Shedding light on the crystallographic etching of graphene at the atomic scale

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Owing to the unique electronic properties of graphene, as for example the high intrinsic carrier mobility, the interest in this novel sp^2 carbon material has rapidly expanded since it was first isolated [1]. However the gapless band structure of truly two-dimensional graphene makes it unsuitable for direct use in graphene-based field effect transistors. Thus, the integration of graphene into semiconducting nanoelectronics necessitates the fabrication of graphene nanoribbons (GNRs) where the lateral quantum confinement opens a band gap. The fabrication of GNRs with a well-defined and regular edge structure without defects is a prerequisite to reduce edge effects [2, 3]. Conventional methods for GNR fabrication, e.g. electron beam lithography, produce GNRs with significant edge roughness. GNR with desired shapes may be produced via chemical routes [4, 5] or scanning tunnelling microscope lithography [3].

Recent research into the channelling of few layer graphene via catalytic hydrogenation using metallic catalyst nanoparticles shows that this technique is potentially a key engineering route for the fabrication of GNRs with atomic precision [6, 7]. In this technique metal catalyst particles are deposited onto a graphite or graphene sheet and exposed to hydrogen at elevated temperatures. The catalyst particles help to dissociate hydrogen, which then reacts with carbon from a graphite step edge forming methane. Thus the catalyst particle takes up carbon from a graphite step and an etch channel is produced.

We have studied the catalytic hydrogenation utilizing gas phase prepared cobalt nanoparticles as catalyst for carbon gasification and etch channel formation in hydrogen atmosphere. The onset temperature for cobalt catalyzed carbon gasification in hydrogen atmosphere was found to be 600°C, i.e. much lower than that reported for iron (900°C, [6]) and nickel (700°C, [7]). Aberration corrected high resolution transmission electron microscopy (HRTEM) studies were performed to directly determine the etch direction(s) and to investigate the catalyst particles before and after the hydrogenation reaction. The development of aberration corrected microscopes enables researchers to investigate samples that are sensitive to high energy electron radiation damage, so called “knock-on damage”, at lower accelerating voltages without the loss of resolution. In our studies the HRTEM investigations were performed at 80 kV accelerating voltage.

It is known that the removal of one carbon atom from an armchair edge costs less energy than from a zigzag edge during carbon gasification reactions. Thus zigzag channels, i.e. channels along the $\langle 11\bar{2}0 \rangle$ directions, are preferred and also experimentally observed in most cases after the catalytic etching, since an armchair site will be etched away more easily [7, 8]. Typical bending angles of 60° and 120° are expected. 30° bends are observed less frequently, since this would involve a change from a $\langle 11\bar{2}0 \rangle$ to a $\langle 10\bar{1}0 \rangle$ direction or vice versa. However, in our experiments etching along armchair edges is observed more frequently for small nanoparticles. An example is given in Figure 1 showing a HRTEM micrograph of two etch tracks formed by Co nanoparticles at 600°C. Fourier enhancement of the micrograph allows one to identify the

graphene structure and determine the etch direction to be along armchair edges (Figs. 1b and 1c). Figure 1d shows a magnified image of the marked area in Figure 1b to illustrate the graphite structure. The graphite unit cell (green rhombus) and the main crystallographic directions of graphite, i.e. zigzag and armchair edges, are highlighted in yellow and orange, respectively. Recently a change of the "preferred" etching direction was suggested to occur for very small nickel particles (e.g. below 10 nm) [7]. Therefore tailoring of graphene nanostructures, e.g. GNRs, with well-defined armchair edges via the adjustment of nanoparticle size in catalytic hydrogenation may indeed be possible.

References:

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Figures:

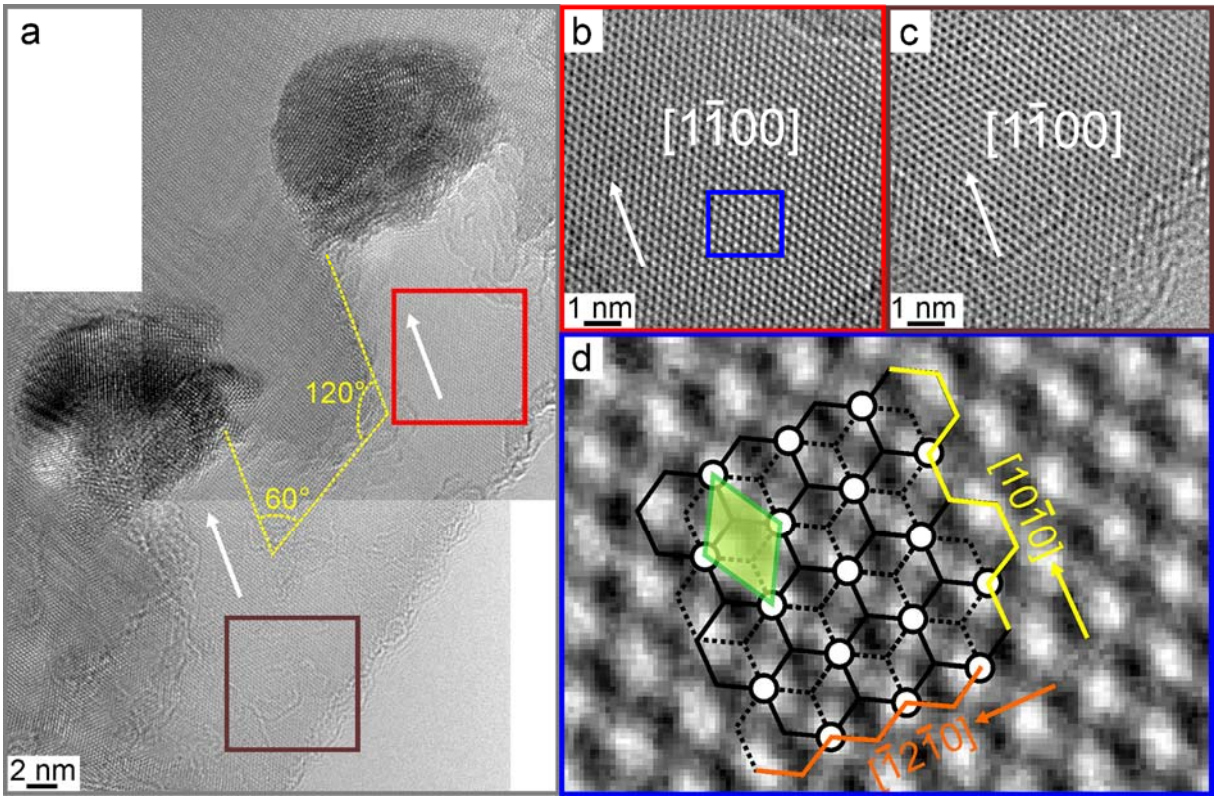

Figure 1: a) HRTEM micrograph of Co nanoparticles etching graphene/graphite. b, c) Fourier enhanced micrographs of the marked areas in a) revealing the graphite structure and etching direction. d) Magnified image of the marked area in b) and illustration of the graphite structure including unit cell (green rhombus) and the main crystallographic directions.