

Electron irradiation of N-heterocyclic carbenes SAMs on gold

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Electron irradiation of self-assembled monolayers (SAMs) is a versatile tool not only for high-resolution classical lithography but also for surface modification of monolayers chemical functionality (chemical lithography), or creation of carbon nanomembranes (CNMs) with potential application in ultrafiltration and nanobiosensing. While the interactions between the electron beam and aromatic or aliphatic thiolate SAMs on gold have been well studied, the behavior of more complex systems such as N-heterocyclic carbenes (NHCs), which are recently attracting growing attention due to their high chemical[1] and thermal stability[2,3], remains unknown. In the current work, we analyze the electron irradiation of SAMs on gold based on the series of NHC molecules featuring (i) different number of benzene moieties (0-2), and (ii) different side groups (methyl, isopropyl) and consequently different packing density[3]. The changes in monolayer thickness and composition are traced by X-ray photoelectron spectroscopy as a function of electron dose. Our results show that irradiated NHC SAMs resemble aromatic systems and cross-linking process could be observed. However, in contrast to thiols on gold[4] or carboxylic acids on silver[5], the molecule-substrate bond is strongly resistant to removal by electron irradiation. Finally, we investigate the possibility of creation of CNMs from series NHC SAMs examining the influence of molecules design on mechanical properties of nanomembranes.

[1] Crudden *et al.*, *Nat Chem.*, **5**, 409-414 (2014)

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[4] Yildirim *et al.*, *J Phys Chem C*, **1**, 567-576 (2017)

[5] Kruk *et al.*, *J Phys Chem C*, **17**, 9310-9318 (2021)