Science Bulletin 64 (2019) 1817–1829

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Review

Low-temperature synthesis of sp^2 carbon nanomaterials

Yu Ding [a,1], Mengqi Zeng [a,1], Lei Fu [a,b,*]

[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
[b] The Institute for Advanced Studies, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 17 August 2019
Received in revised form 30 September 2019
Accepted 8 October 2019
Available online 14 October 2019

Keywords:
Low-temperature synthesis
sp^2 carbon nanomaterials
Graphene
Carbon nanotubes

ABSTRACT

sp^2 carbon nanomaterials are mainly composed of sp^2-hybridized carbon atoms in the form of a hexagonal network. Due to the π bonds formed by unpaired electrons, sp^2 carbon nanomaterials possess excellent electronic, mechanical, and optical properties, which have attracted great attention in recent years. As the advanced sp^2 carbon nanomaterials, graphene and carbon nanotubes (CNTs) have great potential in electronics, sensors, energy storage and conversion devices, etc. The low-temperature synthesis of graphene and CNTs are indispensable to promote the practical industrial application. Furthermore, graphene and CNTs can even be expected to directly grow on the flexible plastic that cannot bear high temperature, expanding bright prospects for applications in emerging flexible nanotechnology. An in-depth understanding of the formation mechanism of sp^2 carbon nanomaterials is beneficial for reducing the growth temperature and satisfying the demands of industrial production in an economical and low-cost way. In this review, we discuss the main strategies and the related mechanisms in low-temperature synthesis of graphene and CNTs, including the selection of precursors with high reactivity, the design of catalyst, and the introduction of additional energy for the pre-decomposition of precursors. Furthermore, challenges and outlooks are highlighted for further progress in the practical industrial application.

1. Introduction

sp^2 carbon nanomaterials have been widely studied due to their unique properties for nearly three decades [1–4]. The sp^2 carbon nanomaterials, mainly including zero-dimensional (0D) fullerene, one-dimensional (1D) carbon nanotubes (CNTs) and two-dimensional (2D) graphene, have attracted great interests in both academy and industry [5–11]. The structure based on a hexagonal network arranged by sp^2 carbon atoms endows them with superior properties, such as excellent electrical and thermal conductivity, outstanding mechanical strength and superlubricity, extraordinary flexibility and high carrier mobility [12–16]. Owing to these unique properties, sp^2 carbon nanomaterials exhibit wide applications in field-effect transistor (FET) [17], capacitor [18], sensor [19], and composites [20]. An essential requirement to achieve the practical applications of sp^2 carbon nanomaterials is to reduce the synthesis temperature for reducing the energy consumption, lowering the cost and improving the safety of industrial production. There are many methods developed for preparing graphene and CNTs, involving arc discharge [21], laser vaporization [22], pyrolysis [23], mechanical and chemical exfoliation of graphite [20], thermal decomposition of SiC [24], chemical vapor deposition (CVD) of hydrocarbons [25,26] and so on. The synthesis processes mainly include the following elementary steps: (1) precursors undergo a few steps of reaction and are decomposed into carbon radicals with sufficient energy supply assisted by the catalyst; (2) carbon radicals combine with each other to form crystal nucleus; (3) the formed nucleus continues to combine with free radicals and grows into the desired sp^2 material. In general, the carbon source for the synthesis of sp^2 carbon nanomaterials is hydrocarbon, like alkane (CH_4), whose pyrolysis temperature is above 1000 °C. The high temperature is undesirable for large-scale industrial production of the sp^2 carbon nanomaterials. Besides, once the low-temperature synthesis technology is well established, sp^2 carbon nanomaterials are expected to directly grow on the substrate that cannot bear high temperature, like plastics, which is beneficial to the development of flexible electronic devices. For composites, direct growth of sp^2 carbon nanomaterials on polymers is more favorable to various applications, such as electrode materials and biosensors. Hence, it is critical to achieve the low-temperature synthesis of sp^2 carbon nanomaterials to meet the demands of their future practical applications.

In this review, we summarize the main strategies for low-temperature synthesis of two widely explored sp^2 carbon nanomaterials, graphene and CNTs, which can be seen in Scheme 1. The

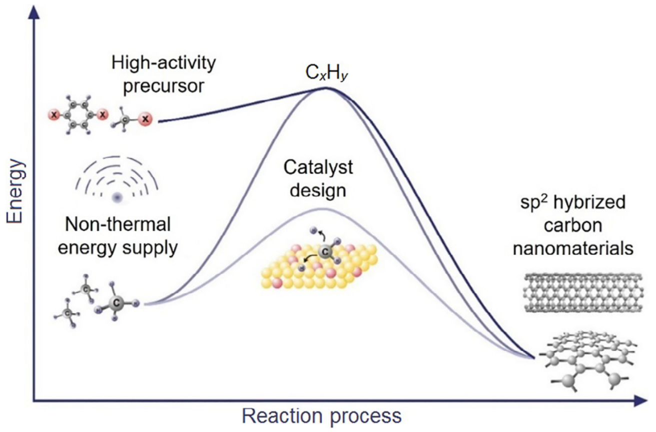
---

SPECIAL ISSUE: Emerging Investigators 2019

[*] Corresponding author.
E-mail address: leifu@whu.edu.cn (L. Fu).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.scib.2019.10.009



Scheme 1. (Color online) Strategies for low-temperature synthesis of sp^2 carbon nanomaterials.

essential factors that influence the growth process are discussed with the mechanisms in detail, including the selection of precursors, the design of catalysts, and the type of energy introduction. It is demonstrated that sp^2 carbon nanomaterials can be obtained at relatively low temperature by choosing the species of carbon source with high reactivity, adjusting the chemical component and physical state of catalysts as well as introducing additional energy for the pre-decomposition of precursors. Moreover, we summarize the challenges and outlook in the low-temperature synthesis of sp^2 carbon nanomaterials.

2. Carbon source selection with high reactivity

The precursor is decomposed into carbon free radicals at the first step in the synthesis of sp^2 carbon nanomaterials, followed by the assembly to form hexagonal carbon clusters. The conventional precursor for preparing sp^2 carbon nanomaterials is CH_4, whose decomposition temperature is generally above 1000 °C [25,27]. Hence, choosing suitable carbon sources with low decomposition energy is crucial to reduce the synthesis temperature. Different from CH_4, other hydrocarbon precursors have been used to synthesize sp^2 carbon nanomaterials at a lower temperature [28,29], such as ethylene, acetylene, as well as solid and liquid carbonaceous compounds. In this section, we will discuss the selection of different precursors for low-temperature synthesis of sp^2 carbon nanomaterials with the related growth mechanism.

