Diazonium derived functionalization of graphene – Big advances with ultra-thin layers

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Aryl diazonium salts are profoundly investigated agents for the functionalization of surfaces, applied typically via electrografting. Using this technique, electrode materials can be refined with a plethora of different functional groups.[1]
Among all electrode materials used so far, graphene is particularly attractive. Flat graphene is thinner than the introduced aryl layers themselves. Therefore, the functionalization of large area CVD-grown graphene on copper using *p*-substituted aryldiazonium salts enables the fabrication of nanometer-thin functional layers. The resulting functionalization is homogeneous over the entire basal plane, chemically accessible and transferable together with the graphene to any substrate.[2][3]
The functional layers can be used to immobilize macro- or biomolecules on graphene by deploying appropriate cross-linking reactions. In this contribution, we demonstrate the linkage of quantum dots as well as PNA single strands. Furthermore, we used the PNA-functionalized graphene to build very simple, yet selective DNA-sensor structures.

Due to the highly reactive aryl radicals generated during the reduction process, the major disadvantage of electrografting is the formation of multi-layers. The diminishing of the layer thickness has been a quest in numerous studies, with top-down and bottom-up approaches being established.[4][5] We compare both and show, that the bottom-up approach using radical-scavengers to catch excessively generated aryl radicals yields the thinnest layers. For our investigations, we used infrared-spectroscopic ellipsometry, electrochemical quartz crystal microbalance measurements, as well as combined atomic-force microscope and infrared spectroscopy experiments.

Figures

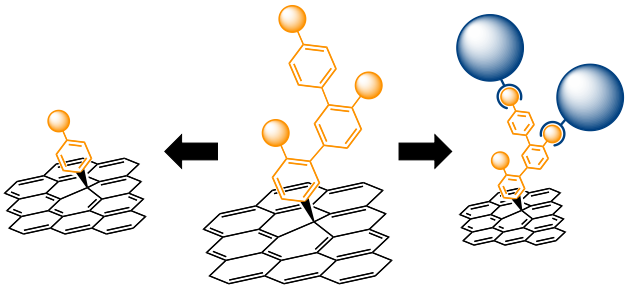

Figure 1: *Middle:* Schematic of aryl-functionalized graphene derived from electrochemical reduced diazonium salts. *Right:* Macro-/biomolecules (blue) immobilized on the functional layers (orange) enabling applications like sensors. *Left:* A major goal is to prohibit chain elongation to reach real monolayer functionalization by radical scavengers.

References

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