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Title: On-surface Synthesis of Atomically Precise Graphene Nanoribbons

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Abstract

The surface-assisted polymerization and cyclodehydrogenation of specifically designed organic precursors provides a route towards atomically precise graphene nanoribbons, which promise to combine the outstanding electronic properties of graphene with a band gap that is sufficiently large for room-temperature digital logic applications. Starting from the basic concepts behind the on-surface synthesis approach, this report covers the progress made in understanding the different reaction steps, in synthesizing atomically precise graphene nanoribbons of various widths and edge structures and in characterizing their properties, ending with an outlook on the challenges that still lie ahead.

1. Introduction

As noted by Andre Geim in his 2011 Nobel lecture,^[1] a driving motivation for the study of thin graphite films and, eventually, of graphene was to explore whether the electrical

conductivity of a semimetal could be modulated by the field effect. The seminal work by his group demonstrated not only that the room temperature conductivity of graphene could be modulated by more than one order of magnitude, but also that the charge carriers were extremely mobile.^[2] Charge carrier mobility is a key figure of merit for the application of materials in transistor channels, which has lead to excitement in the electronics industry and has allowed graphene-based transistors to operate at frequencies above 400 GHz.^[3] Yet, it turns out that the on/off ratio of ~ 10 , despite being a record value for a semimetal,^[1] is far too low for many applications, both in high-frequency signal amplification and in digital electronics.^[4,5] The fact that graphene transistors do not properly turn off is a direct consequence of the lack of a band gap – room temperature digital logic applications are estimated to require band gaps of at least ~ 0.4 eV.^[4] One may therefore wonder: Is it possible to open a band gap in graphene's electronic structure that is sufficiently large for applications without sacrificing the high mobility of its charge carriers?

One way to open a band gap is by lateral confinement of electrons on the nanometer scale, i.e. by cutting graphene into narrow ribbons. This offers the exciting opportunity to tune the value of the band gap to just the right value for the intended application, simply by controlling the width of the graphene nanoribbons (GNRs). However, this path is not quite as straightforward as one might anticipate. While a large number of top-down approaches has been explored,^[6] all of them must confront two major challenges. First, *ab initio* calculations predict that GNRs need to be less than 10 nm wide in order to possess large enough band gaps.^[7] This corresponds to less than 100 carbon atoms across the ribbon, and is out of reach for standard lithographic methods. And second, in these one-dimensional systems even weakly defective edges are predicted to give rise to scattering and localization of electrons.^[8,9] In order to take full advantage of the outstanding electronic transport properties of graphene, the ribbon edges should therefore be made atomically precise.

Cutting graphene nanoribbons with atomic precision is a daunting task. Here, we discuss an alternative approach: stitching up graphene nanoribbons from molecular building blocks. In this context, a GNR can be viewed as a conjugated macromolecule containing some hundred to several thousand atoms. Its large size poses a problem for traditional solution-based polymerization chemistry, which requires reactants and products to be soluble.^[10] This is where the emerging field of on-surface chemistry has come into play, building on pioneering works concerning the surface-supported covalent assembly of networks and conjugated molecular wires^[11–13] as well as surface-assisted cyclodehydrogenation.^[14] **Figure 1a** illustrates the recipe devised for the bottom-up fabrication of graphene nanoribbons, as first reported in 2010.^[15] The building block is a carefully designed molecule that determines the width of the GNR. In this case, 10,10'-dibromo-9,9'-bianthryl (DBBA) yields a GNR with armchair edges and a width N of seven carbon atoms (7-AGNR). The precursor molecule is evaporated onto the crystalline surface of a noble metal, such as Au(111) or Ag(111), under ultra-high vacuum (UHV), which activates the molecule by removal of its halogen atoms. Annealing at a characteristic temperature T_1 allows for the radical intermediates to diffuse and meet on the surface, leading to polymerization into linear chains via aryl-aryl coupling, similar to the classical Ullmann reaction.^[16] The building blocks are now connected by single carbon-carbon bonds. Once the chain formation has completed, the sample is heated further to $T_2 > T_1$, inducing a cyclodehydrogenation reaction that transforms the polymers into the final product: atomically precise GNRs (Figure 1b-d).

