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Purely Armchair or Partially Chiral: Non-Contact Atomic Force Microscopy Characterization of Dibromo-Bianthryl-Based Graphene Nanoribbons Grown on Cu(111)

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ABSTRACT

We report on the atomic structure of graphene nanoribbons (GNRs) formed *via* on-surface synthesis from 10,10'-dibromo-9,9'-bianthryl (DBBA) precursors on Cu(111). By means of ultrahigh vacuum (UHV) non-contact atomic force microscopy (nc-AFM) with CO-functionalized tips we unveil the chiral nature of the so-formed GNRs, a structure which has been under considerable debate. Furthermore, we prove that - in this particular case - the coupling selectivity usually introduced by halogen substitution is overruled by the structural and catalytic properties of the substrate. Specifically, we show that identical chiral GNRs are obtained from 9,9'-bianthryl (BA), the unsubstituted sister molecule of DBBA.

Keywords: graphene nanoribbons, chiral, armchair, on-surface synthesis, bottom-up, non-contact atomic force microscopy, functionalized tip.

The absence of a bandgap in pristine graphene is a severe limitation toward its application in electronics and has triggered intensive efforts to find new strategies to induce a bandgap. Electron confinement in 1D graphene stripes, commonly known as graphene nanoribbons (GNRs), has emerged as one of the most promising approaches. GNRs,

very much like carbon nanotubes, can be classified into three families according to their edge structure, namely armchair, zigzag and chiral.¹ Interestingly, it has first been predicted²⁻⁴ and then experimentally proven⁵ that ribbon width and edge topology fully determine the crucial properties of GNRs such as electronic bandgap or magnetism. GNRs have been fabricated both by top-down (*e.g.* lithography,⁵ sonochemical graphite exfoliation,⁶ or unzipping of carbon nanotubes⁷) and bottom-up approaches like the on-surface colligation of precursor monomers.⁸ However, as the bandgap of GNRs is inversely proportional to their width (and for armchair GNRs furthermore strongly modulated with a period of three carbon atoms in width due to the three inequivalent families of AGNRs),⁹ fabrication accuracy at the atomic level is required, a precision that, so far, can only be achieved by the on-surface bottom-up synthesis from tailored precursor monomers. In this approach, halogen-functionalized precursor monomers are deposited on a surface and thermally activated to react in a two-step process, namely dehalogenation accompanied by intermolecular aryl-aryl coupling and subsequent surface-assisted cyclodehydrogenation.⁸

Since the pioneering work by Cai *et al.*,⁸ this strategy has been extensively applied to the fabrication of the two prototypical kinds of GNRs, namely armchair and zigzag, with variations in width and the ensuing changes in electronic properties.¹⁰ Furthermore, the formation of chiral (3,1)-GNRs (for the (m,n) notation of chiral GNRs, see Scheme 1) from 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor monomers on Cu(111) has recently been reported, with indications for the chiral (3,1) edge structure deriving from scanning tunneling microscopy (STM) images.^{11,12} Another group, however, reported the formation of (achiral) armchair GNRs (AGNRs) from the very same DBBA precursor on Cu(111), and provided detailed characterization by means of STM, x-ray photoelectron spectroscopy (XPS), and near-edge x-ray absorption fine structure (NEXAFS).^{13,14} Despite this multi-technique approach, and a subsequent controversy between the two contradictory interpretations,^{15,16} the situation has remained unsettled and a different characterization, capable of delving into the intramolecular structure of the GNRs obtained from DBBA precursors on Cu(111), is required.