2.1. Carbon source with an active halogen group

Carbon halides are usually used as liquid precursors in solution reactions due to their low C–X bond energy [30,31]. The C–H bond with the bond energy of 414 kJ/mol is stronger than the C–X bond with the bond energy of 285–340 kJ/mol, making the C–X bond in halogenated hydrocarbon easier to decompose than the C–H bond in alkane. Tetrachloroethylene (C_2Cl_4) can be successfully reduced to free radical C_2 by metallic potassium at a low temperature of 200 °C (Fig. 1a) [32]. The newly formed C_2 can assemble into hexagonal carbon clusters and then grow into multi-wall carbon nanotubes (MWCNTs) when using Fe/Au as catalyst. Hexachlorobenzene (C_6Cl_6) can be reduced to hexagonal carbon clusters by metallic potassium, followed by the assembly into MWCNTs in the presence of Co/Ni catalyst at 350 °C (Fig. 1b) [30]. Both methods required alkali metal catalysts to decompose precursors and form carbon-containing radicals, involving complicated metathesis reactions. Afterward, MWCNTs were synthesized through decomposing carbon tetrachloride (CCl_4) using Fe-encapsulated dendrimers as catalyst under heating at the high pressure without alkali metal (Fig. 1c) [31]. With this method, CCl_4 was decomposed into dichlorocarbene intermediate, and then the as-produced dichlorocarbene was delivered to the

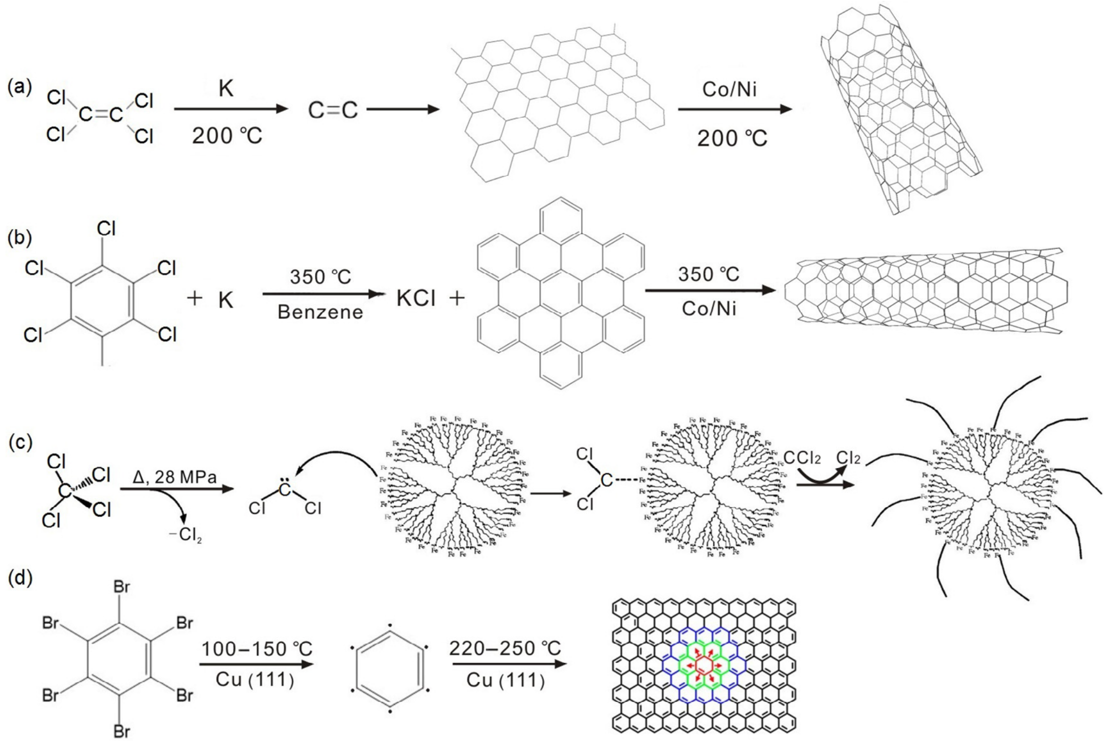


Fig. 1. (Color online) The formation route of sp^2 carbon nanomaterials by using carbon halides as the precursor with a radical coupling reaction at low temperature. (a) C_2Cl_4; (b) C_6Cl_6; (c) CCl_4; (d) C_6Br_6. Reproduced with permission from (a) Ref. [32], Copyright 2002 American Chemical Society (ACS); (b) Ref. [30], Copyright 2000 ACS; (c) Ref. [31], Copyright 2004 ACS; (d) Ref. [33] Copyright 2013 ACS.

encapsulated Fe surface for the nucleation and growth of MWCNTs at 175 °C.

In addition to Cl-containing hydrocarbons, Br-containing hydrocarbons can also serve as precursors with low decomposition energy to synthesize graphene. Monolayer graphene film was synthesized via a mild radical-coupling reaction at the low temperature of 220–250 °C (Fig. 1d) [33]. During the deposition process, the C–Br bond of hexabromobenzene (C_6Br_6) precursors was easy to break, leading to the formation of benzene radicals for coupling together to prepare graphene. The charge carrier mobility of the as-prepared graphene film was 1000–4200 $cm^2/(V\,s)$, indicating the high quality of the obtained graphene film.

Selecting carbon halides as precursors can obtain carbon-containing radicals at a lower temperature, followed by a radical coupling reaction to obtain hexagonal carbon clusters. However, in this process, the halogen atom might be incorporated into carbon clusters, resulting in non-six-membered ring defects and heteroatom doping.

