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Emerging Carbons

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Carbon is a basic element of all known life on Earth. Depending on how carbon atoms bond to each other, manifold types of carbon materials are formed, termed allotropes of carbon. Different allotropes have distinctive physiochemical properties, functions, and applications. Diamond, graphite, and amorphous carbon are the three well known allotropes of carbon since antiquity. The old carbon allotropes have returned to the spotlight of the scientific community since the 20th century, when a new allotrope of carbon, i.e., Buckminsterfullerene (C_{60}), was discovered in 1985.

Featuring a hollow cage-like structure and the presence of conjugated π electrons on the surface, fullerenes exhibit intriguing electronic, superconducting, photonic, and biomedical properties. In 1991, the structure of the carbon nanotube (CNT) was discovered by transmission electron microscopy (TEM) in carbon samples produced by the arc-discharge technique, which is a method used to synthesize fullerenes. The length of CNTs could reach centimeters with diameter down to sub-nanometers, thus exhibiting a high aspect ratio. Further studies revealed that CNTs can be categorized into two types, namely single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Interestingly, the SWNT is akin to a seamlessly rolled-up graphene layer. Depending on the rolling angle and radius, SWNTs can be either metallic or semiconducting. By virtue of different lengths, diameters, and chirality that can be adopted by CNTs, they possess a broad range of physical properties.

Another ground-breaking milestone in the development of the carbon family was in 2004, when Geim, Novoselov, and co-workers used Scotch tape to fabricate graphene, a single layer of sp^2 -bonded carbon atoms arranged in a honeycomb crystal lattice. Graphene is the building block for many other carbon allotropes, such as graphite, fullerene, and CNTs. It has many

unprecedented properties, such as ultrahigh surface area, high electric and thermal conductivities, high Young's modulus, etc. Featuring a fascinating structure and amazing properties, graphene has not only brought about an upsurge in the study of carbon materials, but also leads the role in the field of two-dimensional (2D) materials.

The carbon allotropes are, and always will be, one of the research hotspots. This is because of our everlasting enthusiasm to design and controllably synthesize new types of functionalized carbon materials, the ambition to develop mass-production methods for achieving commercialization, and the desire to make the best of carbon materials in diverse applications. Since this field is highly dynamic and fast-involving, we intend to provide a timely themed issue, with a compilation of recent review articles related to carbon materials.

This special issue covers a broad range of carbon nanomaterials research, including controlled growth, scalable synthesis, and their multifunctional applications. The contributions come from members, alumni, and collaborators of the Center for Nanochemistry (CNC) at Peking University, which was founded in 1993 and celebrated its 25th anniversary in 2018, and of the Beijing Graphene Institute (BGI), which was founded as a "spin-off" from CNC/Peking University in 2018. The broad research activities at the CNC and BGI cover research and development on various carbon materials from 1D to 2D in the carbon allotropes. This special issue was organized to focus on these carbon nanomaterials while commemorating the 25th anniversary of CNC and the founding of the BGI.

Toward Controllable and Scalable Syntheses

Achieving controlled synthesis and large-scale production of carbon nanomaterials with high quality is prior to their structural and property studies as well as their practical applications. Among the diverse synthetic strategies, the chemical vapor deposition (CVD) method has been the most attractive one to produce graphene hitherto, mainly because of its potential ability to produce large-area high-quality graphene film, which is beneficial for property and application studies. Though great progress has been made, researchers are still pursuing to perfect this technique in all aspects. For example, Zhongfan Liu and co-workers (article number 1803639) discuss the direct CVD growth of graphene on commercial glass substrates, with a focus on their growth methods and mechanisms. Various growth techniques are introduced in this review, including direction thermal CVD growth, molten-bed CVD growth, metal-catalyst-assisted growth and plasma-enhanced growth. Their advantages and disadvantages are also summarized and compared, providing a valuable guideline for researchers of interest.

