

Graphene Nanoribbons Via Crystal Engineering

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A new synthesis of graphene nanoribbons has been reported by Rubin and coworkers which combines the advantages of straightforward organic synthesis, intelligent crystal engineering, and high-yielding solid state transformations.¹ By carefully selecting simple aryl diyne monomer (**6**, Fig. 1), the authors report a crystal structure with very short intermolecular distances that favors topochemical polymerization in the crystalline state to long polydiacetylene (PDA, **7**) chains. These rigid polymers can then be dispersed in an organic solvent, patterned onto a substrate and undergo full graphitization at moderate temperatures (300°C, **8**). This work represents a significant step forward as it proves that intelligent monomer design and crystal engineering can obviate the need for pyrolytic temperatures, tedious lithographic manipulation of graphene and the use of complex organic precursors and solution phase oxidative dehydrogenation.

As progress accelerates to establish graphene as a post-silicon electronic material, interest has grown in the synthesis and applications of graphene nanoribbons (GNRs).² Two dimensional graphene sheets are ballistic conductors in all directions with a zero-energy Dirac point. For applications in transistors and related nanoelectronics, the development of a narrow but distinct bandgap in graphene is paramount. It has been established that confining the sheet in one direction to a narrow strip with a high aspect ratio offers the creation and control of a bandgap with energy inversely related to GNR width. GNRs have already shown good performance in OFET applications but the production of atomically precise ribbons on scale remains a significant barrier to the utility of nanoribbon transistors.

GNRs exist in the often-explored frontier between small molecule and bulk material. From an electronics standpoint, this is where the action is. Where molecules like GNRs, Fullerenes, and monodisperse carbon nanotubes prove that confinement of materials dimensions and expansion beyond molecular architectures offers up

best-of-both-worlds characteristics. As with other carbon nanostructures, the approach towards graphene nanoribbons has been attempted in a top-down manner, taking advantage of the easily available larger carbon structures which form easily under high energy conditions and subtractively modifying them to arrive at a more controlled, homogeneous sample. Equally appealing is the bottom-up strategy: using the hefty tool of wet chemical synthesis that is by nature precise to the atomic scale but becomes much more demanding at the enormous molecular weights of the nanomaterial size-regime.

In a top-down sense, GNRs have been accessed most often by cutting graphene using electron beam, helium ion or metallic nanowire lithography to offer GNRs as narrow as 5nm. Throughput of these methods is limited by the deposition of an oriented, graphene target and the fabrication of nanoribbons one-by-one. The gold standard of atomistic control in a top-down method is scanning tunneling microscopy (STM) lithography. Using an STM tip to modify single-layer graphene offers true atomistic control of both size and edge architecture in the ribbons produced, however this is a very time consuming and expensive process which shows no promise for applications beyond the laboratory scale.³

Carbon nanotubes, available in large quantities from CVD, have also been employed as feedstock for the synthesis of nanoribbons. Chemical oxidation has shown high conversion of CNTs to water soluble GNRs but these oxidized nanoribbons show poor conductivity. Localized plasma etching to open followed by sonication to “unzip” CNTs proved highly efficient for the synthesis of ribbons with widths from 10-30 nm. While these nanotube modifications give higher yields with less manipulation than the destructive etching of graphene, their precision is limited by the continuing challenges in availability of homogenous CNTs by which their width limits are defined.³

As materials scientists push the limits of lithography to smaller and smaller scales, synthetic chemists are proving to be more relevant in the world of nanomaterials by doing the opposite, expanding chemical reactions to the size regime of carbon materials. While systems like STM lithography can manipulate atoms with complete precision, they do so one at a time at the location of the microscope tip. A

well-designed chemical reaction will break and form bonds with the same precision at analogous sites on millions of molecules in solution. As such, huge inroads have been made towards the application of synthetic chemistry techniques to the field of nanomaterials.