So far, the only technique capable of providing ultimate resolution at the single bond level is nc-AFM with functionalized tips under UHV conditions.¹⁷ In this paper, we provide nc-AFM data that clearly reveal the formation of chiral (3,1)-GNRs (**5**) after deposition and thermal activation of DBBA (**1**) on Cu(111), as schematically shown in Scheme 1. Furthermore, to shed light on the growth mechanism and the effect of halogen functionalization, we show that identical (3,1)-GNRs of similar lengths are obtained from 9,9'-bianthryl (BA) (**2**), the unsubstituted sister molecule of DBBA. Additionally, we study the growth process by analyzing the intermediate stage composed of partially cyclodehydrogenated GNRs. Our results resolve the controversy around the nature of the GNRs obtained from **1** on Cu(111), and highlight the possibility of using halogen-free chemistry for the on-surface synthesis of atomically precise GNRs.

Scheme 1. Reaction scheme for the formation of chiral (3,1)-GNRs (**5**) from DBBA (**1**) and BA (**2**) precursor molecules. See text for details.

RESULTS

We have deposited submonolayer amounts of the DBBA precursor monomer **1** on a Cu(111) surface held at room temperature (RT), and subsequently post-annealed slowly (1.2 °C/min) up to 250 °C following the recipe explained in Figure S1 of the Supporting Information. Figure 1a shows an STM image of the resulting structures. Three main structures can be discerned, namely short GNRs – either entirely flat (structure I) or with bright protrusions on top (structure II) – and short chains of evenly-spaced units (structure III). Under certain tip conditions (see inset of Fig. 1a), the GNRs exhibit an asymmetric appearance which previously has been attributed to chiral edges,¹¹ but also to an armchair termination possibly decorated with Br adatoms or modulated in appearance due to a structural mismatch with the underlying substrate surface.^{14,15}

Figure 1. Structures formed upon deposition of DBBA (I) on Cu(111) and subsequent annealing to 250 °C. a) STM images reveal short, entirely flat GNRs (I), GNRs with additional protrusions (II), as well as linear assemblies of regularly spaced building blocks (III). Tunneling parameters: 1 V, 50 pA (a); 60 mV, 10 pA (inset)). b) nc-AFM frequency-shift image at constant height of a short, flat GNR (species I), revealing that its atomic structure is the one of a three-unit (3,1)-GNR (z offset -40 pm at tunneling setpoint 10 mV, 2 pA). c) Image (b) with structural model overlaid. d) Tunneling current map measured simultaneously with (b) at bias voltage of 10 mV.

To unambiguously unveil the origin of the asymmetric appearance of structure I (inset of Fig. 1a), we have performed nc-AFM measurements with a CO-functionalized tip.¹⁷ The resulting constant-height frequency-shift image and the simultaneously obtained image of the tunneling current are presented in Figures 1b and 1d, respectively. The frequency-shift image undoubtedly reveals the (3,1) chirality of the corresponding GNR. A

schematic model of a three-units (3,1)-GNR is given as overlay on the frequency-shift image in Fig. 1c. Similarly, Supporting Figure S2 shows a combination of STM and nc-AFM images of a type II GNR. With STM one can readily observe the presence of bright double maxima on the ribbon segments of type II, a behavior already reported by both Simonov *et al.*¹⁵ and Han *et al.*¹² and assigned to tilted anthracene groups due to the steric hindrance between neighboring H atoms. However, differing orientations of the molecular units have been proposed by the two groups, according to their respective models of the final GNR structure. Panels d-f in Supporting Figure S2 show the nc-AFM scan of the lower half of the GNR of type II shown in panel a and the simultaneously measured tunneling current image, which reveal a fully aromatic ribbon segment with chiral edges in the region appearing flat in the STM topography (Fig. S2b). By superposition of a structural model to the frequency-shift (Fig. S2e), the current (Fig. S2f), and the STM images (Fig. S2c) we can indeed assign the bright maxima to unreacted anthryl ends that are tilted out plane. The existence of these maxima implies that consecutive bianthryl units along the chiral ribbon are coupled by one covalent C-C bond (at the 2,2' positions), as schematically shown for polymer **4** in Scheme 1, which corroborates the model proposed by Han *et al.*¹² and rules out the alternative model put forward by Simonov *et al.*^{13,15}

We note that the nc-AFM data reported in Fig. 1b and Fig. S2 also allow to unravel the chemical nature of the (3,1)-GNR edges, because nc-AFM with sensitized tips has been shown to distinguish between radical, H- or H₂-terminated edges.¹⁸ The lack of a depression (indicative for an edge C radical) or a brighter maximum (indicative for a CH₂ edge) indicates the saturation of all edge C atoms with single H atoms, which preserves the *sp*² hybridization of the C atoms and the aromaticity of the entire ribbon structure (Figure 1b).