2.2. Carbon source with primitive aromatic structure

Apart from selecting a precursor which possesses low decomposition energy, an aromatic compound with hexagonal structure can also be used as a precursor for lowering the growth temperature [34,35]. The traditional CVD reaction contains complicated dynamic processes, including the adsorption of precursor molecules, dehydrogenation, and assembly of carbon-containing free radicals. According to the density functional theory (DFT) calculation by Choi et al. [35], the adsorption energy of sp^2-hybridized aromatic molecules on the Cu catalytic substrate surface was ten times higher than that of hydrocarbon precursors like CH_4 or C_2H_2. The reason was that the London dispersion force would result in much stronger adsorption of aromatic precursors on the metal surface. Moreover, the magnitude of the adsorption energy determines whether the subsequent reaction is desorption or dehydrogenation. When the adsorption energy is lower than the energy barrier against dehydrogenation, the adsorbed molecule tends to desorb. Since large-sized molecules have more electron delocalization motion, they have exhibited more pronounced charge density fluctuations that increase their London dispersion power, thus increasing the adsorption energy. From the calculation results, it was more difficult for CH_4 to dehydrogenate than large-sized molecules like C_6H_6 and $C_{18}H_{14}$, because its dehydrogenation barrier of 1.53 eV was much higher than the desorption barrier of 0.17 eV. For $C_{18}H_{14}$, the dehydrogenation barrier was lower than the desorption barrier, which facilitated the dehydrogenation. Therefore, the growth of sp^2 carbon nanomaterials using aromatic compounds as the carbon source can proceed at a much lower temperature.

Early in 2004, *p*-xylene has been used as the carbon precursor to synthesize single-walled carbon nanotubes (SWCNTs) in a liquid solution through ultrasonic method at room temperature [36]. Limited by the technical level at the time, the growth mechanism of SWCNTs was unclear. Subsequently, many researchers began to focus on aromatic compounds whose basic structures are similar to those of graphene for the low-temperature growth, such as benzene, naphthalene and toluene. For instance, monolayer graphene flakes with excellent quality have been synthesized from benzene at a low temperature of 300 °C [37]. Continuous monolayer graphene has been synthesized in a temperature range of 300–600 °C by using naphthalene as the carbon source and Cu as the catalyst (Fig. 2a) [38]. All the C–C and C–H bonds in the naphthalene molecule are sp^2 hybridized and the benzene rings in the molecule resemble the basic unit of graphene. The α and β C–H bonds in naphthalene molecular are less stable than the C–H bonds in benzene [39], which is beneficial to promoting the formation of graphene at low temperature. The quality and layer number of the resulting graphene film were demonstrated by Raman spectra and transmission electron microscopy (TEM) characterizations, as shown in Fig. 2b and c. When the temperature was higher than 500 °C, the synthesized graphene was of high quality. As the temperature dropped, the catalytic activity of Cu reduced, resulting in

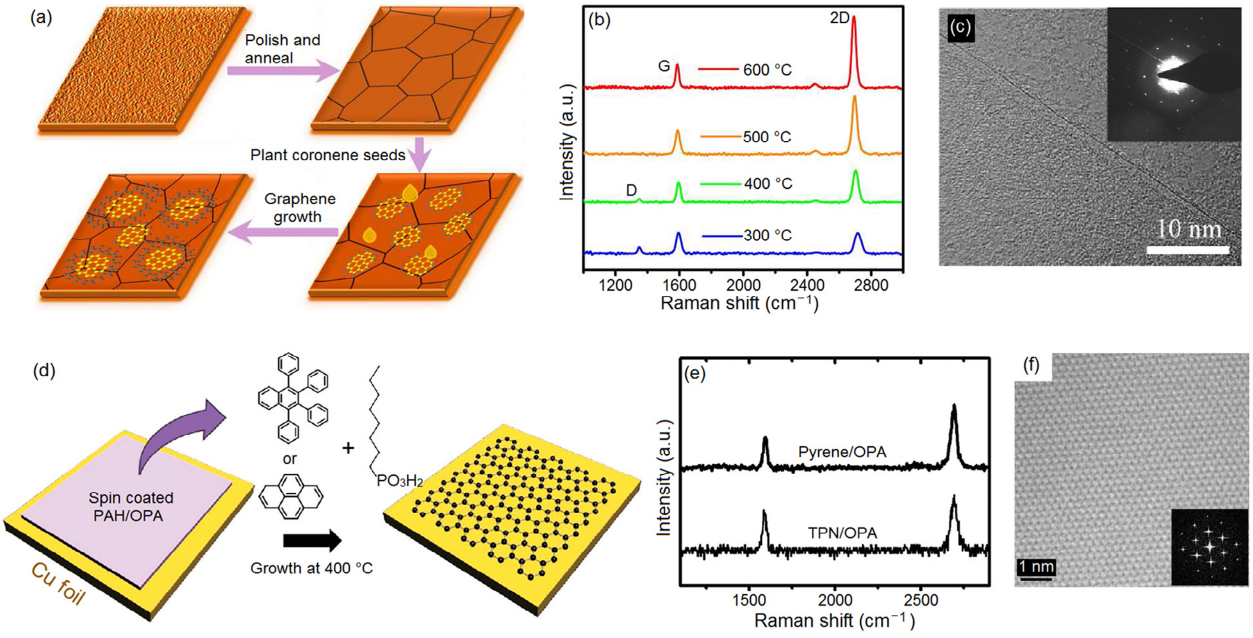


Fig. 2. (Color online) The formation route of graphene by using carbon source with primitive aromatic structure at low temperature. (a) Schematic illustration of low-temperature graphene growth on Cu foil using coronene as nucleation seeds. (b) Raman spectra of graphene grown at 300–600 °C with coronene as seeds and naphthalene as the solid precursor. (c) TEM image of monolayer graphene. The inset shows the SAED pattern. (d) Schematic illustration of high-quality graphene growth on Cu surface at 400 °C using PAH/OPA heterogeneous solid carbon sources. (e) Raman spectra of transferred pyrene/OPA- and TPN/OPA-derived graphene on SiO_2 substrate. (f) HR-TEM images of TPN/OPA-derived graphene at 400 °C. Reproduced with permission from (a–c) Ref. [38], Copyright 2013 Royal Society of Chemistry (RSC); (d–f) Ref. [40], Copyright 2016 Wiley.

incomplete dehydrogenation of carbon-related radicals and the existence of significant defect confirmed by the Raman peak at ~1350 cm^{-1} (Fig. 2b). The high-resolution TEM (HR-TEM) indicated that the graphene gained at 400 °C was monolayer (Fig. 2c), and the selective area electron diffraction (SAED) showed only one set of hexagonal diffraction spots, indicating that the investigated area was single crystalline.