The benefits of the bottom-up approach are obvious: By design of the molecular building block, the width of the GNRs is defined down to the single atom, providing ultimate control over the band gap. And by starting with highly purified batches of molecules, GNRs with correspondingly low numbers of defects can be obtained. In the five years since the first example shown in Figure 1, progress has been made on many fronts, including the

understanding of the different on-surface reactions, the repertoire of available GNRs and the characterization of their properties. Here, we review this progress, ending with an outlook on the challenges that lie ahead.

2. Stages of on-surface synthesis

2.1 Building block design

Top-down approaches tend to struggle with producing GNRs that are narrow enough to exhibit significant electronic band gaps. In the bottom-up approach this is not an issue, as exemplified by the case of the 7-AGNR with a band gap in excess of 2 eV (more details in section 3). The challenge is rather to tune the band gap to technologically useful values in the range of 0.5 – 1.5 eV by designing both the width and the edge structure of the GNRs accordingly.

Much of the initial work has focused on GNRs with armchair edges. Starting with poly-*para*-phenylene, which may be regarded as a 3-AGNR, 5,7,9 and 13-AGNRs have been synthesized successfully (see **Figure 2a**).^[13,15,17–19] The size of the precursor molecule is ultimately limited by the requirement that the entire molecule must evaporate upon heating, not decompose in the crucible. Alternatives to molecular beam epitaxy (MBE), such as electrospray deposition^[20] or laser-induced desorption,^[21] offer ways to overcome this limitation, as does the concept of hierarchical growth,^[22] These routes are yet to be explored in the context of the on-surface synthesis of GNRs. Note also that the width of the GNR may be larger than the width of the precursor molecule. This is illustrated by the cases of 7- and 9-AGNRs, where the wider 9-AGNR is synthesized using a smaller precursor that enters the polymer in two alternating orientations (Figure 2a). Further important factors relevant to monomer design, such as the adsorption configuration, mobility and reactivity of the precursor on the surface of choice, will be discussed in the following sections.

The bottom-up approach is not limited to armchair edges, though. Figure 2b shows a class of “chevron-type” GNRs with a more exotic, but completely regular edge structure that is clearly

out of reach for top-down approaches.^[15] Besides access to specialized edge structures, monomer design also provides an atomically controlled substitutional ‘doping’ mechanism by replacing carbon atoms with heteroatoms, such as boron or nitrogen.^[23–26] The doping level is defined simply by the number of carbon atoms that are replaced. And by growing GNRs from different molecules in succession, atomically sharp transitions from one doping level to another can be achieved.^[24]

Most recently, substantial efforts have been directed towards the synthesis of graphene nanoribbons with zigzag edges (ZGNRs), since they are predicted to host spin-polarized edge states.^[27] In this context, note that the carbon-halogen bonds in the precursors shown in Figure 2 necessarily point along an armchair direction of the hexagonal carbon lattice. In order to obtain ZGNRs, growth must therefore not proceed *along* the direction of the carbon-halogen bond, but at an angle of either 30° or 90°. Figure 2c shows examples for both of these approaches. In contrast to armchair edges, pure zigzag edges cannot be achieved by relying solely on dehydrogenative cyclization of phenyl subgroups, which has prompted the introduction of methyl groups for molecule **12** to obtain pristine 6-ZGNRs.

2.2 Dehalogenation

In the Ullmann coupling strategy discussed here, the metal substrate plays a crucial catalytic role. Density functional theory calculations indicate that the dehalogenation barriers of iodobenzene and bromobenzene are reduced from more than 3 eV in the gas phase to 1 eV and below, when adsorbed on the (111) surfaces of the coinage metals.^[28] This is necessary in order to prevent desorption of monomers before dehalogenation and to avoid undesirable side reactions during the following polymerization stage. Dehalogenation barriers are generally lower for iodine than for bromine and decrease with increasing reactivity of the clean metal surface in the sequence Au, Ag, Cu.^[28]