The most widely applied synthetic strategy towards graphitic materials is the use of Scholl cyclodehydrogenation to effect the planarization and aromatization of a suitably flexible polyaryl precursor (**4** to **5**). The cyclodehydrogenation of hexiphenyl benzene, for example, leads to the graphene fragment hexaperibenzocoronene. If this motif is extended in one dimension, as has been shown with polyphenyl polymers synthesized with aryl-aryl palladium couplings, Diels-Alder polymerization (**3** to **4**), or aryl-alkynyl couplings followed by annulation. This process allows for exact edge control by the careful monomer design. However, to achieve high molecular weights, and therefore longer nanoribbons, in all cases solubility has to be enhanced by the addition of long and flexible side chains such as dodecyl or hexa(ethylene oxide) which, while useful in the flask, enshroud the graphitic cores of these ribbons and obscure them in devices.³⁻⁴

The report from Rubin Lab takes a fundamentally different approach towards the bottom-up synthesis of GNRs, foregoing the convenience of solution phase polymerization and solubilizing moieties for the power found in the preorganization and low entropy of a crystal lattice. Rubin turned to topochemistry as a new method to access a GNR precursor. In 2006, Goroff and coworkers showed that the combination of careful crystal engineering and the reactivity of dialkynes can make topochemical polymerization to carbonaceous chains very efficient by cocrystalizing diiodobutadiyne **1** (Fig. 1) with N,N'-biscyanobutanyl oxalamide **2** to spontaneously form iodopolydiacetylene poly-**1** in the crystal lattice.⁵