As mentioned above, polycyclic aromatic hydrocarbons (PAH) have stronger adsorption energy, which can greatly reduce the synthesis temperature of sp^2 carbon nanomaterials owing to enhanced London dispersion forces [35]. However, structural defects and disordered stacks will occur when large molecules are bonded to each other, affecting the quality of sp^2 carbon nanomaterials. Adding aliphatic hydrocarbons in PAH is an effective strategy to reduce the formation of defects because the small aliphatic carbon fragments can fill up the defect sites. As can be seen in Fig. 2d, pyrene ($C_{16}H_{10}$) or 1,2,3,4-tetraphenylnaphthalene (TPN, $C_{34}H_{24}$) was used as the main carbon source for graphene growth at a temperature of 400 °C [40]. The defect density in graphene could be reduced by adding a small amount of 1-octylphosphonic acid (OPA) to the PAH source. Composed of a short carbon chain with a solubilizing phosphorous group, it could rend the compound in the system. Both Raman spectroscopy and HR-TEM characterizations showed that the quality of graphene was extremely high after the addition of OPA (Fig. 2e, f). Furthermore, researchers also studied the effects of different configurations of PAH on the synthesis of sp^2 carbon nanomaterials [34]. The results showed that the specific molecular structure of the precursor played a decisive role in reducing the growth temperature. Among the three configurations of terphenyl, *p*-terphenyl and *m*-terphenyl were suitable precursors for monolayer graphene growth at 400 °C, whereas *o*-terphenyl and anthracene were not suitable to achieve graphene growth at such low temperature. In the reaction process, the skeleton of *p*-terphenyl and *m*-terphenyl can get flattened after being absorbed on the Cu surface, and the intermolecular dehydrogenation and the formation of enlarged aromatic system contribute to an energy gain and the successive attachment of terphenyl molecules. Hence, large-size graphene sheets can be produced. Conversely, *o*-terphenyl tends to undergo an intramolecular dehydrogenation and form a new central C6 ring. The as-resulted triphenylene was a planar and stable benzenoid structure, which went against the growth of graphene. These results emphasize the importance of the choice of suitable precursor with specific molecular structure and spatial configuration for the synthesis of sp^2 carbon nanomaterials at low temperature.

Precursors with the aromatic structure were also widely used to synthesize graphene nanoribbons (GNRs) at low temperature. The main methods for preparing GNRs include liquid-phase synthesis and surface-mediated synthesis. Liquid-phase synthesis relies on an organic coupling reaction, in which the target molecules are precisely constructed at the atomic level to achieve the control of the structure of GNRs. These small molecule precursors with aromatic components are able to form polyarylene structures by Suzuki-Miyaura coupling polymerization [41,42] and the Diels-Alder polymerization [43], and then form GNRs by cyclodehydrogenation (intramolecular Scholl reaction). These methods attracted great attention owing to their great potential in controlling the width of synthesized GNRs. The length control of GNRs was still a challenge. Recently, a living annulative π-extension (APEX) polymerization technique has been developed to the rapid and modular synthesis of GNRs at 80 °C, which achieved the controlling of their length, as well as width and edge structure [44]. The living polymerization utilized a silicon-containing compound benzonaphthosilole as a monomer and phenanthrene as an initiator. The silicon-containing group in the monomer coupled with the active K-side reaction of the initiator under the catalysis of silver and palladium salts in *o*-chloranil and 1,2-dichloroethane at 80 °C (Fig. 3a–f). After coupling, a new fused aromatic ring and a new K region (**1a**) were formed, resulting in subsequent APEX reactions to the synthesis of a fjord-type GNR. The length of GNRs can be controlled by simply changing the initiator-to-monomer ratio, thus achieving the synthesis of GNR block copolymers. When the ratio of monomer to initiator molar concentration increased from 10:1 to 500:1, the GNR molecular weight gained from 2.9 to 150 kDa and the length extended from 3 to 169 nm. The precise liquid phase synthesis of GNRs with controllable length, width and edge structure established the foundation for further exploring physical and chemical properties of GNRs.

The reactivity of oligophenylene precursors and their compatibility with reaction conditions are essential factors for limiting the liquid phase reactions. In contrast, there exists strong intermolecular π–π stacking between precursor molecule and the GNRs, and the solubility of them in the conventional organic solvent is poor, which makes it difficult for subsequent processing for electronic device applications. To solve this issue, the surface-mediated synthesis became another option for low-temperature growth of GNRs. Surface-mediated synthesis consists of several steps as follows. Aromatic precursors with halogen groups are deposited on the metallic surface by thermal sublimation under ultra-high vacuum conditions at first, then precursor monomers undergo polymerization and cyclodehydrogenation under heating, finally forming the desired GNRs. This method has been applied for fabricating many different GNRs with armchair edges in a temperature range of 200–440 °C [46–49], but it is not suitable for the synthesis of GNRs with zigzag edges, because aryl-aryl coupling is likely to take place along the armchair direction rather than the zigzag direction. As a matter of fact, GNRs with zigzag edges are also important and they are predicted to exhibit spinpolarized electronic edge states, playing a key role in graphene-based spintronics research [50]. Therefore, it is essential to prepare GNRs with zigzag edges. Researchers specifically designed precursor monomers by adding carbon functions at the edges of the monomers to complete the tiling toolbox needed for the fabrication of zigzag structures [45]. Fig. 3g illustrated the fabrication steps of suitably designed molecular precursors **1a** to GNRs with zigzag edges. Monomer **1a** was deposited on the clean Au(1 1 1) single-crystal surface, and then was activated by dehalogenation. It underwent polymer formation via radical addition at 475 K (step 1 in Fig. 3g). Further, the intermediate molecule was heated to 625 K for cyclodehydrogenation, then the final ZGNR was successfully formed (step 2 in Fig. 3g). The height was obviously reduced after the cyclodehydrogenation, indicating a complete planarization of the linear structures (Fig. 3h and i). Thence, GNRs with zigzag and armchair edges can be synthesized by designing different structures of aromatic precursors, whose length and width are also controllable. With this method, GNRs obtained on catalytic metallic surfaces are more beneficial to the electronic device applications.