This trend is supported by experimental evidence from scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). At room temperature, the carbon-iodine bond is already broken on the (111) surfaces of all three metals.^[29] The carbon-bromine bond is reported to be cleaved on the Cu(111), Cu(110) and Ag(110) surfaces,^[30] while it remains intact on Au(111) and Au(110).^[30–33] The Ag(111) surface can be considered intermediate, since room temperature coincides with the onset of carbon-bromine bond scission.^[30,34] After dehalogenation, the halogen byproducts remain adsorbed on the surface up to temperatures beyond 200°C.^[13,30,33,35] The next stage of the synthesis, the polymerization of radical intermediates, thus occurs in the presence of the halogen atoms and it remains to be clarified whether the halogens play a significant role in this process as well. In this respect, the synthesis of one-dimensional GNRs differs from the synthesis of two-dimensional covalent organic frameworks, where steric hindrance from halogen clusters trapped within the network is clearly detrimental to long-range order.^[36] Finally, the cyclodehydrogenation stage has been shown to involve desorption of halogens X in the form of hydrogenated species XH, which in turn allows to use the detection of these species as a marker for the onset of the cyclodehydrogenation reaction.^[37]

2.3 Polymerization

Besides catalyzing the dehalogenation of precursors, the metal surface also needs to allow for the radical intermediates to diffuse and couple. Modeling this process for the sizeable precursor molecules shown in Figure 2 is complex due to the large number of degrees of freedom involved. For the simple case of phenyl radicals, however, *ab initio* studies have been performed.^[28,38] Barriers for sliding diffusion are found to range from 0.2 eV on Au(111) to more than 0.4 eV on Cu(111), while coupling of radicals is found to be almost free of barriers, once the two radicals are sharing the same metal atom as the bonding partner.^[28,38,39]

The barriers involved are therefore below the dehalogenation barriers on Au(111) and Ag(111), while they are very similar to the dehalogenation barrier on Cu(111).

This suggests that, with the exception of iodine on Cu(111), dehalogenation is the rate-limiting step of the self-assembly, at least for small molecules. Experimental results for the 7-AGNR seem to indicate that this still holds for DBBA: polymerization is found to occur already near room temperature on Cu(111), as compared to $\sim 200^{\circ}\text{C}$ on the noble Au(111) surface.^[32] Yet, this picture may be too simplistic, as metal adatoms present on the Cu(111) and Ag(111) surfaces have been observed to participate in the coupling process.^[40]

Molecular geometries give rise to new intricacies as well. For example, the dibromo-anthryl molecule (not shown) adsorbs flat on the surface, while the anthryl units in DBBA **3** are both tilted out of plane due to steric hindrance between their “inner” hydrogens (Figure 1a). This allows for an unhindered approach of two bianthryl radicals at the polymerization stage, while the approach of two anthryl radicals is sterically hindered. All precursors shown in Figure 2 exhibit some degree of out-of-plane tilt upon adsorption – with the exception of precursor **2**, which does not require any dehydrogenation.

Other obstacles to achieving the desired polymers may include the existence of unforeseen inequivalent molecular conformations on the surface or even just a lack of purity of the precursor molecules. Purity is particularly important with respect to mono-halogenated species, since these terminate chain growth and can be highly enriched upon sublimation deposition due to their lower molecular weight.

The experimentally accessible parameters for polymerization are the annealing temperature and annealing time. In a study performed for the 7-AGNR on Au(111), GNR length is found to follow an Arrhenius-like trend, where the length initially increases with polymerization temperature with a characteristic activation energy that describes the dehalogenation and mobility of the precursor monomers.^[19] However, for polymerization temperatures exceeding 175°C , GNR length starts to decrease significantly, indicating the onset of a new reaction that

terminates polymer growth. A possible explanation is provided by STM-based observations of DBBA precursors sporadically undergoing cyclodehydrogenation already during annealing at 200°C.^[41] The resulting hydrogen on the surface may, irreversibly, passivate the radical termini of the growing polymer chains, hence terminating their growth.

At this point, a general caveat about temperature measurements in the context of on-surface synthesis may be in order. Temperatures are usually measured either using optical pyrometers, which need to be calibrated for each substrate to provide absolute values, or using thermocouples that are positioned close to, but not in direct contact with the sample surface on which the reactions occur. When comparing temperatures reported by different groups, care should thus be taken in order to ensure that they are indeed measured in comparable ways.

