Materials with Atomic Precision: The Case of Graphene Nanoribbons*

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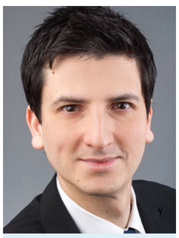

Carlos-Andres PALMA

Summary: In the quest for materials with structural control down to the atomic scale, the synthesis of defect-free graphene nanoribbons sets itself apart since it has led to unprecedented advances in condensed matter physics and graphene electronics. To leverage the precision synthesis of these carbon nanostructures into technologies such as quantum information, materials science solutions for processing must be sought as well. Thus, similar to wafer and thermoplastic processes, answers could lie in engineering macroscopic states of matter, albeit with atomic resolution.

Materials science interlaces physics and chemistry, which might suggest that a materials scientist's expertise lies in both and neither. Many ingredients have been highlighted, however, which define materials science as a unique discipline in its own right. Some of these, apart from synthesis, are processing and modeling. Other essential features of materials science become particularly obvious for polymers when, for example, analyzing the mechanical properties of plastic composites by drawing analogies with metals and alloys. Focusing on the element carbon immediately highlights the often-overlooked role of macromolecular synthesis. Here, the control of function starts at the molecular level as exemplified by the degree of branching and/or cross-linking affecting the thermosetting or thermoforming of a polyolefin. With respect to processing, one must be able to create a macroscopic state of matter such as fibers or sheets with defined morphology. Thus, achieving structural and functional control of materials at different length scales is a key specialty of materials science.

Generally, organic polymers owe their existence to the extremely flexible binding ability of carbon, but materials science also comprises cases consisting only of carbon. Soot or carbon fibers, while being of immense technical importance, remain structurally ill-defined, as opposed to their congeners, the carbon-based allotropes such as fullerenes, carbon nanotubes and graphenic sheets. They have prompted the notion of a 21st-century Carbon Age although, admittedly, not all hypes have become true when scientific excitement was replaced by a more realistic application-oriented view. Turning to graphene as the two-dimensional (2D) material archetype, its performance in devices depends sensitively upon how it is fabricated and processed. Alongside the advent of 2D semiconductors, graphene was heralded as a unique material for field effect transistors (FETs). Thus, a high charge carrier mobility was believed to be favorable for rapid switching while its vanishing band gap would lead to low on/off-current ratios and a current being always on. Overcoming this drawback and opening the band gap required a fundamentally different concept, that is geometric confinement leading toward graphene nanoribbons (GNRs) as quasi-one-dimensional semiconductors. Theory recognized the exciting electronic properties of GNRs since the work of Fujita and Dresselhaus in 1996 together with Louie in 2006. GNR fabrication was then sought by various methods such as chemical or radiation-induced slicing of carbon nanotubes or graphene, posing new challenges due to the limited control of GNR structure down to the atomic level. Here, however, a new aspect is absolutely necessary which considers the precision synthesis of GNRs as macromolecules with defined length, width, edge type and elemental doping. This is not the place to describe such chemistry in detail. It might, instead, suffice to pinpoint some of its key features: GNR synthesis comprises a precursor-protocol in which three-dimensional macromolecules are made from twisted benzene rings. Due to their carefully designed connectivity, the precursors are then subjected to planarization in an oxidative process. Such a controlled two-step scheme can be realized by classical solution-reactions, but also, as has been proven by the Fasel group in their pioneering work, after deposition of precursor molecules on catalytic metal surfaces. The width and edge structure of GNRs govern their spin and electronic properties. For example, zigzag edges may exhibit spin-polarized transport (half-metallicity) while GNRs with armchair edges present near-metallic to semiconducting behaviors. In addition to their edges, GNRs feature end structures known as termini which may host topological end states. One way to understand such states outside topological band physics, is to consider the quinoid–benzenoid electronic transition in a conjugated polymer such as polyphenylene. Therein, different electronic structures are possible, one of which may lead to electronic states localized at the termini. A similar electronic transition leads to end states at the termini in GNRs which are accessible by precision synthesis, and this strategy for the engineering of topological states is now unique to chemistry and physics.