2.3. Carbon source with a carbon chain skeleton

Many polymers with giant carbon chain skeleton are expected to prepare graphene at low temperatures, such as polymethylmethacrylate (PMMA) and polystyrene (PS) [51–53]. Compared with hydrocarbon, the decomposition temperature of polymers is much lower (200–300 °C), which may lower the temperature in the first step of the precursor decomposition in the synthesis process of sp^2 carbon nanomaterials [54]. On this basis, the C–H bond energy of PMMA (283–288 kJ/mol) and PS (292–305 kJ/mol) are weaker than that of the typical hydrocarbon like CH_4 (410 kJ/mol), C_2H_2 (443 kJ/mol) and C_2H_4 (506 kJ/mol), contributing to the reduction of dehydrogenation energy [55]. As a result, the growth

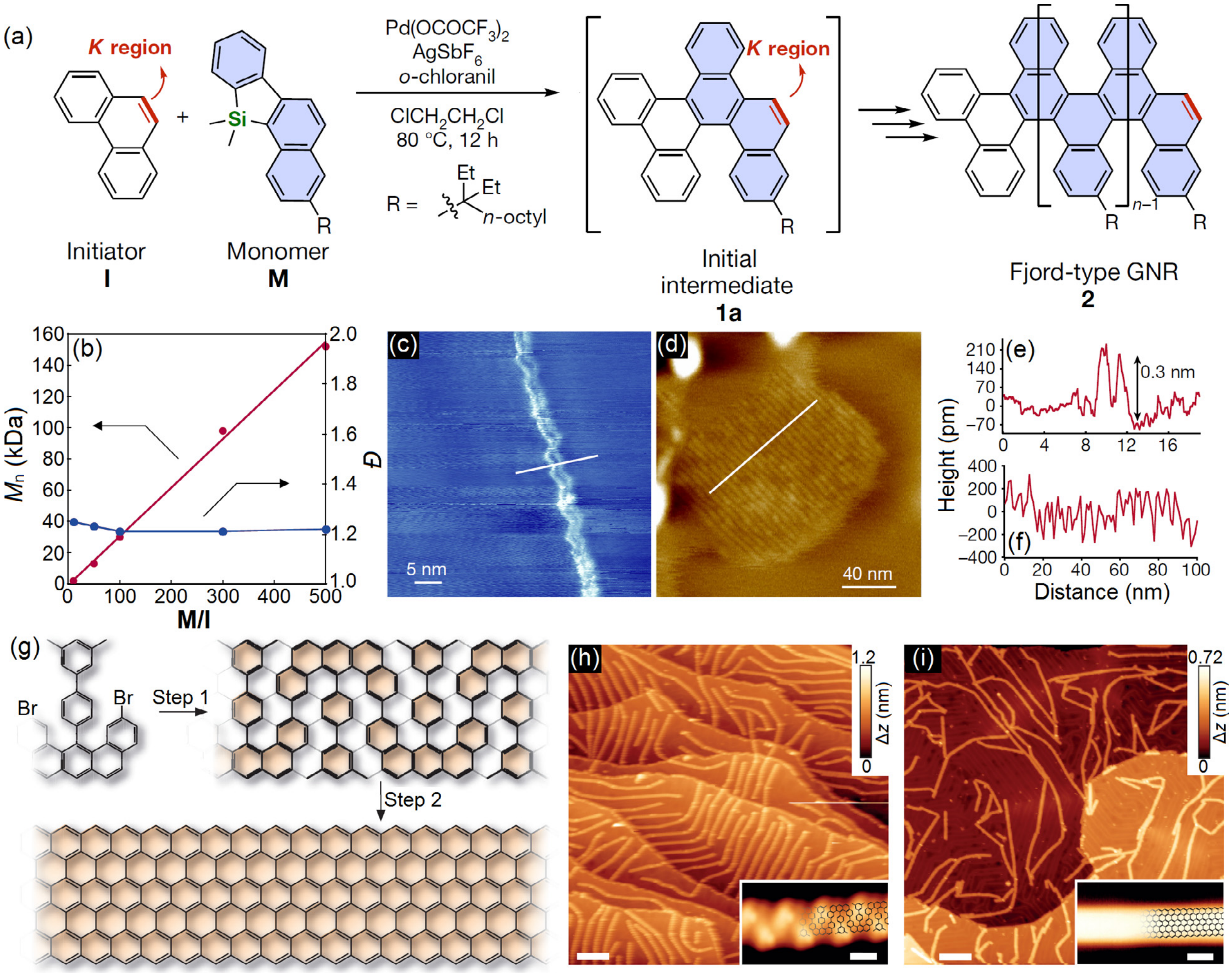


Fig. 3. (Color online) The formation route of GNRs by using carbon source with primitive aromatic structure at low temperature. (a) Living APEX polymerization using phenanthrene as the initiator and benzonaphthosilole as the monomer. Reaction conditions: Monomer (1.0 equiv.), $Pd(OCOCF_3)_2$ (1.0 equiv.), $AgSbF_6$ (2.0 equiv.), *o*-chloranil (2.0 equiv.), $ClCH_2CH_2Cl$, 80 °C, 12 h. (b) M_n ($Đ = M_w/M_n$) profiles versus **M**/**I** in the conversion of the monomer in the living APEX polymerization. (c) STM image of fjord-type GNR ($M_n = 1.5 \times 10^5$ Da, $Đ = 1.22$) deposited on HOPG (voltage = 1.0 V, current = 50 pA, temperature = 78 K). (d) AFM height image of GNR ($M_n = 1.5 \times 10^5$ Da, $Đ = 1.22$) on HOPG. Cross-sectional height profile taken along the white line in *c* (e) and *d* (f), perpendicularly to the observed stripes. (g) Synthetic strategy to obtain GNRs with zigzag edges, Monomer 1a owns an additional dimethyl-biphenyl group in the interior of the U-shape, which is designed to synthesize a 6-ZGNR upon polymerization (step 1) and subsequent cyclization (step 2). (h) Large-scale STM image of the Au(1 1 1) surface after the deposition of monomer **1a** held at 475 K. (i) Large-scale STM image of the Au (1 1 1) surface after annealing at 625 K. Reproduced with permission from (a–f) Ref. [44], Copyright 2019 Springer Nature; (g–i) Ref. [45], Copyright 2016 Springer Nature.

temperature of monolayer graphene can be reduced to 800 °C using PMMA and PS as precursors [37]. The growth of graphene can still be achieved when the temperature is as low as 400 °C, while the quality degrades owing to the residual disordered hydrocarbon. PS was also used to prepare monolayer and few layers of graphene via coating on the bulk stainless steel sheets and alloy nanofibers at the temperature below 400 °C, significantly improving the resistance to corrosion [52]. Except for directly acting as the carbon source, PMMA was reported to be used as a matrix host to introduce additional carbon sources to improve the quality of graphene [53]. High-quality monolayer graphene was obtained by using chlorobenzene as the carbon source at low temperatures of 180 °C. When the temperature raised to 400 °C, the disordered multilayered graphene film was obtained, where the decomposition of PMMA resulted in a high carbon concentration.

