Distance-Dependence of Chemical Interactions and Image Contrast Reversal in Noncontact Atomic Force Microscopy: A Case Study on Highly Oriented Pyrolytic Graphite

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The structural and chemical nature of surfaces governs a material's ability to interact with its surrounding. Designing nanodevices requires tailoring surfaces to meet specific needs and revealing underlying fundamental principles, which determine surface reactivity at the atomic scale. A particularly interesting case occurs when the surface site exhibits varying attraction with distance. To shed light on this issue, noncontact atomic force microscopy experiments combined with scanning tunneling microscopy experiments have been carried out where the evolution of the atom-specific chemical interaction leads to contrast reversal in the force channel. Due to the importance of sp^2-hybridized carbon surfaces in functional nanostructures, we have used highly ordered pyrolytic graphite surface and metal probe tips as the model system. Our experiments reveal that at larger tip-sample distances, carbon atoms exhibit stronger attractions at hollow sites while upon further approach, hollow sites become energetically more favorable. The analysis suggests the fundamental factors promoting contrast reversal are local varying decay lengths and an onset of repulsive forces that occurs for distinct surface sites at different tip-sample separations. In addition to these, a change of the hybridization state of carbon atoms from sp^2 to sp^3 under the influence of an approaching reactive probe can also result in contrast reversal. Our experiments address the unexpected nature of contrast reversal due to different governing mechanisms, which are determined by local properties of the sample as well as interacting materials. Combined with in-depth computational analysis, such experiments will lead to a deeper understanding of the fundamental effects that govern how materials interact with their surroundings at sub-nanometer scale. Entangling these fundamental principles with design will enable fabrication and synthesis of better nanodevices with graphene and other layered materials as well as nanotubes.

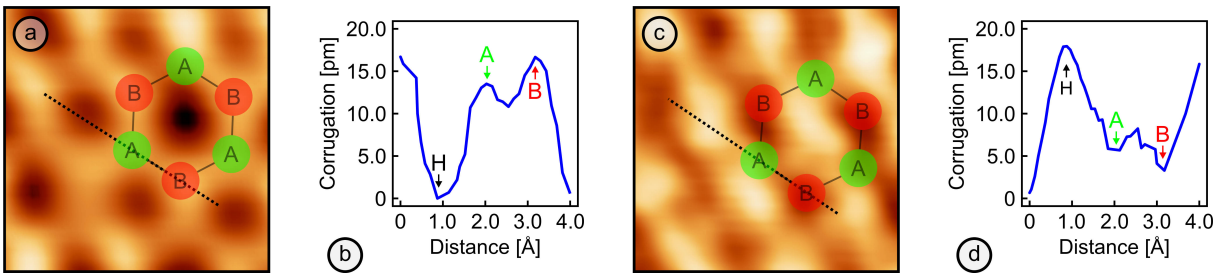

Figure 1: NC-AFM images (a, c) and related cross sections (b, d) of highly oriented pyrolytic graphite. (a) 7.1 Å × 7.1 Å large NC-AFM image revealing A and B type carbon atoms (i.e., carbon atoms that either do or do not have a neighbor in the layer below) as different peaks while hollow positions appears as pits on the surface. (b) Line profile as indicated in a) (c) NC-AFM image sized identical as in a), but recorded with smaller tip-sample separation, revealing inversed contrast. (d) This line profile reveals that A and B type carbon atoms are now imaged as different minimums while the hollow position appears as a protrusion.

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