Functionalized graphene and new carbon hybrid materials

Rolf Mülhaupt*

Freiburg Materials Research Center and Institute for Macromolecular Chemistry of the University of Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Email: rolf.muelhaupt@makro.uni-freiburg.de

The development of functionalized single and multi-layer graphenes offers new opportunities for designing unconventional nanostructured carbon materials and carbon dispersions, which are readily tailored to meet the demand of highly diversified technologies. Applications range from automotive and aerospace engineering to energy technology and biomedicine. In contrast to most other carbon nanoparticles, graphenes represent two-dimensional carbon macromolecules which can be assembled and processed using technologies established for functional polymer processing. Bottom-up and top-down strategies have been explored for graphene synthesis. In comparison to chemical vapor deposition and polymerization of precursors, the exfoliation of graphite and graphite oxide (GO) represents a very attractive and versatile route to graphenes. At the Freiburg Materials Research Center, as part of the BMBF-funded project on Functionalized Graphenes ("FUNgraphen"), the ancient GO synthesis combined with chemical and thermal reduction have been scaled-up successfully in order to produce functionalized graphenes. In the thermal reduction process the functional group content and pore formation are readily controlled by the reduction temperature. In high shear mixers, GO as well as graphite are exfoliated. Small amounts of functional groups render graphene amphiphilic. As a consequence, stable concentrated graphene dispersions and pastes are ontained. Moreover, nanopores and polar groups enable easy decoration of graphenes with various metal nanoparticles and polymers. Such dispersions of functionalized graphenes and decorated graphenes have been processed by means of a novel 3D microextrusion process. In this layer-by-layer ("additive") processing, frequently being referred to as 3D printing", very complex functional carbon and carbon hybrid architectures can be manufactured in a single step. As a function of the 3D positioning of the nozzle, it is possible to print free standing films, porous scaffolds and even hybrids and multi-component composites.This includes simultaneous 3D dispensing of a great variety of other materials ranging from polymers to ceramics and metals. Multi-site catalysts with well-defined pore sizes are 3D printed and tailored for application as catalysts and nanostructured electrodes. Applications include graphene-supported Fe-hydrogenation catalysts with magnetic catalyst recovery. Graphene gels using graphene polyelectrolyte complexes have been implemented in this 3D printing process. Multicomponent 3D dispening has been demonstrated to enable printing of batteries in a single step. This presentation will highlight the graphene research and carbon 3D printing of functional carbon materials and systems, illustrated by recent advances at the Freiburg Materials Research Center.

F.J. Tölle, M. Fabritius, R. Mülhaupt, Aqueous and non-aqueous emulsifier-free graphene dispersions with high graphene content for printing electronics and freestanding graphene films, Adv. Funct. Mater. 2012, 22:1136-1144.

M. Stein, J. Wieland, P. Steurer, F. Toelle, R. Mülhaupt, B. Breit, Iron Nanoparticles Supported on Chemically-Derived Graphene: Catalytic Hydrogenation with Magnetic Catalyst Separation Advanced Synthesis & Catalysis (2011), 353(4), 523-527.