Another kind of carbon precursor with a carbon skeleton structure is the metal–organic frameworks (MOFs), which is not only carbon source but also metal catalyst. By varying the metal ions/clusters and organic linkers, MOFs with different structures can be synthesized. There have been many researches focusing on the fabrication of sp^2 carbon nanomaterials from MOFs [56–59]. N-doped CNTs (N-CNTs) with excellent electrocatalytic activity was prepared via the high-temperature pyrolysis of zeolitic imidazolate frameworks (ZIFs) in the presence of H_2 above 600 °C [57]. Further, CNTs with various oriented assembled architectures and heteroatom doping were successfully obtained by modulating the corresponding MOFs through a low-temperature (430 °C) pyrolysis process [58]. During the pyrolysis process, the metal ions/clusters were firstly reduced into metal nanocatalysts in the atmosphere of Ar. Then these nanocatalysts further catalyzed the residual organic units into N-CNTs. Fe, Co and Ni catalysts can be obtained by the pyrolysis process, which have a high catalytic activity in the synthesis of N-CNTs. Simultaneously, there are rich hexatomic or N-heterocyclic carbon rings in organic ligands in MOFs, directly acting as the basic units of CNTs to reduce the energy barrier of the cyclization, leading to the formation of CNTs at a lower temperature. However, not all the MOFs are capable of synthesizing CNTs by the pyrolysis reaction. Selecting MOFs with rich hexatomic or N-heterocyclic carbon rings from organic ligands and nanocatalysts can effectively prepare CNTs at the low temperature. Using MOFs to prepare CNTs and its complexes with different architectures broadens their application in the energy storage and conversion.

3. Catalyst design to reduce the energy barrier of the reaction

Catalysts play an important role in the growth of sp^2 carbon nanomaterials. Choosing different catalysts is capable to change the reactivity, reduce the reaction barrier and meanwhile tune the reaction path and selectivity towards precursors. Up to now, many transition metal and noble metal catalysts have been used to promote the decomposition of carbon sources and the later nucleation and growth, including Ni [17,60], Cu [25,61], Fe [62,63], Co [64,65] and Pt [66,67]. In the initial stage, precursor molecules can be decomposed into carbon radicals on the surface of the catalyst, then diffuse over the surface of the catalyst or dissolve into the catalyst. When the amount of carbon radicals increases to a critical concentration, they would agglomerate with each other to form sp^2 bond, thus forming crystal nuclei on the surface of the catalyst. Finally, the continuously supplied carbon radicals are connected to the formed crystal nuclei and further grow into sp^2 carbon nanomaterials. As the "container" of the whole reaction process, different catalysts exhibit various growth behaviors, including surface self-limitation growth and precipitation on the surface, which primarily depends on the carbon solubility of the metal catalysts. Therefore, the composition and physical state of the catalyst can be adjusted to prepare the sp^2 carbon nanomaterials at a lower temperature.

3.1. The composition design of catalyst

Generally, graphene films could be successfully synthesized by using Cu and Ni as catalysts [25,60,68]. Due to the low catalytic activity of Cu, the growth temperature is relatively high (over 1000 °C) to obtain high-quality graphene. In the meantime, the low solubility of carbon in Cu would lead to monolayer graphene by the self-limiting surface reaction. At lower temperature, Co, Ni and Fe possess higher catalytic activity than Cu for the decomposition of carbon source, whereas the high solubility of carbon in these catalysts leads to the formation of multilayer graphene. Therefore, designing multi-component alloy catalysts is an effective strategy to overcome the shortcoming of single-component metal catalyst and reduce the growth temperature. Due to the synergy effect of the two kinds of metal catalysts, the catalytic activity can be improved at low temperature, and the reaction path can be changed by adjusting the solubility of carbon. On one hand, adding metal with high activity into the metal with low carbon solubility can reduce the growth temperature. Cu-Ni alloy has been widely used as a catalyst for growing graphene films [69–71]. Adding a small amount of Ni into Cu would enhance the catalytic activity with the maintaining of low carbon solubility to obtain uniform monolayer graphene. It was reported that monolayer graphene was obtained on Cu-Ni alloys substrate at 600 °C when the compositions of Ni was less than 20 at.% (Fig. 4a) [72]. According to the experiment results and DFT calculation, the addition of Ni can facilitate the adsorption and decomposition of C_2H_2, thereby improving the catalytic activity. On the other hand, low-temperature growth of high-quality graphene can be achieved by adding the metal with low carbon solubility into the catalyst with high activity. For example, Au-Ni alloy was used to synthesize graphene film at 450 °C, in which the monolayer coverage reaches 74% [73]. The effect of the inactive Au decorated on the majority of the highly active Ni surface sites was to lower the solubility of carbon and suppress the nucleation of carbon species at step edges or defects. Compared with the pure Ni, the graphene nucleation density on Au-Ni alloy decreased and the domain size increased to 20 μm at 450 °C, as can be seen in Fig. 4b. In the same way, Cu-Co alloy was also developed for the growth of uniform, high-quality graphene at 750 °C [74]. As shown in Fig. 4c, Cu was decorated on the highly reactive sites of Co to reduce the hydrocarbon dissociation rate and carbon solubility. Compared with Co, a continuous monolayer graphene film without any multilayer region was observed on Cu-Co alloy,