Today, harnessing GNR design at the atomic scale, but beyond the traditional armchair and zigzag edge paradigm, has led to new materials and opened doors to novel phases of matter as well as quantum phenomena. A typical case is sawtooth edges bearing zigzag moieties along a ribbon. The precise synthesis of the sawtooth pattern allows for coupling between localized spins at the zigzag moieties, and ultimately creates spin chains connected through GNR backbones. Such complex edge structures of GNRs have led to the expression of quasiparticles such as massive Dirac fermions. Nanostructures realizing Heisenberg and Kondo spin chains are now customarily designed, and future exotic phases of matter together with their quantum critical phenomena are on the horizon. Furthermore, decorating the peripheries of GNRs with small conjugated molecules adds to the tunability of the spin degree of freedom. This method showcases GNRs as scaffolds mediating interaction between molecular spins, wherein microsecond-long spin coherence times at room temperature have been demonstrated. The strategy of peripheral decoration can be further employed to define new platforms for molecular electronics by lateral fusion of GNRs through molecular bridges. On the other hand, longitudinally combining ribbons of different widths and band gaps affords diodes at the molecular level. Such GNR heterostructures have been fabricated, both on catalytic metal surfaces and in solution, and their photodiode behavior has been studied.

Precision synthesis grants access to a wide range of hitherto elusive physical phenomena along with proofs-of-concept for applications. In many cases, one would want to make GNRs as extended as possible but still solution-processable and prone to de-aggregation from dispersion since stacking of GNRs influences their band gap. This method, which brings us back to the issue of processing, was implemented for achieving single-electron GNR FETs. Other applications mandate transferring of GNRs from catalytic metal surfaces to target device interfaces which affords device configurations based upon van der Waals contacts or top contacts to GNRs. These efforts are a step forward to efficiently contacting single GNRs for FETs towards building circuitry. At the same time, new processes defining precise GNR assemblies could emerge to complement labor-intensive tasks of GNR transfer and circuit integration. Thus, GNR-precursor formation on insulating interfaces has been evidenced and employed for GNR growth directly on device interfaces. Recent strategies propose molecular crystallization as a route to GNR fabrication whereby nanometer-thin nanowire crystallites are placed between electrodes. Such protocol expands existing surface and solution synthesis methods and may alleviate device processing by capitalizing on the long-range ordering accessible from supramolecular organization of suitable GNR precursors.

With the right resources at hand for precious material integration in devices, the central question regards the feasibility of processing carbon architectures for complementing future silicon and quantum roadmaps. Carbon-based spins, while not currently on the map of viable qubit elements for quantum computing, exhibit significant open-shell singlet to triplet splitting, enabling spin preparation at room temperature. This presents a promising avenue for molecule-derived qubits, provided appropriate interfacing and sufficient spin stability. Thinking ahead, colossal challenges still remain toward real-world applications. Specifically, quantum technologies rely on intricate circuitry for spin superposition, logic operations, readout and so on. A case thus emerges in favor of designing future carbon nanostructures to complement the function of circuitry, complete with qubits, their coupling, and readout terminals. This could require processes for cutting and stitching molecules into ultracomplex architectures through the use of atomically sharp probes, electron beams or focused photons. Alternatively, layer-by-layer supramolecular organization may be harnessed to fabricate vertical circuitry.

