

## Functionalization of Graphene

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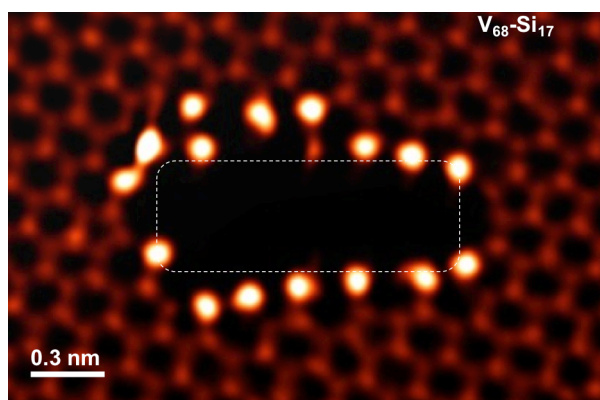
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Experimental results and calculations based on imaging of functionalized graphene with stable nanopores, the smallest rotor and ‘super’ crown ethers will be presented and discussed. It is argued that the stabilization of nanopores in graphene is a critical issue that must be resolved to enable functionalization of graphene. Small holes in graphene are known to be subject to reconstruction and partial or total filling by diffusing carbon or other adatoms (known as the self-healing process) (1-3). Using medium-angle annular dark-field (ADF) imaging in an aberration-corrected scanning transmission electron microscope (STEM), we found that silicon atoms stabilize graphene nanopores by bridging the dangling bonds around the perimeter of the hole (4). STEM imaging was performed using a fifth-order aberration-corrected STEM (Nion-UltraSTEM100) with a cold field emission electron source. The microscope was operated at 60 kV to prevent knock-on damage to graphene. The angular range of the collected electrons in medium-angle ADF mode was 58–200 mrad semiangle. Theoretical calculations reveal the underlying mechanism for this stabilization effect is that Si atoms bond strongly to the graphene edge and their tetrahedral coordination preference (5, 6) forces adatoms to form dendrites sticking out of the graphene plane, instead of filling into the nanopore. All carbon dangling bonds in the nanopore seen in Fig. 1 are passivated by silicon atoms. Although a number of bonding configurations are observed, all the Si atoms are calculated to have binding energies larger than 5 eV. Smaller holes stabilized by silicon were also observed. Fig. 2 shows three silicon atoms replacing a single hexagonal ring of carbon atoms in a graphene layer. Under the electron beam, this silicon trimer rotates as a single unit in stepwise jumps while the surrounding carbon atoms remain fixed (7). Theoretical calculations indicate that the energy barrier to rotate the trimer is about 2 eV, corresponding to a tangential force of only 4.3 nN parallel to the graphene layer. This small force, provided by an electron beam to any of the three silicon atoms, generates a torque on the trimer and results in a rotation of 60° in about 140 femtoseconds and demonstrates that the ultimate miniaturization of a mechanical device (switch, oscillator, stirrer) down to a triangular arrangement of three atoms is possible.

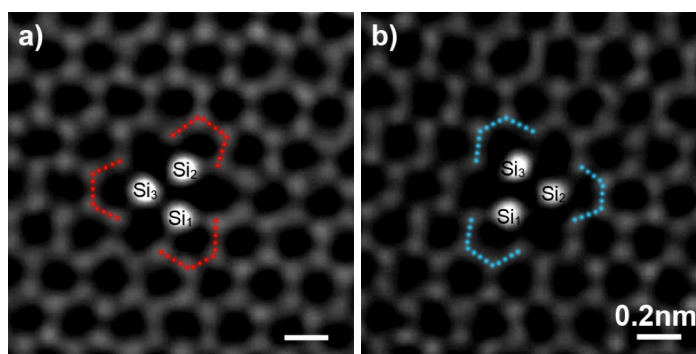
Oxygen atoms were imaged in graphene (Fig. 3) only at the edges of small holes in highly stable crown ether configurations within the 2D graphene layer (8). Oxygen and carbon in the ether configuration at graphene or graphene oxide zig-zag sheet edges have been proposed to exist but, until this investigation, have not been imaged by electron microscopy. Density functional calculations indicate that the crown ether configurations in graphene should exhibit selectivity for different cations depending on the crown ether ring size, a key property of individual crown ether molecules, but in graphene have the added property of being rigid and planar, prized features sought in preorganized receptors for selective ion binding. Calculations indicate that these “super crown ethers” provide unprecedented binding strength and selectivity. Thus, new supramolecular materials in which metal ions are trapped into arrays within the graphene plane are possible. These new materials should provide electrical, magnetic and optical functionality to graphene.

## References:

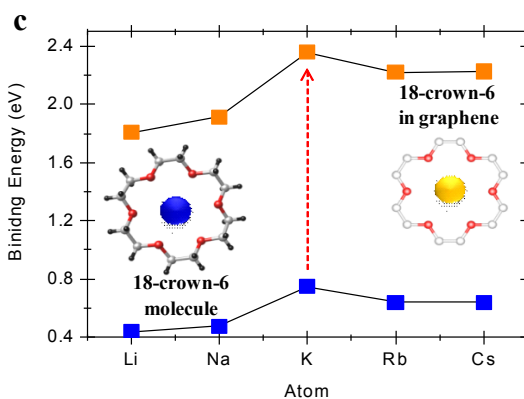
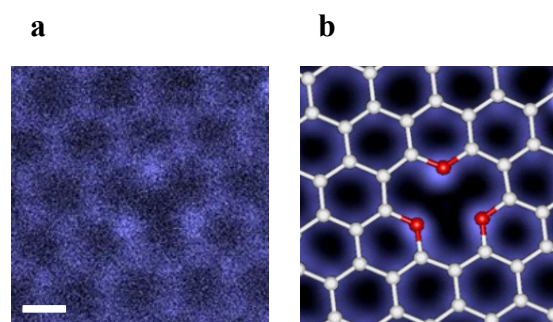
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**Figure 1.** ADF image of a graphene nanopore passivated with 17 Si atoms. [4]



**Figure 2.** STEM ADF image of a silicon trimer in graphene nanopore (a) before and (b) after one stepwise rotation. [7]



**Figure 3.** (a) Experimental STEM-ADF image of crown ether in graphene. (b) Calculated structure overlaid on experimental image. (c) Calculated binding energy of metal ions in 18-crown-6 in graphene compared with of flexible 18-crown-6. [8]