Hybrid Doping Strategy for Few-Layer Graphene via a Combination of Intercalation and Surface Doping

Ahmed E. Mansour1, Ahmad R. Kirmani1, Stephen Barlow2, Seth R. Marder2, Aram Amassian1\*

1King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), and, Division of Physical Science and Engineering (PSE), Thuwal, 23955-6900, Saudi Arabia
2Center for Organic Photonics & Electronics and School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA, 30332-0400, USA

Chemical doping of graphene is a viable route towards increasing its conductivity and tuning its work function, which are important metrics for a wide range of applications including transparent conducting electrodes (TCEs). However, dopants are typically present at the surface of the graphene sheet, making them highly susceptible to degradation in environmental conditions. Few-layer graphene (FLG) is a resilient form of graphene exhibiting higher conductivity and performance stability under stretching and bending as contrasted to single-layer graphene (SLG). In addition, FLG presents the advantage of being amenable to bulk doping by intercalation.

Herein, we report a hybrid doping approach of FLG combining surface doping by (metal-) organic molecules and intercalation (bulk) doping using small molecules such Br2 and FeCl3 targeting the bulk of FLG. We show that a combination of these two doping modalities together works synergistically in enhancing the electrical conductivity and tuning the work function. The depth variation of the chemical composition of the two dopants ions is revealed via angle-resolved x-ray photoelectron spectroscopy (AR-XPS) which shows the predominant presence of the intercalant in the bulk (between the graphene sheets) of FLG and the larger molecular dopants primarily present on the surface of the top-most layer.

A systematic characterization of the electrical transport properties and the electronic levels using Hall effect measurements and Photoemission spectroscopy, respectively, show that intercalation doping is predominantly responsible for the increase of electrical conductivity by increasing the carrier density from ~3×1013 cm-2 to ~6×1014 cm-2. Further doping of the intercalated FLG with surface molecular dopants, leads to an additional increase in the carrier density due to charge transfer without reducing the carrier mobility due to effective screening of the charge dopant ions at the surface. Furthermore, the surface dopants effectively shift the work function through the formation of surface dipoles.