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In contrast to solid substrates, Lei Fu and Jinxin Liu (article number 1800690) focus on the CVD growth of graphene on liquid surfaces, highlighting their advantages in growing highly uniform graphene films and forming unique graphene grains. Four aspects regarding this topic are comprehensively discussed, including controlled growth, etching, self-assembly, and delivery of graphene onto a liquid surface. In another review, Hailin Peng and co-workers (article number 1800996) discuss the growth mechanism and three engineering principles for large-scale graphene production, including process, equipment, and critical parameters. This is followed by highlighting the recent progress on large-scale production of graphene films with homogeneity control. Feng Ding and co-workers (DOI: adma.201801583) specifically target at the mechanisms of 2D materials grown by the CVD method. They provide a complete picture regarding the kinetic studies of 2D materials, including their growth modes, experimental factors that affect the growth kinetics, the etching process, as well as the growth mechanisms of multilayered and polycrystalline 2D materials.

In addition to 2D graphene, researchers are also interested in making polymeric graphene bulk materials with a 3D crosslinked network. Yongsheng Chen and co-workers (article number 1802403) present a review related to this topic. They first summarize the theoretical work on predicting various structures of graphene bulk materials. Then, the experimental synthesis strategies are discussed, with a focus on two methods, namely CVD and crosslinking using graphene oxide directly. Lastly, some applications of 3D graphene materials are given.

Meanwhile, the fast advancement of various characterization techniques, such as aberration-corrected TEM, has inspired some interesting work. For example, Mark H. Rummeli and co-workers (article number 1800715) study the chemical interactions between an electron beam and graphene. After introducing the general principles of aberration-corrected TEM, they summarize various chemical phenomena induced by the interaction between the electron beam and the graphene, including etching of the graphene edges, formation of carbon chains and defects, generation of fullerene from graphene flakes, and generation of graphene from amorphous carbon.

Besides graphene, Jin Zhang and co-workers (article number 1800805) provide a review related to the chirality-controlled synthesis of SWNTs. They firstly introduce the growth modes and catalytic mechanisms for the nucleation and growth processes of SWNTs. With these fundamentals, the recent progress on the chirality-selective synthesis of SWNTs on various templates, such as predefined molecular seeds, transition metals, W-based alloy catalysts, and so on, is summarized. Particularly, the key factors designating the chirality of SWNTs are highlighted. Qingwen Li and co-workers (article number 1800750) summarize the recent progress in studies related to semiconducting SWNTs, with a special focus on their solution processing strategies. They first discuss some solution-based purification methods to obtain pure semiconducting SWNTs, particularly highlighting the conjugated-polymer-based sorting strategy. Then, they present the solution-based deposition and shape control of semiconducting SWNT thin films on surfaces. Applications of purified semiconducting SWNTs in next-generation electronics are also introduced.



Jin Zhang obtained his B.S. and M.S. degrees at Lanzhou University in 1992 and 1995, respectively, and completed his Ph.D. degree with Prof. Hulin Li and Prof. Zhongfan Liu at Lanzhou University and Peking University in 1997. After a two-year postdoctoral fellowship at the University of Leeds, UK, he returned to Peking University where he was appointed Associate Professor (2000) and promoted to Full Professor in 2006. In 2013, he was appointed as Changjiang professor. His research focuses on the controlled synthesis and spectroscopic characterization of carbon nanomaterials.



Hua Zhang obtained his B.S. and M.S. degrees at Nanjing University in 1992 and 1995, respectively, and completed his Ph.D. with Prof. Zhongfan Liu at Peking University in 1998. As a Postdoctoral Fellow, he joined Prof. Frans C. De Schryver's group at Katholieke Universiteit Leuven (Belgium) in 1999, and then moved to Prof. Chad A. Mirkin's group at Northwestern University in 2001. After working at NanoInk Inc. (USA) and at the Institute of Bioengineering and Nanotechnology (Singapore), he joined Nanyang Technological University in July 2006. His current research interests focus on the (crystal-)phase engineering of nanomaterials and controlled epitaxial growth of heterostructures, including the synthesis of ultrathin two-dimensional nanomaterials (e.g., metal nanosheets, graphene, metal dichalcogenides, metal-organic frameworks, covalent organic frameworks, etc.), novel metallic and semiconducting nanomaterials, novel amorphous nanomaterials, and their hybrid composites for various applications such as catalysis, clean energy, (opto-)electronic devices, nano- and biosensors, and water remediation.