2.4 Cyclodehydrogenation

The last stage of the on-surface synthesis is the (cyclo-)dehydrogenation of the readily formed polymer chain. The details of this reaction naturally depend on the chosen precursor. For the 7-AGNR, a careful *ab initio* study reveals a six-step reaction that proceeds first along one edge of the GNR only, and is catalyzed by the substrate in two ways: On the one hand, van-der-Waals interactions naturally favor flat conformations of the polymer chain, thus lowering the barrier for removal of the “inner” hydrogens that enforce non-planarity.^[42] On the other hand, radical intermediates are considerably stabilized by metal-organic bonds. The catalytic influence of the substrate is confirmed experimentally by the fact that cyclodehydrogenation on Cu(111) completes already at 250°C, as compared to 400°C on Au(111).^[32]

During cyclodehydrogenation, a substantial amount of hydrogen is produced on the surface - e.g., 8 hydrogen atoms per DBBA monomer for the 7-AGNR. It is therefore important that the polymerization and dehydrogenation stages are well-separated. If they overlap, the growth of

the polymer chain can be stopped by atomic hydrogen from the surface forming C-H bonds at the radical termini of the polymer chain (see also section 2.3).^[41]

At this point it is important to note that the “outer” hydrogen atoms at the GNR edges are not affected by the cyclodehydrogenation reaction,^[42] which has been demonstrated beautifully by comparison of di-, mono and de-hydrogenated edge carbons in high-resolution atomic force microscopy (see also Figure 1c-d).^[43] Only annealing at significantly higher temperatures eventually leads to fusion of GNRs via cross-dehydrogenative coupling and thus provides access to GNRs with multiples of the original width, e.g., $N=7 \rightarrow N=14, 21$.^[44-46] This strategy has been employed to obtain 6-AGNRs from lateral fusion of 3-AGNRs (poly-*para*-phenylene) on Cu(111).^[44] Since the synthesis of 3-AGNRs does not involve cyclodehydrogenation, the improved separation between polymerization and cross-dehydrogenative coupling may contribute to the comparatively large lengths of the GNRs observed. Yet, precautions need to be taken in order to direct the random fusing of GNRs. While parallel pre-alignment of GNRs favors lateral fusing,^[44] it does not provide control over the width of the product. Further strategies, such as substrates with terraces of specific widths, will likely be required in order to produce monodisperse GNRs in this manner.

3. Properties

3.1 Electronic band gaps

Theoretical predictions of the electronic structure and, in particular, the band gap Δ of atomically precise GNRs have predated their experimental realization by many years.

Commonly used theoretical frameworks range from Clar’s theory^[47] over tight binding^[27] and density functional theory (DFT)^[7,48] to many-body perturbation theory in the GW approximation,^[49] all of which agree on some basic qualitative results.

GNRs with armchair edges are found to be divided into three separate families, depending on whether their width N is of the form $N=3p-1$ (small- Δ), $3p$ (medium- Δ) or $3p+1$ (large- Δ),

where p is an integer. *Within* each family, Δ increases monotonically as GNR width is decreased (see **Figure 3a**). However, decreasing the width atom by atom corresponds to alternating *between* families, which can give rise to a decrease in Δ as well. These predictions are in line with first experimental measurements of Δ for atomically precise AGNRs via scanning tunneling spectroscopy (STS), reporting 2.3 eV (Figure 3b),^[50] 1.4 eV^[19] and 1.4 eV^[18] for the $N=7$, 9 and 13-AGNR adsorbed on Au(111), respectively. Note that the 13-AGNR belongs to the large- Δ family, while 9-AGNR belongs to the medium- Δ family, which explains the similarity of their band gaps despite the substantial difference in width. For the chevron-type GNR obtained from precursor **7**, a band gap of 2 eV has been inferred from STS measurements on Au(111),^[51] but conflicting results from two-photon photoemission spectroscopy^[23] and (inverse) photoemission spectroscopy^[52] have also been reported. Moving from armchair edges to zigzag edges is associated with a dramatical change in electronic structure. In contrast to AGNRs, the band gap of ZGNRs is predicted to increase *monotonously* with decreasing width. But, interestingly, the electronic states close to the Fermi level are localized near the zigzag edges, and the corresponding bands show very little dispersion. Following early theoretical investigations of these flat bands,^[53] the synthesis of materials with a high “flatness index” η_α ^[54] has become a priority in carbon nanomaterials research, in particular since these states have been predicted to undergo spontaneous magnetization.^[27] Within the tight binding framework, η_α of the recently synthesized 6-ZGNR^[55] (Figure 2c) is very close to the highest possible η_α predicted for $N=7$,^[54] thus making the 6-ZGNR an excellent candidate for the study of magnetism at graphene zigzag edges.