Looking back at GNRs from the previous settings, one cannot help but wonder if sp^2-carbon is a destination or placeholder for future carbon materials. Once control over sp^2-carbon materials is established, a next promising step would be conversion to sp^3-carbon. What π orbitals have achieved for electron mobility and low band gaps in graphenic materials, could be accomplished by σ orbitals for (electron-) phonon mobility and large band gaps in their sp^3-carbon analogs, *graphanic* materials. The latter two attributes are sine qua non ingredients for conventional superconductors and nitrogen-vacancy (NV) spin centers, which are established elements of superconducting qubits and optically addressable qubits. In addition, *graphane*-derived macromolecules could become important electrically and optically insulating components of circuitry. Many materials are expected to derive from cyclic sp3-carbon structures, starting from quantitatively hydrogenated GNRs and their nanodiamond counterparts, to diamond nanothreads and elusive solids such as body-centered cubic carbon. Whether high-temperature superconductivity or aligned NV spin centers for quantum information can be realized with nanostructured *graphanes* is uncertain: what can be expected are new prospects originating from chemistry, physics and engineering of multitalented carbon architectures.

Materials science has undeniably shaped the Silicon and Plastic Age, and it will continue to influence a Carbon Age following trends in synthesis, modeling and nanofabrication. Present-day advancements in graphene nanoribbons underscore that groundbreaking physics and chemistry demand structural control down to the atomic scale. The role of materials science in unlocking the societal benefits of such control is now vital. Looking forward, unique opportunities emerge for materials science to shape the next age of materials with atomic precision, carbon or otherwise, wherein innovation in synthesis and atomic-level processing are likely crucial. Ω

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The E-MRS 2024 Spring Meeting and Exhibit will be held at the Convention & Exhibition Centre of Strasbourg (France) from May 27 to 31, 2024.

It is expected that this 2024 edition will be the largest in Europe in the field of Materials Science and Technology.

The Spring Meeting is a major conference with over 2500 attendees coming from all over the world every year. The Conference will consist of 21 parallel symposia with **invited speakers, oral and poster presentations**, including one plenary session, an exhibition of products and a series of workshops. The high quality scientific program will address different topics organized in six clusters covering the fields of:

1. Decarbonized energy and sustainability;
2. Materials for human well-being;
3. 2D materials and surfaces: synthesis, characterization and perspectives;
4. Advanced characterization of materials;
5. Materials sciences for cultural heritage;
6. Electronics, magnetics and photonics.

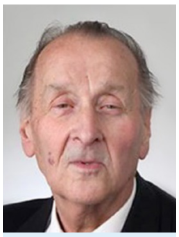
The focus of the scientific program will be both on fundamental investigations and technological applications, providing an international forum for discussing recent advances related to the different aspects to be considered to promote innovation.

The deadline for abstract submission is set at January 18, 2024. This will be an exciting event which should not be missed!

The full conference program is available HERE.

Artificial Intelligence: European Regulations

Paul Siffert, E-MRS and Jacques Amouroux, Université Pierre et Marie Curie



Paul SIFFERT

Jacques AMOUROUX

The general public discovered last winter the revolutionary possibilities offered by Artificial Intelligence (AI) when the media announced the availability of ChatGPT developed by the OpenAI company. In response to a question this software immediately gives a well-written report. High school students quickly rushed to this innovation to have part of their homework done without any effort. This generated an immediate strong reaction from the education community.

In fact, even the newspapers reported that Bill Gates did not expect such a breakthrough. Today, professionals appreciate this progress but observe that the text cannot integrate the 'atmosphere' of the context.

Actually, the research on AI goes back about ten years and, for example, OpenAI was founded in 2015 in San Francisco as a non-profit organisation by well-known investors including Elon Musk.

At present, about $100 billion is invested in AI yearly, from the following regions: USA (50%), China (15%) and Europe (5%), the last being nearly the same as the UK and Israel. Today, in many areas the presence of AI is already very visible through the involvement of industries, in medicine, and the replacement of repetitive jobs, etc. Concerns have arisen throughout the world, even among the initiators of this revolution, including Sam Altman, the current CEO of OpenAI, about the negative effects of AI on many jobs.

Today, two major models on the future developments of AI clash, including, for example, with regard to the effect on jobs:

1. Effects of AI on Employment

Drastic Changes

Arthur D. Little had already sounded the tocsin a few years ago: 300 million jobs risk drastic changes. Very recently, the media reported that the World Bank believes that AI "carries substantial risks of disruption of labour markets". Reportedly, McKinsey & Company estimates that worldwide productivity gains will be between $2400 and $4000 billion.