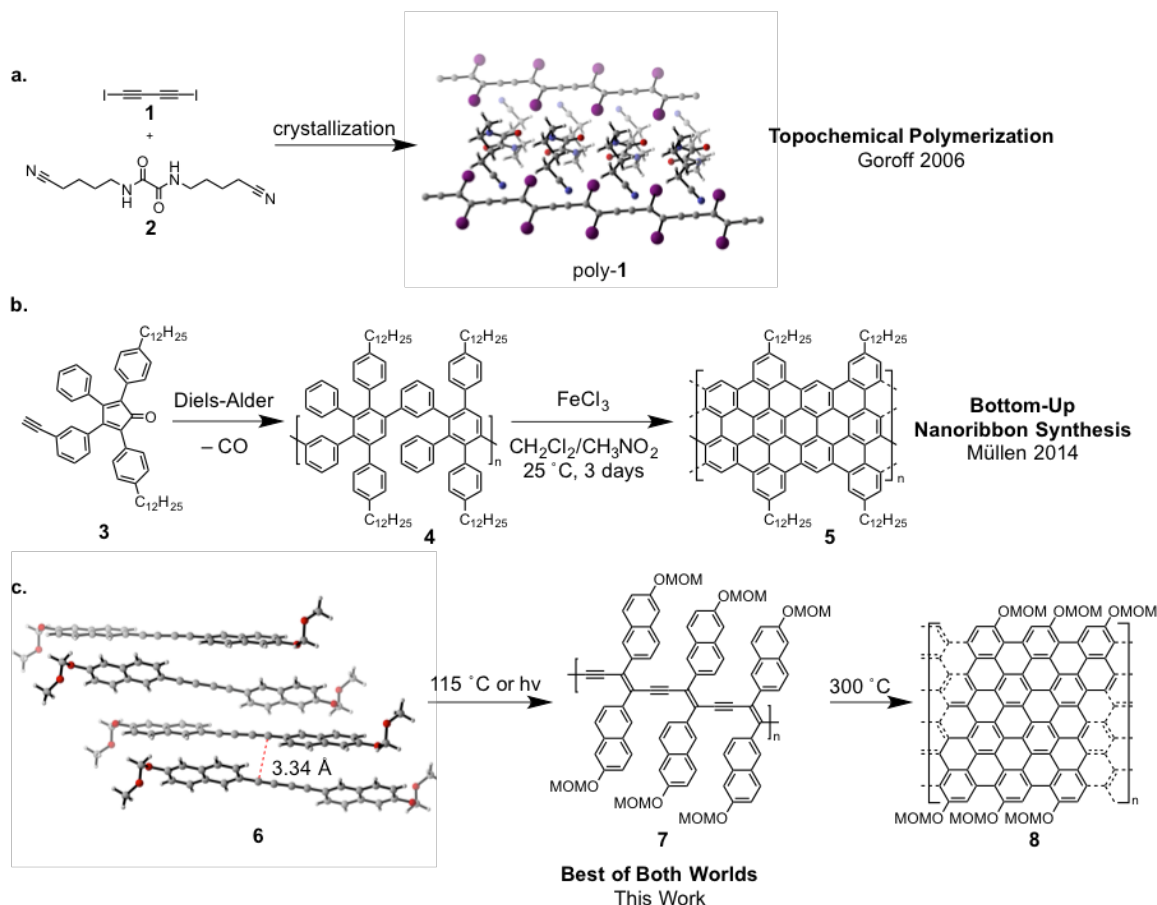


Figure 1. Evolution of design **a.** topochemical polymerization of a diacetylene **b.** solution synthesis of a graphene nanoribbon **c.** topochemical synthesis of a graphene nanoribbon.

For other typical synthetic GNRs the challenge lies in synthesizing a monomer with high solubility and molecular weight that can polymerize efficiently in solution. Thus the organizational energy is contained within the covalent bonds and limited by bond forming efficiency. For Rubin, the challenge was somewhat reversed, the monomer could be simple, but to achieve similar organization, the careful selection of aryl groups and functionalization of the termini was necessary to achieve the appropriate crystal geometry and facilitate an efficient topochemical polymerization to PDA. This was brilliantly achieved by applying their experience in crystal engineering of polyacetylenes.⁶ The straightforward synthesis of several aryldiynes and investigation by X-ray crystallography to determine the C1–C4 (electrophile–

nucleophile) distances. Rubin and coworkers reasoned that naphthalene moieties, with slightly less aromatic stabilization, would impart more reactivity than benzene in the final cyclodehydrogenation step, and so set about synthesizing a class of dinaphthyldiynes, arriving in short order at 6,6'-bismethoxymethyl ether functionalized **6** with a remarkably short (3.34 Å compared to 4.49 Å in the Goroff PDA) C1–C4 distance.

This investment of effort into monomer design facilitates a remarkably straightforward route to the desired nanoribbons. Indeed the simplicity of the synthesis allowed for access to 5.5g (60% overall yield from commercial material) of crystalline material that polymerized with full topochemical conversion to the corresponding PDA **7** spontaneously under ambient light and temperature (slow), with UV irradiation (fast) or heating to 115°C (fast). These polymerized crystals can be separated from the aggregate by sonication and suspension in an organic solvent. Thus, the polymer, confirmed by UV-vis-NIR and Raman spectroscopy and lacking excessive solubilizing chains, can be deposited on a desirable surface. After deposition, applying heat considered mild by graphene synthesis conventions (300 °C) converts the PDA chain to GNR **8** as confirmed by Raman, UV-vis-NIR, and selected area electron diffraction. Extensive microscopic analysis reveals the existence of individual ribbons with widths of less than 2nm, much smaller than available by top-down methods. The length of these ribbons confirms *a posteriori* the high degree of the topochemical polymerization. The on-silicon patterning by selective adsorption of a PDA suspension followed by gentle annealing to form GNRs allowed for the construction of a proof-of-principle FET (using a tangled bulk of nanoribbons, not a single isolated ribbon) with an $I_{\text{on}}/I_{\text{off}}$ ratio of 5 and a charge mobility of $\sim 0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These values are comparable with literature standards.¹

What has really been demonstrated in this report is the utility of a new philosophy of bottom-up graphene synthesis, one where synthetic design prevails over synthetic rigor. After encountering a monomer which aligns correctly in the crystalline state, it is only necessary to apply mild heat or UV light to transform with very high efficiency

a molecule with a molecular weight of 422 g/mol available on the gram scale to a precisely defined, semiconducting carbon material which can be freely deposited and patterned. From the synthetic chemists perspective, this is a triumph of retrosynthetic creativity, and from the materials scientists point-of-view it is a simple and straightforward demonstration that through careful system design, the energy contained within sp-hybridized carbons and a crystal lattice can compete with the thermal energy in a CVD furnace for an up-and-coming material.

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