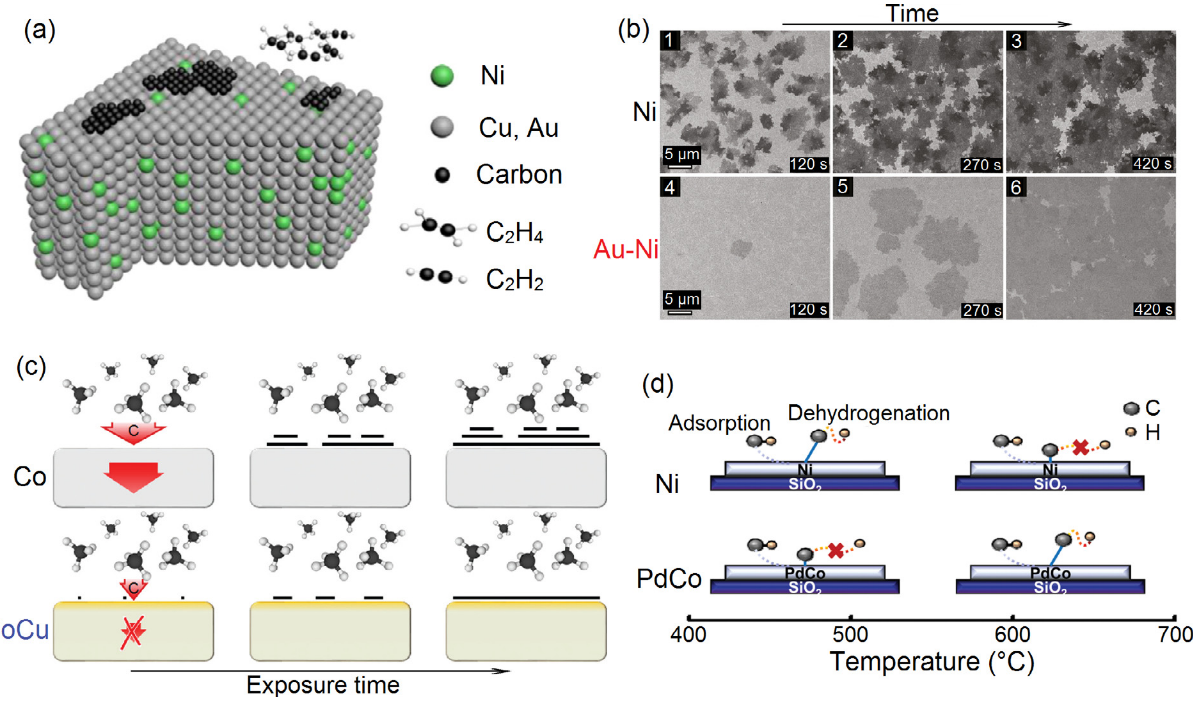


Fig. 4. (Color online) Graphene growth on the metal catalyst with the composition design at low temperature. (a) Schematic illustration showing the growth process of monolayer graphene on Ni-diluted solid solution of Cu-Ni alloy thin film. (b) SEM images of graphene synthesized from acetylene by low-pressures CVD at 450 °C for different growth time of 120–420 s on Ni (1, 2, 3) and Au-Ni catalyst (4, 5, 6), respectively. (c) Schematic illustration of the graphene growth mechanism on Co and Co-Cu catalysts. (d) Schematic illustration of different gas reactions on Ni and Pd-Co alloy surface involving adsorption, dehydrogenation, and desorption. Reproduced with permission from (a) Ref. [72], Copyright 2013 Elsevier; (b) Ref. [73], Copyright 2011 ACS; (c) Ref. [74], Copyright 2017 RSC; (d) Ref. [75] Copyright 2011 American Institute of Physics Publishing.

demonstrating the growth of high-quality graphene at low temperature. Besides, noble metal alloy catalysts were also used to reduce the growth temperature of graphene. Few-layer graphene films were formed on Pd-Co alloy catalyst at a temperature as low as 400 °C (Fig. 4d) [75]. Owing to the reduction of the density of states (DOS) in d-electron at the Fermi level, the alloy of Pd and other metals (Co, Ni, Cr) revealed better catalytic performance than the pure Pd [76,77]. Pd-Co alloy catalyst was more effective for dehydrogenation at a lower temperature below 500 °C. Later, the decomposed carbon would be incorporated into Pd-Co alloy to form nanoscale aggregates, resulting in the growth of the graphene at low temperature.

3.2. The physical state design of catalyst

In addition to changing the solubility and decomposition efficiency of carbon sources by designing the composition of the catalyst, liquid metal was also added into the metal catalyst to change its physical state from the solid to liquid to promote the carbon diffusion for lowering the synthesis temperature. Ga, as a liquid metal, has a long melting range from 29.8 to 2403 °C, and it can lower the melting point of the transition metal catalyst by forming the alloy. Large-area, uniform and monolayer graphene was prepared on a homogeneous liquid Ga-Cu alloy at 800 °C (Fig. 5a) [78]. The Ga-Cu alloy sustained its liquid state at 800 °C, which serves as a container to dissolve carbon atoms, facilitating the diffusion rate of carbon species at the same time. The rapid diffusion of carbon species on liquid surface contributed to the growth of uniform graphene film with low defect density at a reduced temperature. The added liquid metal also forms carbon-containing compounds during the growth of graphene. Strict monolayer graphene with 100% surface coverage was successfully synthesized by Ga-Ni alloy at 600 °C [79]. During the growth of graphene, Ga-Ni alloy formed an anti-perovskite layer ($GaCNi_3$) with carbon species, which shielded and blocked the precipitation of excess dissolved carbon fragments from the catalyst during the cooling process (Fig. 5b). Same as mentioned above, the molten surface of Ga-Ni alloy favored a higher diffusion rate of absorbed carbon species.

Apart from alloying with other metals, the liquid metal itself also has high catalytic activity for graphitization. It is reported that nanographene has been synthesized by using CBr_4 as the precursor and Ga as the catalyst at a temperature of 200 °C [80]. The efficient precipitation of carbon atoms toward the surface at such a low temperature indicated the high catalytic efficiency of Ga. It is worth mentioning that Ga is in liquid state at room temperature, which enhances the mass transport of carbon atoms and improves graphene growth kinetics. A near-room-temperature (50–100 °C) growth of graphene was successfully achieved by using Ga as an efficient catalyst under CH_4 atmosphere [81]. In this strategy, the graphene nucleus islands were pre-formed at high temperature and then the carbon atoms attached to the island edges to form graphene on sapphire and polycarbonate at low temperature (Fig. 5c). The main advantage of using a molten Ga catalyst was the enhanced absorption of CH_4 on Ga at a lower temperature, which led to a surprisingly low reaction barrier of ~0.16 eV below 300 °C. The faster growth kinetics due to low reaction barrier and the preset graphene nuclei facilitate the direct synthesis of graphene on many kinds of substrates at 50–100 °C, which significantly promotes the integration of graphene in electronic devices.