Studying the electronic structure of metal-adsorbed ZGNRs is challenging, which brings up the role of the substrate that has been neglected in the discussion so far. For armchair GNRs, both experimental indications and DFT calculations support a picture of weak hybridization and a lack of charge transfer, at least when adsorbed on the noble Au(111) surface.^[19,50]

Quantitative predictions of quasiparticle energies still make it necessary to account for the screening by the metal. For 7-AGNRs on Au(111), the band gap Δ , defined as the difference between the ionization potential and the electron affinity, is predicted to be reduced by more than 1 eV compared to its gas phase value.^[26,50] Yet, qualitative features are often readily understood from calculations for freestanding AGNRs.

The low-energy states localized at zigzag edges, however, interact even with the noble Au(111) surface, as evidenced from the qualitative disagreement between STS data and theoretical predictions for free-standing GNRs.^[43] This issue has been investigated experimentally for the short zigzag edge found at the termini of 7-AGNRs by transferring individual GNRs onto monolayers of NaCl using the tip of an STM (Figure 3c).^[56] Upon transfer, qualitative agreement with the predicted electronic structure is restored. We note here that dispersion-corrected DFT calculations, incorrectly, predicted negligible interaction between monohydrogenated graphene zigzag edges and the Au(111) surface.^[57] This demonstrates the theoretical challenge involved in accurately describing the adsorption regime falling in between physisorption (dominated by dispersion forces) and chemisorption (dominated by chemical bonds).

3.2 Effective masses

The effective mass m^* of charge carriers is another important figure of merit, since it enters the charge carrier mobility. Effective masses have been determined for the 7- and 9-AGNR by measuring the dispersion of electronic bands close to the Fermi level. Investigations have relied both on area-averaging techniques, such as angle-resolved photoemission spectroscopy (ARPES), which is enabled by parallel alignment of GNRs on vicinal metal surfaces,^[50,58] and on Fourier-transformed scanning tunneling spectroscopy (FT-STs), which is performed on individual GNRs.^[19,59] While some questions regarding discrepancies between ARPES and FT-STs results remain to be answered,^[59] we note that the FT-STs results of $m^* = 0.4 m_e$ for

the 7-AGNR and $m^* = 0.1 m_e$ for the 9-AGNR are in good agreement with theoretical predictions.^[19,59] Here, m_e is the free electron mass and m^* the effective mass of both valence and conduction band. For AGNRs with smaller band gaps, effective masses are expected to decrease even further as valence and conduction band approach the Dirac point of graphene.

3.3 Band shifts in heterojunctions

Atomically precise doping of GNRs can be a versatile tool for band alignment with electrode materials or for modifying the band gaps of GNRs. STS and electron energy loss spectroscopy (EELS) have been used to investigate substitutional nitrogen doping of chevron GNRs (see Figure 2d), which leads to a downshift of bands by an energy in the range of 0.1-0.3 eV per nitrogen atom.^[23,24] Yet, except for the overall shift, the electronic band structure near the Fermi level remains almost unaffected. Careful observers will notice that in the monomers shown in Figure 2b, nitrogen actually does not replace a carbon atom, but a C-H group. In chemical terms, the nitrogen atoms end up carrying a lone electron pair that is orthogonal to the π -system of the GNR and is therefore not donated to the carbon skeleton. In contrast, the substitutional boron doping in molecule **4** results in the introduction of a deep acceptor band that is predicted to reduce the band gap by more than a factor of two.^[26] For the sake of clarity, we would like to stress that the ‘doping’ levels considered here correspond to several at% and are thus not comparable to doping levels in the semiconductor industry.