Increase in the Number of Jobs

At the World Economic Forum in Davos, Switzerland, in 2020, it was said that in 2025, 85 million jobs will disappear, but 97 new jobs will be created. Historically, every industrial revolution has led, after a transition period, to a substantial increase. In a report in the Artificial Intelligence Index Report, it is noted that two-thirds of today's jobs did not exist in 1940. Will that still be true for the present major industrial revolution?

2. The European Parliament Position: The AI ACT

As early as April 2021, the EU began discussions for a legislative act defining the rules for the use of AI The European Parliament will vote on it before the end of this year, which will be a world first. In the USA, meetings between industry leaders (Microsoft, Google, OpenAI) and the administration are currently taking place to remind them of their responsibilities in the face of this promising and worrying technology. The European project does not conceive of the text as a whole but takes into account the risks vis-à-vis society and democratic values. Thus, several categories are planned:

AI Act: different rules for different risk levels

The new rules establish obligations for providers and users depending on the level of risk from artificial intelligence. While many AI systems pose minimal risk, they need to be assessed.

Unacceptable risk

Unacceptable risk AI systems are systems considered a threat to people and will be banned. They include:

- Cognitive behavioural manipulation of people or specific vulnerable groups, for example, voice-activated toys that encourage dangerous behaviour in children.
- Social scoring: classifying people based on behaviour, socio-economic status, or personal characteristics.
- Real-time and remote biometric identification systems, such as facial recognition.

Some exceptions may be allowed. For instance, "post" remote biometric identification systems where identification occurs after a significant delay will be allowed to prosecute serious crimes but only after court approval.

High risk

AI systems that negatively affect safety or fundamental rights will be considered high risk and will be divided into two categories:

1. AI systems that are used in products falling under the EU's product safety legislation. This includes toys, aviation, cars, medical devices, and lifts.
2. AI systems falling into eight specific areas that will have to be registered in an EU database:
   - Biometric identification and categorization of natural persons.
   - Management and operation of critical infrastructure.
   - Education and vocational training.
   - Employment, worker management and access to self-employment.
   - Access to and enjoyment of essential private services and public services and benefits.
   - Law enforcement.
   - Migration, asylum, and border control management.
   - Assistance in legal interpretation and application of the law.

All high-risk AI systems will be assessed before being put on the market and also throughout their lifecycle.

Generative AI

- Generative AI, like ChatGPT, would have to comply with transparency requirements:
  - Disclosing that the content was generated by AI;
  - Designing the model to prevent it from generating illegal content;
  - Publishing summaries of copyrighted data used for training.

Limited risk

Limited risk AI systems should comply with minimal transparency requirements that would allow users to make informed decisions. After interacting with the applications, the user can then decide whether they want to continue using it. Users should be made aware when they are interacting with AI. This includes AI systems that generate or manipulate image, audio, or video content, for example, deep fakes.

Some aspects of this bill generate strong opposition, for example from the Corporate European Observatory. In Washington, the leaders of the GAFAM*, Larry Page, Tim Cook, Mark Zuckerberg, Jeff Bezos, and Bill Gates, have been invited to the Oval Office in the White House to discuss their responsibilities in the context of this revolution. Similarly, industry leaders have recently briefed members of the US Congress on the current capabilities of AI and its continuing development.

Conclusion

Brussels authorities are proud to announce that they are on the front edge of establishing the first world regulations on AI through their Act in order to protect the population against excessive unregulated developments. However, some are surprised by this very fast regulation of a new game not yet fully established. In addition, no leading teams are really present in this world game. Ω

N.B.: References in this article to the opinions expressed by individuals or companies and to publicly announced meetings and events reflect the content of various news reports in the general media as observed by the authors.

*Google, Apple, Facebook, Amazon, and Microsoft

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