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Study of the steric hindrance in grafting reactions

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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.

References

[1] Kuila, Saswaa Bose, Ananta Kumar Mishra, Partha Khanra, Nam Hoon Kim and Joong Hee Lee, Prog. Mater. Sci., 57 (2012) 1061.
[2] Kazukuni Tahara, Yuki Kubo, Benjamin Lindner, Shingo Hashimoto, Shingo Hirose, Anton Brown, Brandon Hirsch, Lakshya Daukiya, Steven De Feyter and Yoshito Tobe, Langmuir, 35 (2019) 2089.
[3] Miriam C. Rodríguez González, Anton Brown, Samuel Eyley, Wim Thielemans, Kunal S. Mali and Steven De Feyter, Nanoscale, 12 (2020) 18782.

Figures

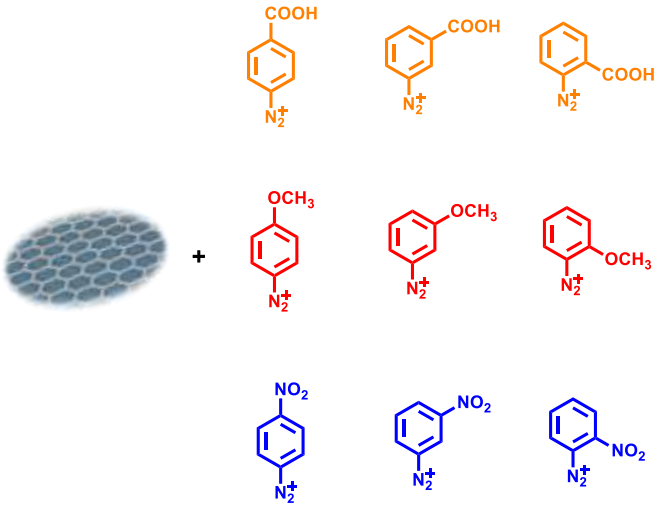

Figure 1: Molecular structures of the diazonium salts used in the study.