

Electronic defect states in graphene nanoribbons induced by surface confined hydrogenation

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On-surface synthesis is considered as an efficient strategy for preparing atomically precise graphene nanoribbons (GNRs) [1]. By means of this method, several strategies can be implemented to fine-tune the electronic structure of supported GNRs: for instance, introducing dopant heteroatoms within the carbon backbone, or controlling structural parameters such as width and edge symmetry. Up to now, substitutional doping of the GNRs has exclusively relied on the introduction of boron [2], nitrogen [3], and sulphur [4]. However, in most cases, the band gap of doped ribbons remains unchanged in magnitude. Our research focuses on hydrogenating GNRs, as a way to purposefully tailor the band gap. In this process, hydrogen interacts with GNRs to induce coordination change from sp^2 to sp^3 within the carbon backbone and therefore modify their electronic structure. To date, the results of the hydrogenation reaction and its consequences on the electronic properties of GNRs have merely been studied through theoretical calculations [5,6].

Here, we report on surface-confined hydrogenation studies of 7-armchair graphene nanoribbons (7-AGNRs). GNRs are prepared following a well-known method [1], and partially hydrogenated by exposure to activated hydrogen atoms. The occurrence of the hydrogenation process is traced and verified through two vibrational spectroscopies, i.e., high resolution electron energy loss spectroscopy (HREELS) and inelastic electron tunnelling spectroscopy (IETS). Scanning tunnelling microscopy (STM) is initially used to compare the evolution of the electronic contrast between the pristine and hydrogenated 7-AGNRs (Figs. 1a,b). d^2I/dV^2 mapping is then utilised to identify the hydrogen adsorption and to reveal the precise nature of the hydrogen coordination sites. Using bond-resolved scanning tunnelling microscopy (BRSTM) imaging, two main features can be discerned, namely, edge hydrogenation sites (Figs 1c, d) and basal plane hydrogenation sites (Figs 1e, f). In addition, by controlled STM manipulation experiments whereby C-H bonds are selectively cleaved, we are able to propose a hydrogenation mechanism. The modification of the electronic properties is monitored by scanning tunnelling spectroscopy (STS), revealing the inclusion of defect states within the band gap. Finally, density functional theory (DFT) calculations are used to further confirm our proposed mechanism. In all cases, our experiments demonstrate the successful modification of the electronic properties by edge and basal-plane hydrogenation.

Fig. 1 Representative STM images of 7-AGNRs. Constant current STM images acquired (a) before and (b) after hydrogenation. Constant current STM and off-phase dI/dV BRSTM images with a CO-functionalized tip acquired on the hydrogenated 7-AGNRs show (c, d) edge defects marked by arrows, and (e, f) a basal plane defect marked by an arrow.

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