Toward Multifunctional Applications

Featuring their fascinating structures and exceptional properties, carbon-based materials are promising in a wide range of applications. Liming Dai and co-workers (article number 1801526) review the use of carbon-based metal-free catalysts (CMFCs) in the field of energy conversion and storage. They first highlight the superiority of CMFCs over other conventional catalysts, such as noble metals and metal oxides. Then they introduce three design strategies to prepare CMFCs, including controlled doping, nano-meso-macro structure design and chemical functionalization. This is followed by examples of

using CMFCs in different reactions involved in the energy conversion and storage process.

Francesco Bonaccorso and co-workers (article number 1801446) discuss the application of carbon-based materials as photocathode electrocatalysts for the hydrogen evolution reaction (HER). They first justify the carbon-based semiconductors as promising candidates through energy-band diagrams. They also introduce the criteria for evaluating the performance of photocathodes, the key processes for ensuring the proper functioning of the photocathodes, as well as the valuable guidelines for achieving efficient and durable device operation.

Yingying Zhang and co-workers (article number 1801072) focus on the application of carbon materials in flexible and wearable electronics. They discuss the synthesis of various carbon-based materials, and their applications in flexible devices, such as pressure sensors, humidity sensors, electrochemical sensors, flexible conductive electrodes, etc., as well as the integration of multiple devices for multifunctional wearable systems. Di Wei and co-workers (article number 1800716) discuss the applications of carbon nanomaterials in wearable batteries. They summarize the most recent progress in this field in terms of materials fabrication, and structure design and optimization of wearable energy-storage systems.

Hui-Ming Cheng and co-workers (article number 1800863) highlight the regulating role of CNTs and graphene in lithium batteries, which is comprehensively discussed, in terms of electrochemical reactions, electrode structures, and integrated cell design. Fei Wei and co-workers (article number 1800680) specifically focus on the use of CNTs, one of the strongest materials, to store mechanical energy. They first summarize the typical materials for storing mechanical energy. Then they highlight the theoretical and experimental studies on the mechanical properties of CNTs and their assemblies. Diverse strategies of using CNTs to store mechanical energy are subsequently discussed.

Hua Zhang and co-workers (article number 1800696) review the recent studies in graphene-based noble-metal nanocomposites for electrocatalytic applications. They first discuss the synthetic methods for various types of graphene-based noble-metal nanocomposites. Then, the performances of these materials in various electrocatalytic reactions are summarized and

compared. Particularly, the functions of noble metals and graphene, as well as their synergistic effects are highlighted. Yuliang Zhao and co-workers (article number 1800662) present a comprehensive review on the application of graphene as a smart platform for stimuli-responsive drug delivery and combined cancer therapy. The design principle is firstly introduced, which is followed by several examples of graphene-based materials utilized in multiple combined therapies.

Carbon nanomaterials are of great research interest in the past few decades. The everlasting goal is to achieve controlled synthesis of carbon nanomaterials at large scale and with high quality, and to further improve their physiochemical properties. Despite great achievements, challenges still exist. So far, it is still problematic to scale up the production of CNTs and graphene with controlled structures. Moreover, carbon nanomaterials generally face the problem of becoming aggregated during the synthesis process. Typically, 1D CNTs are prone to aggregate into networks, while 2D graphene sheets tend to stack together. The severe aggregation will deteriorate their properties and future applications. In addition, making high-quality graphene by the CVD method and its transfer of substrate on a large scale have been perplexing researchers in this field for a long time. Nevertheless, these challenges also pose opportunities and stimulate researchers to continue the studies of carbon materials.

To tackle the critical challenges of 2D graphene material and bridge its industrial applications, BGI was founded to provide the first-class R&D conditions for materials synthesis and characterization, as well as to offer the service of the R&D foundry for industry partners to solve their practical problems with materials solutions. We believe that with our great efforts, the field of carbon materials will continue to develop strongly and perpetually, and attract more and more interest.

Toward this end, we would like to thank all the authors for their great contributions to this themed issue. I hope readers from diverse fields can enjoy these excellent, timely, and representative articles and be inspired from them. Lastly, we would like to thank all the editorial staff members of *Advanced Materials* for their hard work and strong support. The cover page was carefully designed by Dr. Xin Gao, a member of the CNC family.