Regarding structure III, high-resolution STM images (Supporting Figure S3) reveal the presence of adatoms between adjacent units. Owing to their dimensions and uniform apparent height (0.15 nm), the units can be assigned to individual cyclodehydrogenated precursor monomers (**3**, bisanthene) which are self-assembled into linear structures. As stabilizing links, both Cu adatoms intrinsically present on the copper surface and Br adatoms originating from the dehalogenation of **1** have to be considered. It has been shown that Br atoms do not desorb from the Cu(111) surface up to 550 °C,¹³ and that they can stabilize similar structures on Cu(110).¹⁴ Consequently, we assign the adatoms stabilizing the linear bisanthene assemblies III to Br. Note that the presence of ‘bays’ at the non-coordinated bisanthene edges (Supporting Figure S3c) suggests that the Br coordination takes place at the zigzag edges, as schematically indicated in Supporting Figure S3d.

Based on these findings, we can already detail some of the intermediate steps of the growth process of GNR **5** on Cu(111). First, the monomer **1** undergoes dehalogenation, where the two bromine atoms are released to the substrate surface, resulting in biradical **1'** (temperature-dependent XPS measurements determined full dehalogenation at -30°C).¹⁴ Subsequently, the biradical **1'** can either cyclodehydrogenate internally to the bisanthene **3** or form the surface-stabilized biradical **2'**, either *via* a series of hydrogen shifts resulting in the relocation of the radical sites from the 10,10' to the 2,2' positions (a similar phenomenon has been reported by L. Ferrighi *et al.*¹⁹) or *via* hydrogen

passivation of the 10,10' positions and substrate induced C-H activation of the 2,2' positions which are pointing towards the catalytically active substrate. In any case, the surface-stabilized biradicals **2'** can readily undergo aryl-aryl coupling into polymer **4**, and subsequently form GNR **5** *via* cyclodehydrogenation. Alternatively, two monomers **1'** could undergo direct substrate-catalyzed aryl-aryl coupling at the 2,2' positions with the subsequent (or even concurrent) release of hydrogen. Such a sequence of aryl-aryl coupling and dehydrogenation has been reported by Blankenburg *et al.* for the cyclodehydrogenation in armchair GNRs on Au(111).²¹

Figure 2. Chiral (3,1)-GNRs formed by BA (**2**) on Cu(111). a) Overview STM image of the Cu(111) surface after GNR formation revealing short, entirely flat GNRs (I), GNRs with additional protrusions (II), and scattered small units (0.5 V, 110 pA). b) nc-AFM frequency-shift image at constant height of two (3,1)-GNR segments with opposite handedness (z-offset -125 pm at tunneling setpoint 100 mV, 2 pA). c) Tunneling current map at constant height measured simultaneously with the frequency-shift image (bias voltage = 5.1 mV).

