Atomic Defects in Graphene and their Role in Proton Transport and Water Desalination

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Nanoporous graphene is being sought as a membrane material for applications that require proton and ion selectivity, such as used in proton exchange membrane fuel cells and water desalination technologies. Proton transport through single layer graphene is generally associated with a large activation energy barrier; however, this barrier can be significantly lowered in the presence of defects such as atomic-scale vacancies or nanopores. Based on density functional theory (DFT) calculations, an activation energy greater than 3.8 eV is required to transport protons through the aromatic ring within the graphene layer, which can be lowered to 0.68 eV if atomic vacancy defects are functionalized with hydroxyl-terminated functional groups.[1] In this work, we use a combination of experiment and theory to demonstrate the feasibility of creating atomic defects using noble gas ion irradiation and perform quantitative scanning transmission electron microscopy (STEM) analysis from atomically resolved images of the defect structures.[2] Two methods for atomic-scale defect manipulation in graphene are demonstrated. First, an ion microscope equipped with helium and neon ion beams, is used to irradiate pristine single-layer graphene at different ion dose rates. Following ion irradiation, atomic-resolution STEM imaging is conducted at 60kV (e.g., below the knock-on damage threshold for graphene) to quantify defects for ion beam irradiation and plasma treatments. For He^+ irradiation, doses above 10^{16} ions/cm^2 are capable of introducing atomic vacancies, Stone-Wales (SW) defects, and nanopores less than 2 nm diameter. For the case of Ne^+ irradiation, a lower dose 10^{14} ions/cm^2 is required to produce SW defects and nanopores, which is in excellent agreement with ReaxFF simulations.[2] Another method to create defects is using an oxygen plasma treatment, which results in the formation of nanoporous graphene with controllable pore size distributions. Atomic resolution imaging shows that the nanopores are decorate with silicon atoms, which help stabilize the dangling bonds created during oxygen plasma etching. This method can be optimized to control the nanopore size distribution to less than 1 nm, which is the optimal pore size for rejection of small ions while permitting water transport.[3] This work shows how defects can be introduced into graphene and tailored for functional applications.

Research supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Aberration-corrected STEM imaging was conducted as part of a user proposal at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), a U.S. Department of Energy Office of Science User Facility.

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