Incorporation-limiting mechanisms during nitrogenation of monolayer graphene films in nitrogen flowing afterglows

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SUPPLEMENTARY DATA

S1 – PLASMA DIAGNOSTICS

Number densities of key species are extracted using NO titration and line-ratio of particular spectral bands. NO gas is added to the flowing afterglow and the emission intensity of the NO_β band at 320 nm is followed. monitored. Extinction of the emission occurs when the density of N atoms is equal to the density of NO (see **Figure S1**). The titration method allow for the calculation of a constant, $k_{titration}$, that can be used to link the emission intensity of the 580 nm line to the number density of N atoms [1,2]:

$$a\, I_{580} = k_{titration}[N]^2$$

, where I_{580} is the emission intensity of the 580 nm line; $k_{titration}$ is a constant for a given geometry and exposure time of the acquisition; $[N]$ is the number density of atomic nitrogen; a is the coefficient that expresses the transition between the early afterglow and the late afterglow.

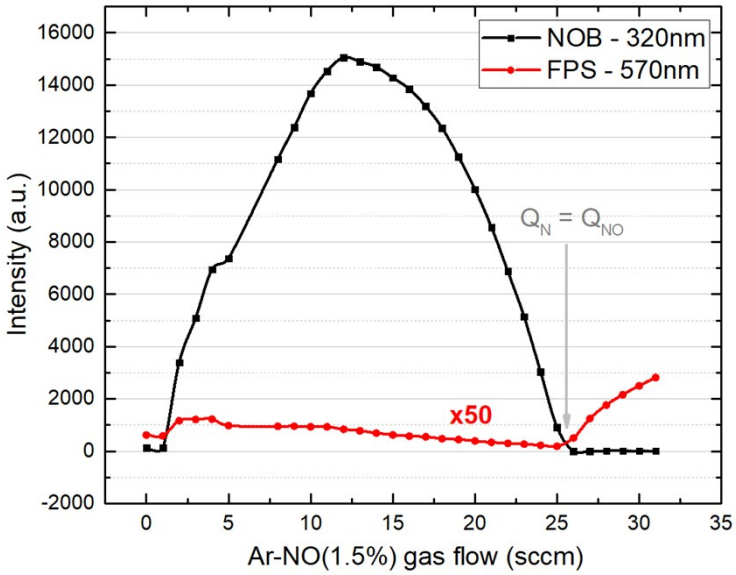

Figure S1 – NO titration. Intensity of the NO_β-320 nm as a function of Ar-NO gas flow. When the gas flow of NO (Q_{NO}) reaches the gas flow of atomic nitrogen Q_N, the loss of N is complete and there is extinction of the NO_β emission.

A given set of experimental conditions with NO in the microwave nitrogen flowing afterglow is chosen as a calibration to obtain the vibrational energy distribution function of the early and late afterglows. As shown in Figure S1, by varying the NO concentration in the microwave nitrogen flowing afterglow, a full extinction of the late afterglow can be seen. From this set of data, constraint linear fitting of the distribution is done over the whole set of conditions. All coefficients are bound between 0 and 1, and the distribution are normalized. In addition, the distribution of the early afterglow is constrained to an exponential decay, with a vibrational temperature of 0.66 eV. The results are shown in Figure S2a for the vibrational energy distribution and in Figure S2b for the a coefficient as a function of the NO concentration.

