Visible-Light Assisted Covalent Surface Functionalization of graphene based materials with Arylazo sulfones

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We present an unprecedented environmentally benign methodology for the covalent functionalization [1] (arylation) of different sp^2 carbon-based materials with arylazo sulfones: from Graphene Oxide, to reduced Graphene Oxide (rGO), considering also the highly oriented pyrolytic graphite (HOPG) as ideal 100% sp^2 substrate. A variety of tagged aryl units were conveniently accommodated at the rGO surface via visible-light irradiation of suspensions of carbon nanostructured materials in aqueous media. Mild reaction conditions, absence of photosensitizers, functional group tolerance and high atomic fractions (XPS analysis) represent some of the salient features characterizing the present methodology. The late stage-functionalization of the modified rGO and a mechanistic proposal based on both experimental as well as spectroscopic analyses completed the study, control experiments for the mechanistic elucidation as Raman analysis on HOPG was successfully achieved [2]. The quantitative analytical determination of the tagged aryl units via XPS, represent a unique combination of factors electing the present methodology as a valuable synthetic alternative to the known protocols [3,4] for the covalent modification of reduced graphene oxide surface.

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References

[1] C. Sauer, Y. Liu, A. De Nisi, S. Protti, M. Fagnogni, M. Bandini, ChemCatChem 2017, 9, 4456-4459
[2] Lombardi L., Kovtun A., Mantovani S., Bertuzzi G., Favaretto L., Bettini C., Palermo V., Melucci M., Bandini M. *Chemistry—A European Journal*, accepted manuscript
[3] Sinitskii, A.; Dimiev, A.; Corley, D. A.; Fursina, A. A.; Kosynkin, D. V.; Tour, J. M. ACS Nano 2010, 4, 1949
[4] Greenwood, J.; Phan, T. H.; Fujita, Y.; Li, Z.; Ivasenko, O.; Vanderlinden, W.; Van Group, H.; Frederickx, W.; Lu, G.; Tahara, K.; Tobe, Y.; Uji-I, H.; Mertens, S. F. L.; De Feyter, S., ACS Nano 2015, 9, 5520

Figures

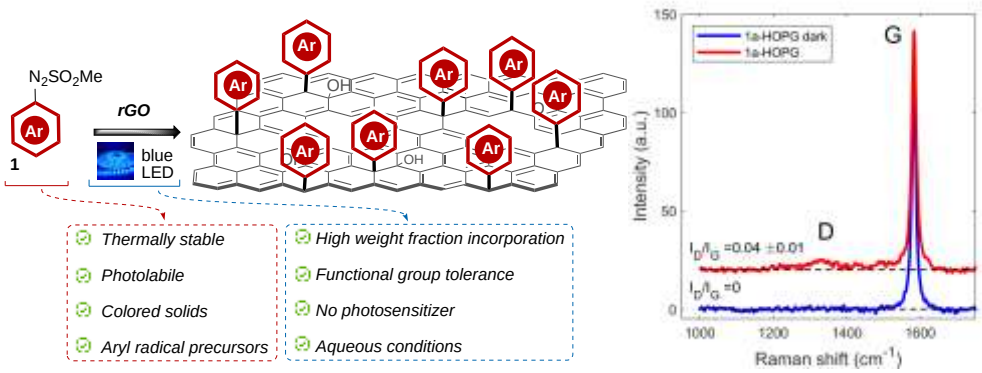

Figure 1: left: schematic representation of the present visible-light assisted covalent arylation of rGO with arylazo sulfones. Right: Raman spectrum of 1a-HOPG dark and 1a-HOPG. Linear background was subtracted, and spectra were shifted for clarity.