Other applications of this doping strategy include the synthesis of atomically sharp junctions between regions with different doping levels, simply by growing one precursor after the other. For reasons detailed above, the monomers shown in Figure 2b yield staggered gap heterojunctions,^[51] commonly referred to as type II. Straddling gap heterojunctions (type I) have been obtained by growing 7- and 13-AGNRs in succession (Figure 3d-e).^[18]

3.4 Optical absorption

As dictated by their electronic structure, the optical absorption of narrow GNRs differs substantially from the one of graphene, which is virtually independent of wavelength.^[60] Since optical probes lack surface sensitivity, measuring the optical response of GNRs makes it necessary to isolate the associated signal from the one of the supporting substrate. This can be achieved via reflectance difference spectroscopy (RDS) by exploiting the fact that one-dimensional systems, such as GNRs, absorb light most effectively when it is polarized along their long axis,^[61] while the (111) surfaces of face-centered cubic crystals are optically isotropic at normal incidence.^[62] For 7-AGNRs aligned on stepped Au(111) surfaces, an optical gap of 2.1 eV has been determined using this technique (Figure 3f).^[63] Interestingly, this finding is in close agreement with *ab initio* many-body calculations for *freestanding* GNRs.^[63] While the electronic band gap Δ of low-dimensional materials is often highly sensitive to screening, the optical gap corresponds to the charge-neutral excitation of an electron-hole pair and is hence affected by screening to a much lesser degree.^[64]

3.5 Vibrational modes

The study of vibrational modes by means of Raman spectroscopy has emerged as a powerful technique for the characterization of sp^2 -hybridized carbon nanomaterials.^[65] In the case of GNRs, spectroscopic fingerprints can be used to determine their width and thus to identify the specific GNR under investigation.^[66] Most notably, armchair and zigzag GNRs host a well-defined, low-frequency radial-breathing-like mode (RBLM), in analogy to the radial breathing mode found in carbon nanotubes. Its frequency is determined by the width of the GNR. For example, the RBLM of the 7-AGNR with a width of 0.74 nm is observed at 396 cm^{-1} , in excellent agreement with predictions based on DFT.^[15] Upon removal or addition of one carbon row (resulting in 6- or 8-AGNRs, respectively), the RBLM is predicted to shift by $\pm 50\text{ cm}^{-1}$.^[66] This is readily resolvable given the narrow peak width of $\sim 25\text{ cm}^{-1}$ observed for the 7-AGNR. Other modes related to the GNR edges have been reported, including C-H

vibrations, as well as the *D*- and *G*-bands familiar from graphene, but a detailed understanding is still lacking. We note that for carbon nanotubes the intensity ratio between characteristic features of the Raman spectrum has been shown to provide estimates for their length.^[67] A similar relation for GNRs would be highly desirable for monitoring the synthesis of GNRs, their transfer onto “technical” substrates as well as device fabrication.

3.6 Electronic transport

The long-term objective of fabricating high performance field effect transistors (FETs) from atomically precise GNRs has not yet been met. First electronic transport experiments on bottom-up fabricated GNRs have, however, already been undertaken.

On the one hand, individual 7-AGNRs have been picked up at one end with an STM tip and the current flowing between tip and substrate through the GNR has been measured as a function of the voltage applied and of the tip-sample distance (Figure 3g-h).^[68] This unique approach provides access to the voltage-dependent tunneling decay length in a precisely controlled experiment under UHV.

On the other hand, GNRs have been transferred to SiO₂ substrates by adapting methods employed for the transfer of graphene from Cu foils (Figure 3i-j), which has enabled the fabrication of GNR FETs.^[69] Yet, the transfer involves coating with polymer films, which inevitably leads to organic contamination. Furthermore, electronic transport is found to be largely dominated by Schottky barriers at the electrodes, signaling a need for improved metal contacts.

4. Conclusions and Outlook

Over the course of the last years, the on-surface bottom-up approach to graphene nanoribbons has proven to be a highly fruitful symbiosis between the powerful machinery of modern organic chemistry and the analytical strength of surface science. It provides GNRs with uniform width and edge structure down to the single atom – a key prerequisite for GNR-based

electronics that makes it possible to treat the GNRs as one *material* in the sense of having one set of well-defined electronic properties (which still is a challenge in the field of carbon nanotubes^[70]). The approach has been adopted by several research groups worldwide and important progress has been made, in understanding the different on-surface reactions, in demonstrating the versatility of the approach by synthesizing a wide range of GNRs and in the measurement of figures of merit. Yet, only a small fraction of the full potential of this new approach has been explored and a great number of challenges still lie ahead.