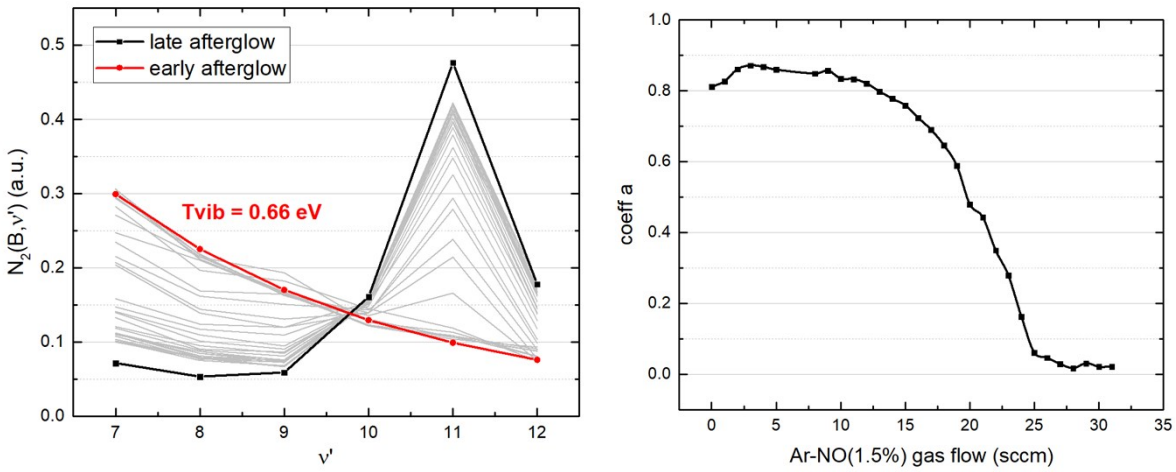

Figure S2 – (a) Evolution of the vibrational energy distribution of the first positive system of N_2 for various concentrations of NO leading to the extinction of the late afterglow. (b) Influence of the NO concentration on the *a* coefficient.

As for the population of $N_2(A)$, it can be obtained from the band ratio [3]:

$$\frac{a\, I_{580}}{I_{316}} = \frac{A_{580}\, k_{01}[N_2][N]^2/(v_{27} + k_{02}[N_2])}{A_{316}\, k_{03}[N_2(A)]^2/(v_{30} + k_{26}[N_2])}$$

Reaction	**Rate constant**
$N + N + N_2 \Rightarrow N_2(B,v) + N_2$	k_{01} = 4.4e-34 ; cm^6s^{-1}
$N_2(B) + N_2 \Rightarrow N_2(A,X) + N_2$	k_{02} = 3e-11 ; $cm^{-3}s^{-1}$
$N_2(A) + N_2(A) \Rightarrow N_2(C,1) + N_2(X)$	k_{03} = 4.1e-11 ; cm^3s^{-1}
$N_2(C,1) + N_2 \Rightarrow$ products	k_{26} = 3e-11 ; cm^3s^{-1}
$N_2(B,11) \Rightarrow N_2(A,v') + hv$	v_{27} = 2e5 ; s^{-1}
$N_2(C,1) \Rightarrow N_2(B) + hv$	v_{30} = 2.7e7 ; s^{-1}

A_{580} = 7.8e4 ; s^{-1}

A_{316} = 1.3e7 ; s^{-1}

S2 – XPS ANALYSIS

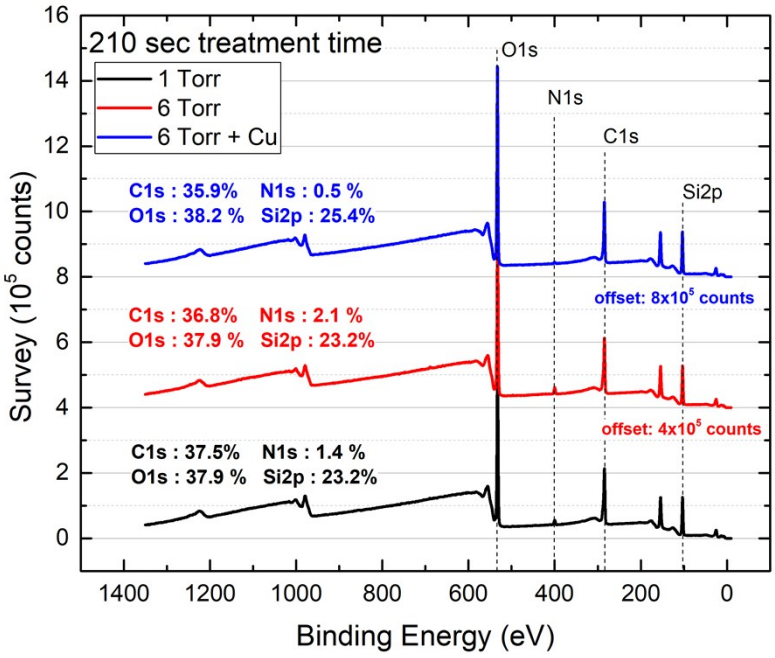

Figure S3– Survey spectra for the 210-treatment time for all conditions.