In the light of this sequence, the immediately arising question is on the function, if any, of the bromine functionalization in this particular case. Apparently, in the present case of DBBA **1** on a Cu(111) surface, the polymerization selectivity usually introduced by the halogen functionalization¹⁰ is overruled by the catalytic activity of the substrate,²⁰ possibly complemented by some impact of the directionality of the substrate, *e.g.* by promoting diffusion along the high symmetry directions, as already speculated by Simonov *et al.*¹⁵ and Han *et al.*^{11,12} In order to corroborate whether bromine functionalization plays a role or not in this particular system, we have repeated the experiments with the precursor monomer BA (**2**), the unsubstituted sister molecule of DBBA. Deposition of **2** on the Cu(111) surface held at RT and a subsequent slow post-annealing up to 250 °C results in the formation of short, fully cyclodehydrogenated GNRs I and some partially cyclodehydrogenated species II as shown in Figure 2a. Such samples do not differ much from the samples prepared with DBBA (*e.g.* Fig. 1), except for the complete lack of the linear structures III assigned to Br adatom stabilized bisanthene (**3**) chains. This can be rationalized by the lack of Br atoms in the case of GNR growth from **2**, which further corroborates the assignment of the adatoms observed in the

linear assemblies III to Br, and not Cu. Closer inspection of the structures I and II by high-resolution STM again reveals an asymmetric (chiral) appearance, as reported for GNRs grown from DBBA.^{11,12,14} Furthermore, nc-AFM images with CO-functionalized tips such as the one presented in Fig. 2b clearly prove that the GNRs obtained from BA exhibit exactly the same (3,1) chirality as the ones obtained from DBBA.

With respect to the DBBA reaction path discussed above, the BA results clearly show that formation of the polymer **4** (and thus the (3,1)-GNR **5**) proceeds *via* the biradical **2'**. Since **2'** is obtained from **2** *via* thermal C-H activation at the 2,2' positions facing towards the catalytically active substrate surface - and at identical temperatures than in the case of DBBA - it is natural to assume that the transformation of **1'** into **2'** does not proceed *via* radical relocation but also *via* direct thermal activation of the 2,2' positions (Scheme 1). In other words, the transition from **1'** to **2'** must proceed in two steps: Hydrogen saturation of the radical positions 10,10' of **1'**, and dehydrogenation of the positions 2,2'. Whether these two steps proceed sequentially or concurrently cannot be answered from our experiments.

As to the length of our (3,1)-GNRs, it can be seen in Supporting Figure S4 that they are rather short. For the case of DBBA as a precursor monomer, we mainly observe the formation of individual planar monomers, and a fast decaying number of GNRs with larger lengths. This distribution resembles the one obtained by Han *et al.* under fast annealing conditions.¹¹ However, our heating ramp was very slow (Supporting Figure S1), similar to the one reported by Han *et al.* for obtaining long GNRs,¹² and we thus discard limited diffusion as the cause of short GNR formation. There are other factors like molecular coverage or monomer purity which can affect the length of GNRs fabricated *via* on-surface synthesis. Similarly, the selectivity to either create bisanthene monomers or GNRs can be steered by the surface orientation or the material of the substrate.^{14,22} In the present case, however, we speculate that passivation of the biradical species with hydrogen originating from low-temperature cyclodehydrogenation plays a crucial role. The detailed XPS analysis reported by Simonov *et al.*¹³ shows an almost linear increase of the C 1s component due to carbons in C[C₃] sites (C atoms with three neighboring carbons and *sp*² hybridized valence electron state, named C2 in ref. 13) and a concomitant decrease of the component due to C[C₂H] sites (a single hydrogen bond and two neighboring carbon atoms, named C1 in ref. 13) at temperatures between room temperature and 200 °C, which is compatible with cyclodehydrogenation proceeding readily already at low temperatures.

This is also compatible with our observation of a significant fraction of unpolymerized bisanthene **3**, the cyclodehydrogenation product of BA (**2**) and of DBBA (**1**) after radical passivation. The following picture thus emerges for (3,1)-GNR growth from DBBA on Cu(111) (Scheme 1): After room-temperature dehalogenation of the precursor **1** into the biradical **1'** and upon subsequent increase of the sample temperature, there is a competition between monomer cyclodehydrogenation into bisanthene **3** and surface-catalyzed dehydrogenation of the bianthryl's inner 2,2'-positions facing toward the substrate, both of which proceed at similarly low temperatures on Cu(111). The hydrogen released in both cases – four hydrogens per monomer in the former case, and two hydrogens per monomer in the latter case – firstly saturates the bianthryl's 10,10' radical positions from the preceding