Despite the success of the aryl-aryl (Ullmann) coupling discussed here, there is no good reason for limiting oneself to this strategy. Organic chemistry clearly has much more to offer and other strategies are being actively explored, including dehydrogenative coupling, Glaser coupling, Bergman coupling as well as cycloaddition and cyclotrimerization.^[28,36,40]

The band gaps reported so far for the 5, 7, 9 and 13-AGNRs still strongly exceed 1 eV, even while adsorbed on the metal substrate. This calls for continued band gap tuning, with the 8 and 11-AGNR of the low-band gap $N=3p-1$ family being particularly promising targets. The advent of zigzag GNRs should enable investigations of the spin physics at zigzag edges, including the long-awaited experimental determination of the spin-spin correlation length along the zigzag edge.^[71]

From a technological point of view, the key milestone is the fabrication of a GNR field effect transistor prototype that truly leverages the advantages of atomically precise GNRs. A first step towards this goal is the transfer of the GNRs onto an insulating substrate after fabrication. While transfer protocols involving polymer film coatings have been demonstrated,^[69] membrane free transfer methods may offer advantages in terms of cleanliness. Indeed, bottom-up fabricated GNRs have been transferred to SiO₂/Si, Al₂O₃ and CaF₂ substrates through a combination of cleaving, etching, cleaning and stamping steps, with Raman spectra suggesting that the transferred GNRs remain intact.^[24] Other approaches, such as undergrowing as-synthesized GNRs with an insulator, are under development. Alternatively,

one may consider devising a strategy for the direct synthesis on the surface of a semiconductor or insulator. In this case, the catalytic role of the metal needs to be taken over by other mechanisms, such as the interaction with surface hydroxyl groups in the polymerization of aryl halides on the rutile $\text{TiO}_2(011)$ surface^[72,73] or the excitation by UV light in laser-induced polymerization of DBBA on mica.^[74] While this alternative route seems promising, the corresponding efforts are still at an early stage.

Other technologically important steps include the relaxation of UHV conditions, which has been pursued with considerable success through chemical vapor deposition of precursor molecules in argon atmosphere at pressures of ~ 1 mbar.^[75] Further tuning of the reaction parameters is needed to increase average GNR length beyond the value of ~ 30 nm achieved so far. And, ideally, both defect density and length of GNRs should be quantifiable through Raman spectroscopy, replacing low-throughput STM.

Once the GNRs are on a substrate suitable for electronics applications, the question arises how to best contact these tiny structures. First bottom-up GNR-FET prototypes demonstrate that this is possible, but also indicate the necessity (and difficulty) of avoiding high Schottky barriers at the metal-GNR contacts.^[69] In this respect, lessons may be learned from more mature areas of research, with strategies, such as edge-contacting for graphene^[76] or end-bonding for carbon nanotubes.^[77] The same applies to the challenge of scaling prototype devices to high integration densities.^[70]

Finally, we would like to point out that the on-surface approach described here is not the only contestant in the race for narrow, low-defect GNRs. It has recently been demonstrated that solution synthesis of GNRs is indeed possible,^[78,79] in some cases even without the need of adding solubilizing side groups.^[52] Narrow GNRs have been grown directly on Ge by CVD, although without atomic width control.^[80] Ballistic transport has been demonstrated in GNRs formed at the sidewall facets of SiC.^[81] And even top-down approaches, such as electron-beam lithography, are still progressing substantially.^[82] Yet, we remain convinced that the on-

surface strategy stands out, both in terms of its versatile chemistry and the unmatched precision of the surface science toolbox, and will continue to push the boundaries of materials science.

