

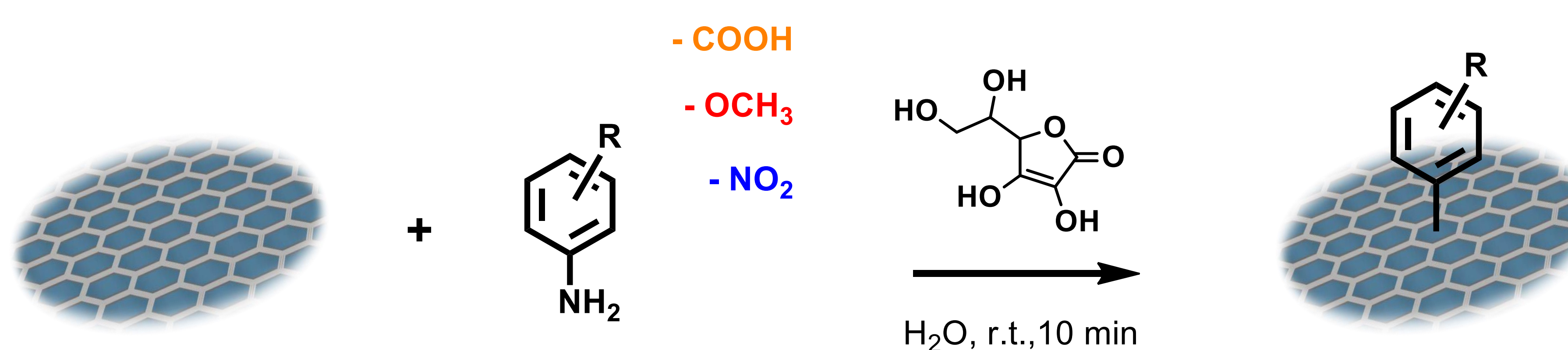
## Study of the steric hindrance in grafting reactions

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### Abstract

Graphitic materials can be modified for tailoring their properties and for the introduction of different functionalities in which, subsequently, other molecules can be anchored. In particular, the electrochemical reduction of different aryldiazonium salts has been shown to be a valuable tool for this purpose.[1] As a result, the diazonium chemistry on carbon surfaces has been studied intensively. The impact of the nature of substituent groups on the grafting density and also the ability of sterically hindering functional groups for circumventing dendritic multilayer growth,[2] has been reported. Herein we report on the influence of the substituent position on the grafting density for three diazonium salts. Among several factors that are at play, we hypothesize that steric hindrance of the radical structure is key to the reaction efficiency. To address this, we have studied the reduction of different aryldiazonium salts in aqueous solution using ascorbic acid as reducing agent.[3] This protocol leads to a self-limiting growth of monolayers with high grafting densities. We have discussed the differences observed in the grafting density, morphology and surface coverage as a function of the position and the nature of the substituent. Differences between grafting efficiencies were assessed by Raman spectroscopy whereas scanning tunneling microscopy (STM) provided nanometer scale insight into the structure of the covalent films.



### Results

Functionalized graphite was characterized by different techniques. In Raman spectroscopy, a slight increment of the  $sp^3$  carbon atom defects (increment of the D band) was obtained. Table 1 provides the  $I_D/I_G$  ratios for the different systems studied here.

