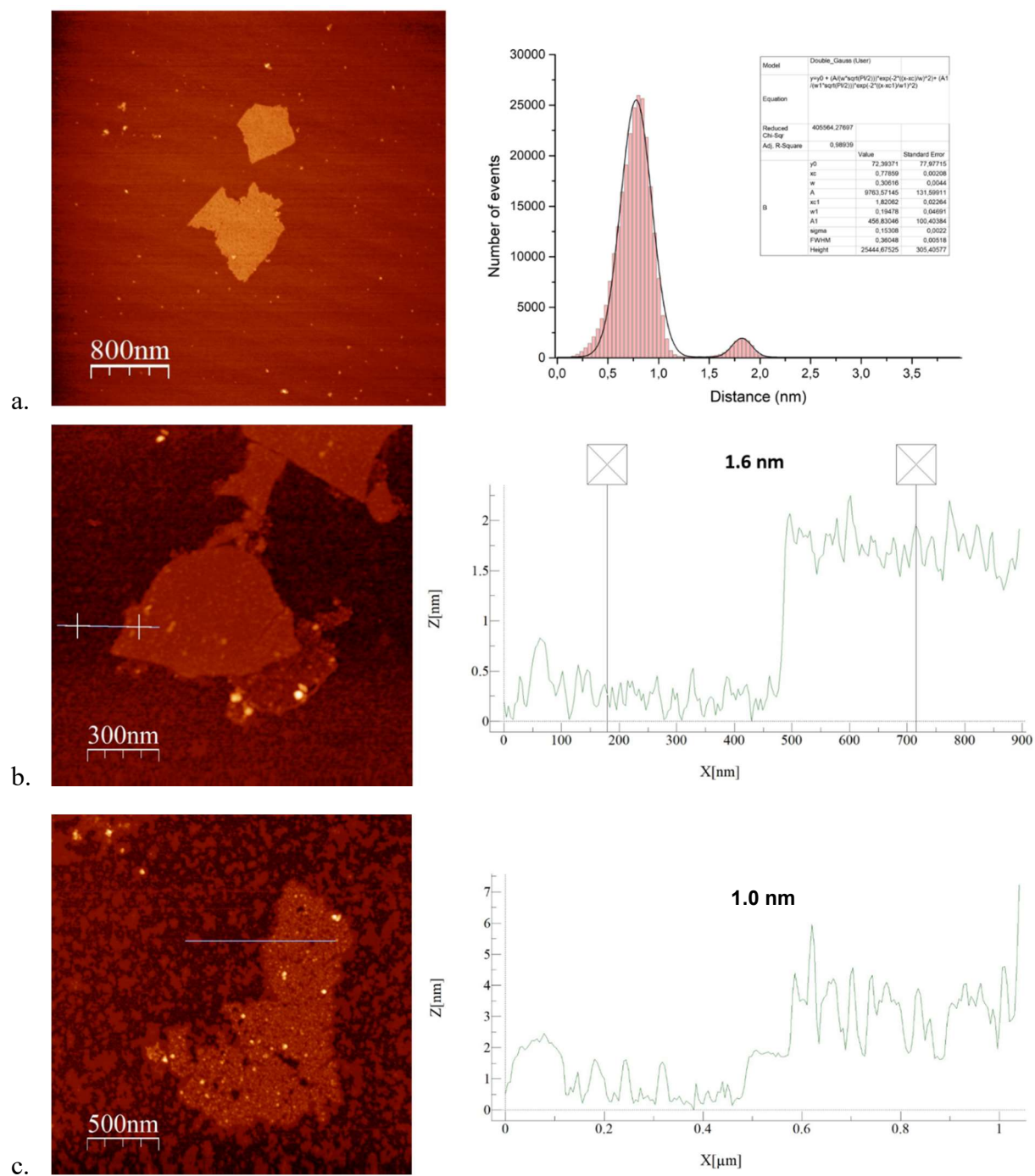


Figure S4. AFM imaging of (a) GO, (b) rGO and (c) B-rGO and layer thickness

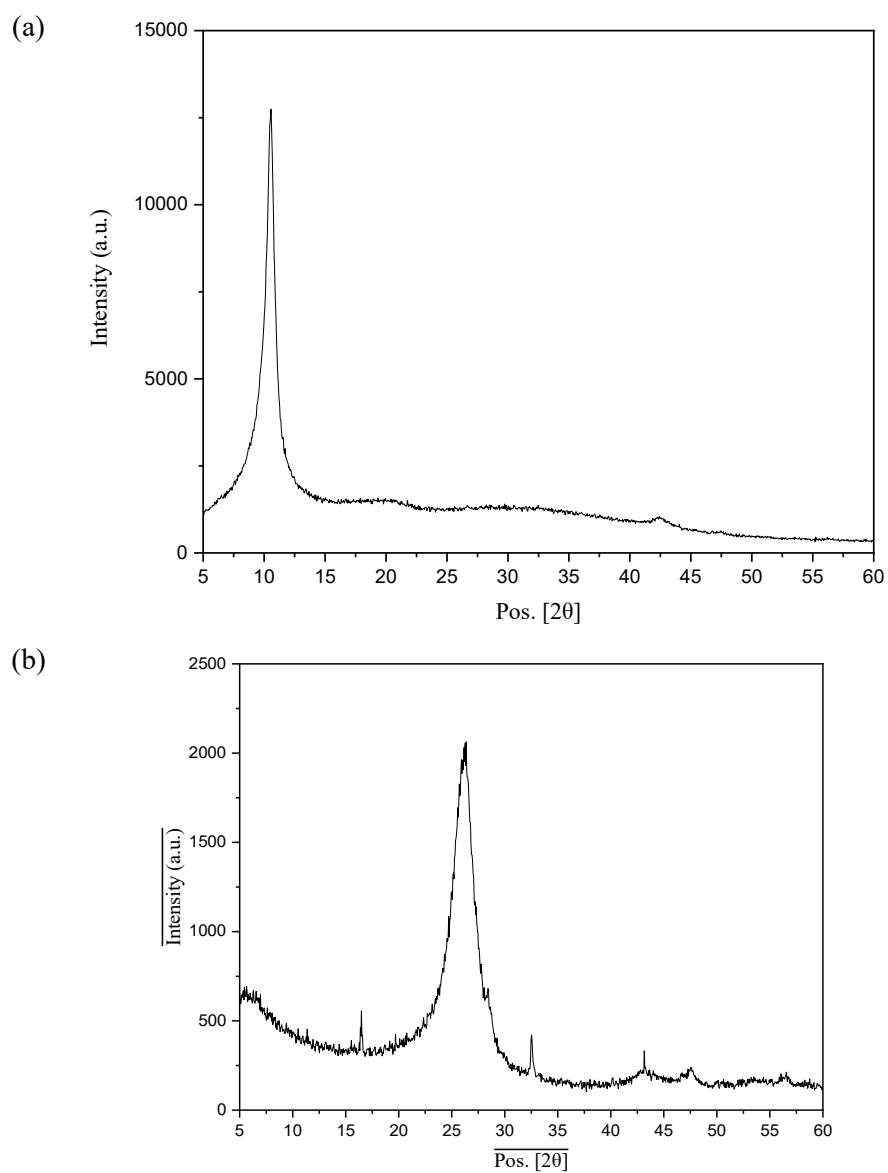


Figure S5. XRD spectrum of (a) GO and (b) B-rGO