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Figure 1. On-surface synthesis of $N=7$ armchair graphene nanoribbons (7-AGNRs). (a) Synthesis steps including surface-assisted dehalogenation of DBBA monomers, polymer growth by radical addition at temperature T_1 and surface-assisted cyclodehydrogenation at temperature $T_2 > T_1$.^[15] (b) Constant-current scanning tunneling microscopy (STM) image of 7-AGNRs on Au(111) with superimposed model (blue) and STM simulation (grey). (c) and (d) Non-contact atomic force microscopy images showing body and terminus of atomically precise 7-AGNR, recorded at constant height with CO-terminated tip.^[43] (a) and (b) reproduced with permission.^[15] Copyright 2010, Macmillan Publishers Ltd. (c) and (d) reproduced with permission.^[43] Copyright 2013, Macmillan Publishers Ltd.

Figure 2. Catalogue of molecular precursors for the on-surface synthesis of atomically precise graphene nanoribbons. (a) Armchair GNRs, including widths $N=3$,^[13,44] 5,^[17] 7,^[15] 7 (B-doped),^[25,26] 9,^[19] and 13.^[18] (b) Chevron GNRs, including substitutional doping with zero,^[15]

one,^[23] two^[23,83] and four^[24] nitrogen atoms per precursor molecule. (c) Zigzag-like GNRs, including widths $N=5$ (with cove defects)^[84] and 6 with and without additional phenyl groups.^[55]

Figure 3. Properties of armchair graphene nanoribbons (AGNRs). (a) Electronic band gap of AGNRs as a function of ribbon width as predicted by many-body perturbation theory, revealing three band gap families.^[49] (b) dI/dV spectra of 7-AGNR on Au(111) (red) together with Au(111) reference (black), revealing a band gap of 2.3 eV.^[50] (c) dI/dV spectra of 7-AGNRs on NaCl monolayer island on Au(111).^[56] Top: Differential conductance spectra measured in the center (blue) and at a zigzag terminus (red) of the 7-AGNR. Electronic decoupling yields a band gap increase to 3.2 eV and a splitting of 1.9 eV for the zigzag end states.^[56] Inset: STM topography recorded at sample bias within the band gap. Bottom: STM topographies of occupied (left) and empty (right) edge state.^[56] (d) Combined on-surface synthesis of 7-AGNRs (top) and 13-AGNRs (center) yields GNR heterostructures

(bottom).^[85] (e) STM topography image of 7/13-AGNR heterojunction with atomically sharp interfaces between segments.^[85] Inset: overview image, showing different segment lengths. (f) Differential dielectric function of 7-AGNRs fitted to reflectance difference spectra, indicating optical transitions at 2.1, 2.3 and 4.2 eV.^[63] (g) Schematic of STM-based conductance measurement on single GNR.^[68] (h) Corresponding tunneling current for varying tip height and sample bias, revealing different decay lengths for probing inside and outside the band gap.^[68] (i) Schematic of GNR transfer to SiO₂.^[69] PMMA is deposited onto the GNRs grown on Au on Mica. Floating the stack on HF delaminates Mica, Au layer is removed by etching and floating PMMA/GNR film is drawn onto the target substrate.^[69] (j) Raman spectra of 7-AGNRs before transfer (yellow), after transfer to SiO₂ (blue) and after lithography (red). The preservation of the radial breathing-like mode at $\sim 400\text{ cm}^{-1}$ indicates the preservation of structural integrity.^[69] (a) reproduced with permission.^[49] Copyright 2007, American Physical Society. (b) reproduced with permission.^[50] Copyright 2012, American Chemical Society. (c) reproduced with permission.^[56] (d) and (e) reproduced with permission.^[85] Copyright 2015, Macmillan Publishers Ltd. (f) reproduced with permission.^[63] Copyright 2014, Macmillan Publishers Ltd. (g) and (h) reproduced with permission.^[68] Copyright 2012, Macmillan Publishers Ltd. (i) and (j) reproduced with permission.^[69] Copyright 2013, AIP Publishing LLC.

TOC Entry

Surface-assisted polymerization and cyclodehydrogenation of molecular building blocks provides a route towards atomically precise graphene nanoribbons that combine the outstanding electronic properties of graphene with a band gap that is sufficiently large for digital logic applications. This report covers the progress made in understanding the on-surface reactions, in synthesizing atomically precise nanoribbons of various shapes and in measuring their properties.

Keyword

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Title On-surface Synthesis of Atomically Precise Graphene Nanoribbons

ToC Figure