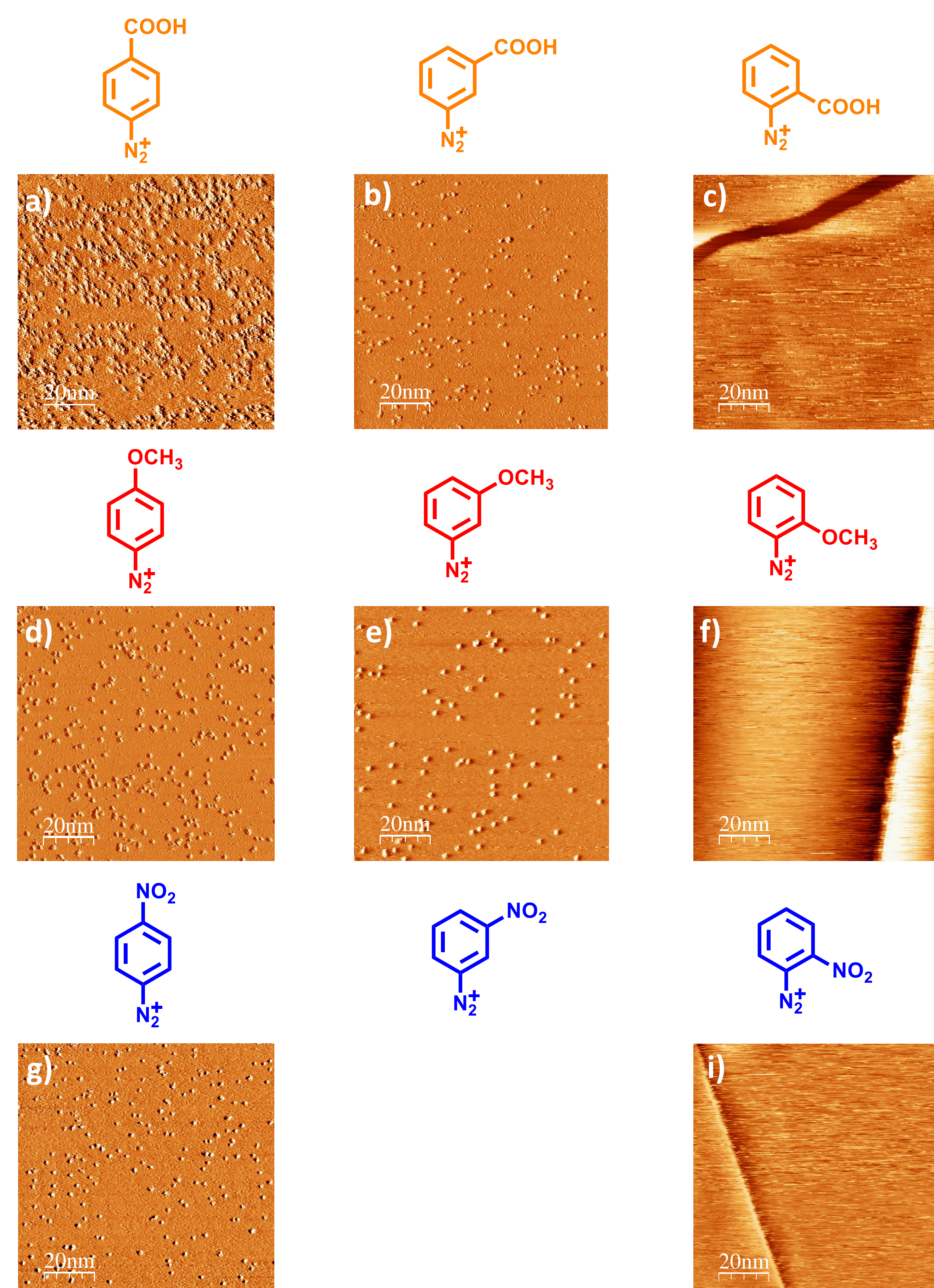
**Table 1.**  $I_D/I_G$  ratio (36 spectra)

	<i>p</i> -	<i>m</i> -	<i>o</i> -
<b>CBD</b>	0.082 ± 0.003	0.050 ± 0.008	0.000 ± 0.001
<b>MBD</b>	0.052 ± 0.011	0.011 ± 0.001	0.000 ± 0.000
<b>NBD</b>	0.040 ± 0.002	0.021 ± 0.002	0.000 ± 0.000

Fig. 1 a-i show representative 100 nm STM images of covalently modified graphite using the different precursors. The images show that the surface is covered with spherical bright features which are attributed to the covalently bound aryl groups. The number of these grafted molecules in an area of 100 nm x 100 nm are summarized in table 2. The trend in the grafting densities obtained from the Raman measurements is confirmed by the STM data wherein the STM images clearly show a decrease in the number of bright features in the following expected order: *para*- > *meta*- > *ortho*-.

**Table 2.** Number of grafted molecules in an area of 100 nm x 100 nm (average of 5 images).

	<i>p</i> -	<i>m</i> -	<i>o</i> -
<b>CBD</b>	693	184	0
<b>MBD</b>	344	100	0
<b>NBD</b>	224	151	0



**Figure 1.** Representative STM images of the covalently modified surfaces. Imaging parameters:  $I_t = 0.08$  nA,  $V_{bias} = -700$  mV.

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### ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the Fund of Scientific Research Flanders (FWO) and KU Leuven - Internal Funds.