N-Heterocyclic Carbene and Olefin Monolayers on Silicon

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Organic overlayers have emerged into a promising surface modification or functionalization tool and N-Heterocyclic carbenes (NHCs) and their close relatives, the N-heterocyclic olefins (NHOs), were found to be particularly suitable in this regard forming highly ordered self-assembled monolayers (SAMs) on metal surfaces that exhibit superior properties to the widely used thiol-based SAMs. As silicon remains the material of choice in today's semiconductor technology a functionalization of its surfaces is of highest interest.

Here, a comprehensive scanning tunnelling microscopy (STM), density functional theory, and X-ray photoemission spectroscopy study of the growth of NHC and NHO monolayers on clean and modified silicon surfaces is presented [1-3]. We demonstrate the formation of highly ordered monolayers binding to the surface via a single Si–C bond (see Fig. 1). The monolayers exhibit high thermal stabilities and show large work function reductions. By systematically varying the sidegroups and the backbone of the molecules and investigating two different molecule classes (NHCs and NHOs), we obtain a profound understanding of the bonding, structure, and assembly of NHCs and NHOs on Si offering guiding rules for a targeted modification of Si surfaces.

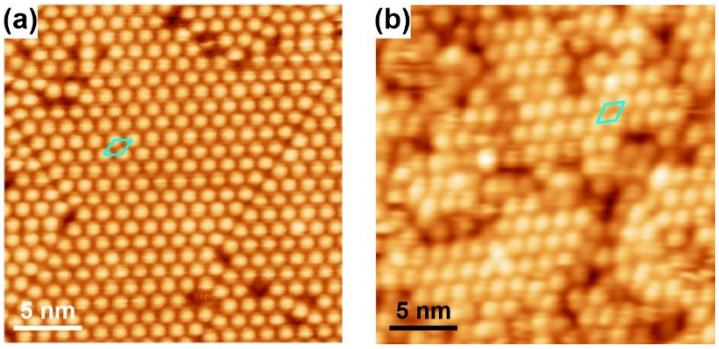

Figure 1: STM images of exemplary ordered monolayers of (a) NHCs and (b) NHOs on silicon [1,3].

[1] M. Franz et al., Nat. Chem. 13, 828-835 (2021).
[2] R. Zielinski et al., J. Mater. Chem. C 11, 7377 (2023).
[3] M. Das et al., Angew. Chem. Int. Ed. 62, e202314663 (2023).
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