Transfer of Electrochemically Amino-functionalized Large Area Graphene

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Abstract

We have investigated the electrochemical grafting of p-aminophenyl residues on CVD grown large area graphene by reduction of the respective diazonium salt (p-aminobenzenediazonium tetrafluoroborate). Before, during, and after electrochemical grafting the samples were characterized with Raman backscattering and infrared spectroscopic ellipsometry measurements (IRSE). The Raman spectra of the pristine graphene show a small D and a pronounced G phonon mode at about 1354 cm^{-1} and 1584 cm^{-1}, respectively. The ratio of the intensity of the D to G mode increases after functionalization by p-aminophenyl. The increase of the D mode is due to chemical binding of the molecules to graphene. This is accompanied by a shift to higher wavenumbers. In addition a new mode arises at 1620 cm^{-1} as a result of C=C ring vibrations. IRSE measurements show vibrational modes that are ascribed to the amino groups of the p-aminophenyl moieties. Subsequently, these amino functional groups were modified by activated p-nitrobenzoic acid via the EEDQ mediated amidation reaction [1]. Raman and IRSE measurements show the successful binding of p-nitrobenzoic acid via amide bond.
Two different approaches were used for the functionalization and modification steps: (i) graphene was transferred to a foreign substrate and then modified. (ii) the functionalization and modification was performed before the transfer process. Interestingly, our data demonstrate that both approaches yield the same result. Hence, the transfer of functionalized and modified graphene is now possible, which opens the prospect to use the modified graphene as tailored modular building block for sensing application on any foreign substrate.

References

[1] X. Zhang, G. Sun, K. Hinrichs, S. Janietz, J. Rappich, Infrared spectroscopic study of the amidation reaction of aminophenyl modified Au surfaces and p-nitrobenzoic acid as model system., Phys. Chem. Chem. Phys. 12 (2010) 12427–12429.