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Stabilization of Nanopores in Graphene

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Progress has been made in experimental studies exploring a wide variety of methods for introducing nanopores in graphene. However, it is observed that small holes in graphene are subject to reconstruction and partial or total filling by diffusing carbon or other adatoms [1-2]. Stabilization of pores for extended periods of time has not been achieved so far.

Using a combination of aberration-corrected scanning transmission electron microscopy and density-functional calculations, we show that Si atoms stabilize graphene nanopores by bridging dangling bonds along the perimeter of the pore. We find the Si-passivated pores survive intact even under the microscope's intense electron beam. Density-functional calculations show that Si atoms are strongly bound to graphene nanopores. Our molecular dynamics simulations show that addition of C adatoms form dendrites sticking out of the graphene plane due to the strong preference of Si atoms for tetrahedral coordination, instead of filling into the nanopore. The resulting stabilized pores of specific size and shape provide an optimal approach for sustainable graphene-based molecular translocation devices.

Figure 1 a-c shows annular dark-field (ADF) Z-contrast images of Si atoms decorating graphene multivacancies. For a hexavacancy, the addition of three Si atoms can effectively stabilize the defect structure by bridging the dangling bonds on neighboring perimeter C atoms, forming characteristic five-member rings (4 C + 1 Si). Precisely the same arrangement occurs naturally in a decavacancy where just four Si atoms provide optimal passivation. Calculated lowest-energy atomic configurations are overlaid on the observed images in Figure 1 d-f. The relaxed structural models of V_6-Si_3 and V_{10}-Si_4 are depicted in Figure 1 g-h, where V indicates the number of carbon vacancies. Small pores with diameters of ~0.2 and ~0.4 nm, respectively, are formed with curved armchair-type edges (indicated in red) passivated by Si atoms.

We find that it is possible to passivate the chemical bonds around the perimeter of pores in graphene. However, our results have shown that not all elements are effective in this role. For example, hydrogen will bond at pore edges, but it does not stop carbon adatoms from filling small holes in graphene. Our experimental and theory investigations demonstrate that Si is particularly effective in this role. This stability can be understood in terms of the fact that Si atoms prefer tetrahedral coordination so that C adatoms that bond to them do not lie in the graphene plane.

References:

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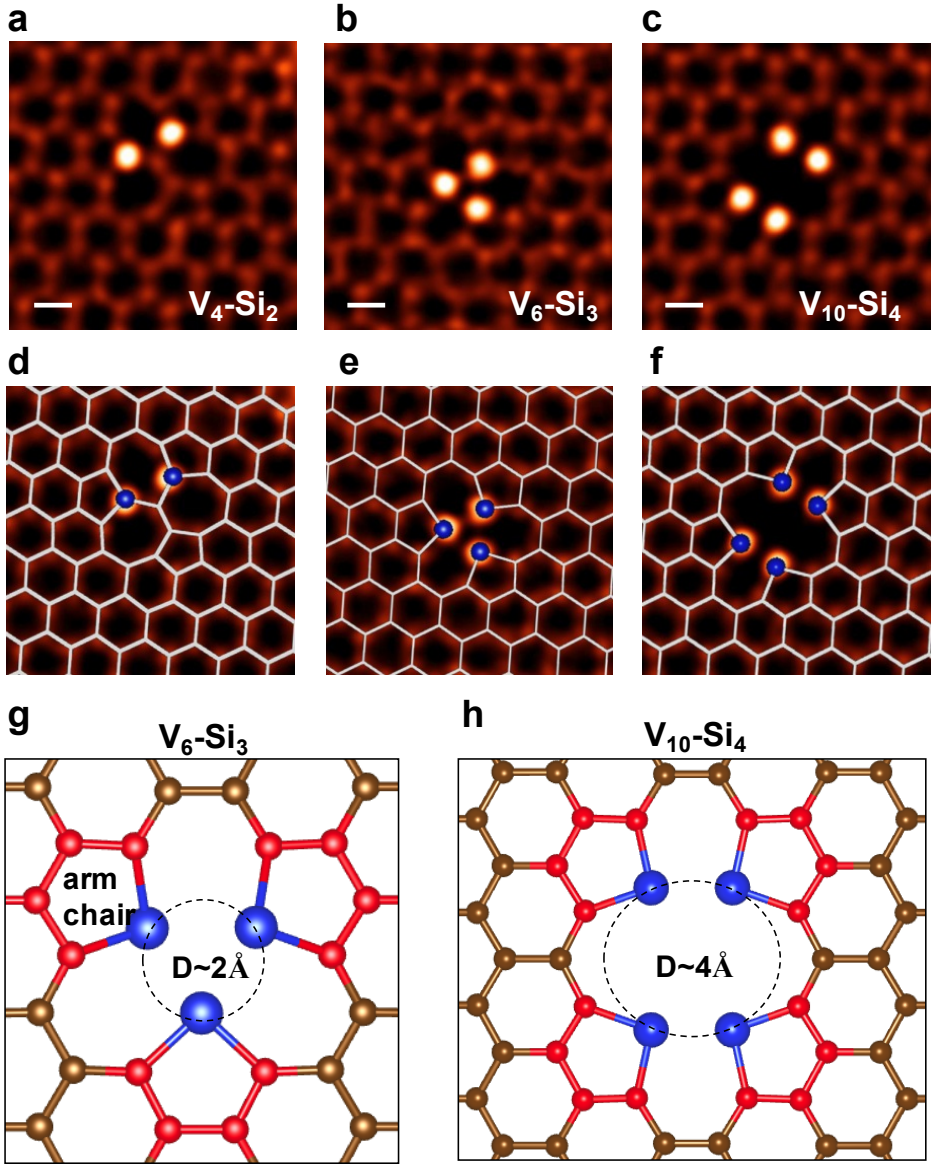

Figure 2. Si atoms stabilize graphene multivacancies. (a)-(c) HAADF images. (d)-(f) calculated structures overlaid on experimental images. (g)-(h) Expanded view of calculated Si-stabilized pores.

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