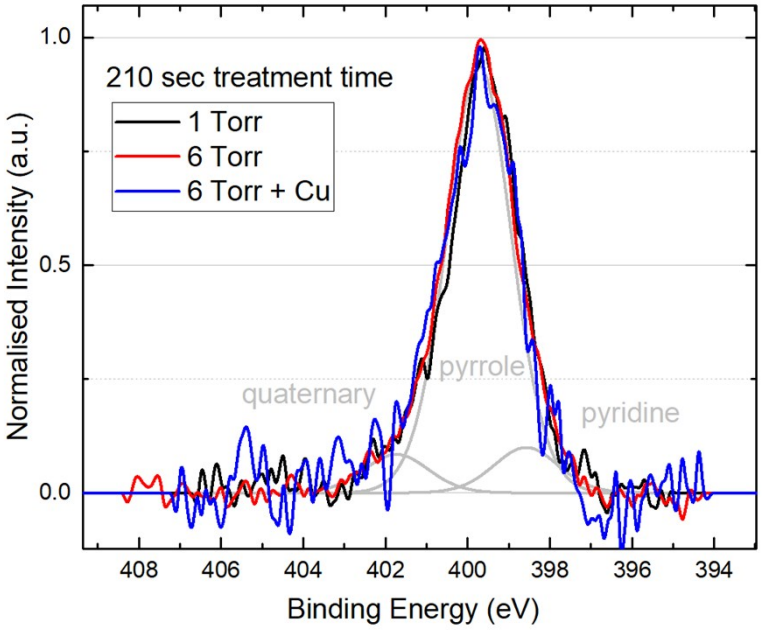

Figure S4 – Normalized high-resolution N1s XPS spectra for the 210-treatment time for all studied conditions.

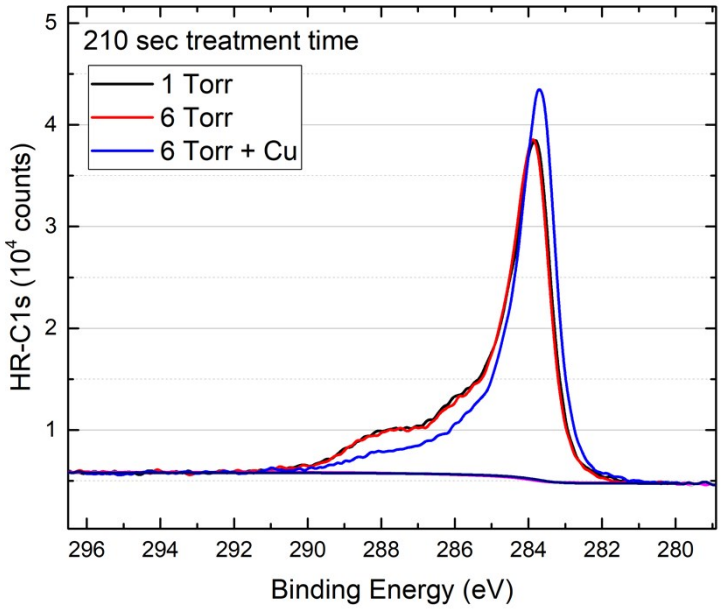

Figure S5 – High resolution C1s spectra for the 210-treatment time for all conditions.

REFERENCES

1 H. Zerrouki, A. Ricard and J. P. Sarrette, Determination of N and O-atoms and N2 (A) metastable molecule densities in the afterglows of N2-H2, Ar-N2-H2 and Ar-N2-O2 microwave discharges, *Contrib. to Plasma Phys.*, 2014, **54**, 827–837.

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3 A. Ricard, S. Oh and V. Guerra, Line-ratio determination of atomic oxygen and N2 (A) metastable absolute densities in an RF nitrogen late afterglow, *Plasma Sources Sci. Technol.*, 2013, **22**, 035009.