dehalogenation step. With increasing temperature, polymerization of **2'** into **4** proceeds as long as the radical positions of the terminal oligomer unit remains active. Due to the significant availability of hydrogen from premature monomer cyclodehydrogenation, however, growing oligomers can be rapidly passivated, resulting in rather short polymer segments. Finally, the polymer **4** is thermally brought to cyclodehydrogenation into the final (3,1)-GNR structure **5**. Note that this scenario is based on the (reasonable) assumption that the strong binding of the biradical species **1'** and **2'** to the metal surface lowers their cyclodehydrogenation barrier compared to the one of the polymer **4**. As shown by previous work of Treier *et al.*²⁰ and Blankenburg *et al.*,²¹ sterically induced strain indeed weakens the involved C-H bonds and consequently the corresponding cyclodehydrogenation barrier. Finally, we note that the (3,1)-GNR length distribution obtained for the halogen-free precursor monomer BA peaks at two molecular units (Supporting Figure S4), *i.e.*, we obtain slightly longer oligomers from the halogen-free molecule. This is a minor difference, but it could imply that, for this particular case, bromine adatoms may negatively affect the growth of (3,1)-GNRs on Cu(111).

CONCLUSIONS

We have shown, by means of nc-AFM with CO-functionalized tips, that the GNRs resulting from a slow annealing of DBBA precursor monomers deposited on Cu(111) exhibit chiral (3,1) edges. This settles a dispute in the recent literature on bottom-up GNR growth on Cu(111).^{11–16} Furthermore, we have shown that identical (3,1)-GNRs are obtained from the halogen-free sister molecule BA, proving that halogen functionalization plays no role in this system. This suggests that GNR growth *via* selective C-H activation, covalent coupling and cyclodehydrogenation may also be achieved using unsubstituted precursors monomers. Finally, we have shed light on the growth mechanism, which involves passivation of the radical positions resulting from dehalogenation with hydrogen originating from premature monomer cyclodehydrogenation and from surface-catalyzed dehydrogenation of the bianthryl's inner 2,2'-positions facing toward the substrate, aryl-aryl coupling *via* the activated 2,2'-positions, and finally cyclodehydrogenation of the oligomers into the chiral (3,1)-GNRs. We hope that our work will stimulate further investigations of the catalytic activity of the Cu(111) surface in on-surface chemical reactions.

METHODS

The molecular precursors 10,10'-dibromo-9,9'-bianthryl and 9,9'-bianthryl were synthesized following reported procedures.⁸ Purification was carried out by sublimation and slow evaporation from a solution in dichloromethane layered with ethanol. All STM and nc-AFM experiments were carried out under ultrahigh vacuum (UHV) conditions (base pressure 1×10^{-10} mbar) with a low-temperature scanning probe microscope (ScientaOmicron, 5K). The Cu(111) substrate was prepared by repeated cycles of Ar⁺ sputtering and annealing at 450°C. The sample temperature was determined by an infrared pyrometer (emissivity = 0.1; CTlaser 3MH-CF3 by Optris GmbH, Germany). Deposition of the molecular precursors was carried out by thermal evaporation using a 6-fold organic evaporator (Mantis GmbH). Qplus sensors (ScientaOmicron, resonance frequency 23555 Hz, oscillation amplitude ~ 80 pm) equipped with tungsten tips were used as received and conditioned by repeated indentation to the copper surface. Prior to the nc-AFM experiments the conditioned tips were decorated with a CO molecule *via* pick-up from the surface.²³

ASSOCIATED CONTENT

Supporting Information. Annealing ramp used for the growth of the GNRs. Characterization of partially cyclodehydrogenated GNRs. Statistical analysis of GNR length. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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