4. Non-thermal energy supply for the pyrolysis activation of the precursor

During the first step in the synthesis of sp^2 carbon nanomaterials, the required thermal energy can be replaced by introducing energy supply in other types to facilitate the ionization, excitation and decomposition of carbon source, thereby reducing the temperature required for the entire reaction. The energy-assisted approaches contain microwave pyrolysis [82,83], plasma assistance

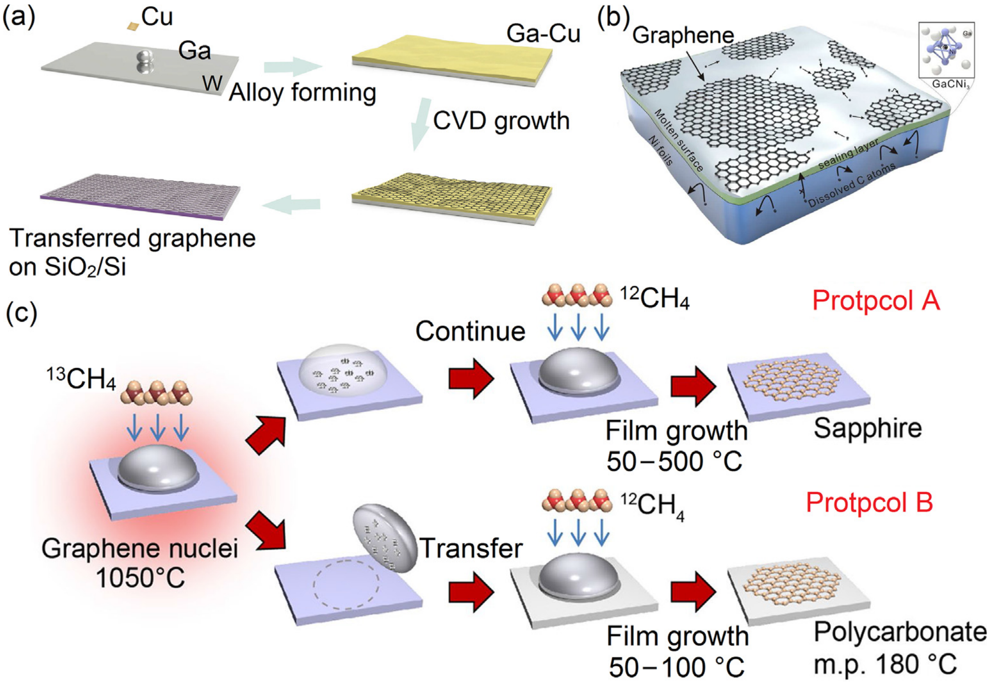


Fig. 5. (Color online) Graphene growth on liquid metal catalyst at low temperature. (a) Schematic illustration of graphene growth over liquid Ga-Cu catalyst. (b) Schematic illustration of graphene growth over liquid Ga-Ni catalyst, which demonstrates the formation of the stable and intense compound $GaCNi_3$ and suppresses the upward precipitation of the excess carbon atoms. (c) Schematic illustration of graphene growth over liquid metal at near room temperature, including two routes (A, B) for different substrates. Reproduced with permission from (a) Ref. [78], Copyright 2016 Elsevier; (b) Ref. [79], Copyright 2015 ACS; (c) Ref. [81], Copyright 2017 Springer Nature.

[84–87], and so on. These approaches are usually combined with CVD, which can deposit activated radical molecules onto the substrate by the vapor phase transport.

4.1. Microwave assistance

Microwave pyrolysis was developed on the base of combining the research of traditional pyrolysis with microwave technology. The microwave, as a high-frequency electromagnetic wave with a frequency between 300 MHz and 300 GHz, is capable of penetrating the whole organic matter so that the energy is quickly transmitted to the functional group of the reactant. In the process of growing sp^2 carbon nanomaterials, the energy of the microwave replaces part of the thermal energy to decompose the precursor at a lower temperature. Moreover, microwave has the advantages of fast speed, immediacy and low cost. As a consequence, microwave pyrolysis is recognized as an attractive alternative for the low-temperature synthesis of sp^2 carbon nanomaterials. Aligned CNTs with high quality were synthesized at 550–650 °C by the microwave pyrolysis of acetylene in N_2 atmosphere, which was catalyzed by ferrocene [88]. The prepared aligned CNTs were densely packed, and some Fe_3C nanoparticles were encapsulated in all parts of CNTs. Apart from gaseous precursors, some macromolecular polysaccharides can also be decomposed by the microwave to synthesize CNTs. The formation of a large number of CNTs on the surface of cellulose bio-chars was demonstrated at 600 °C [82]. The volatile matter derived from cellulose was rich in monosaccharides, including D-glucopyranose and glucopyranose, which can act as carbon sources for the synthesis of CNTs. During the formation of CNTs, the volatiles that were rich in the monosaccharides and hydrocarbons were self-extruded, followed by the condensation and re-solidification of the volatiles on the softened cellulose particles at elevated temperatures. This study may pave the way for the development of the low-temperature production of large-scale CNTs.

4.2. Plasma assistance

Another effective means to lower the growth temperature is plasma-assisted deposition. It aims to use microwave or radiofrequency to create a gas containing the atoms of the desired material, and then form a local plasma. Afterwards, the electrons moving at high speed in the plasma impinge on the neutral reactive gas molecules, making the precursor molecules to become fragments or reactive radicals. In the end, the reactive radicals diffuse into the reactor and move along on the catalytic substrate to realize the nucleation and growth of the materials. The as-formed plasma is highly chemically active, which is easy to react. The high-energy electrons, excited-state molecules, atoms and free radicals in the plasma can promote the decomposition of gaseous carbon sources at a low temperature. Therefore, sp^2 carbon nanomaterials can be prepared at a very low temperature by introducing a plasma in CVD. As early as in 1998, the pioneering work was reported that aligned CNTs have been synthesized over an area up to several square centimeters on Ni-coated glass below 666 °C by plasma-enhanced hot filament CVD [28]. C_2H_2 was used as the carbon source and NH_3 was used as the catalyst and dilution gas. CNTs with controllable diameters from 20 to 400 nm and lengths from 0.1 to 50 μm were obtained in this way. Since then, the synthesis of aligned CNTs at low temperature by different plasma-enhanced CVD (PECVD) methods has been extensively studied. Vertically aligned CNTs were prepared using C_2H_2 as the carbon source and Ni as the catalyst at the temperatures as low as 120 °C by PECVD [89]. It was found that the activation energy was 0.23 eV, which was much lower than the values of 1.5 and 1.21 eV in the reported thermal growth methods [90]. And the activation energy (0.23 eV) was similar to the energy of the surface diffusion of C atoms on polycrystalline Ni (0.3 eV) [91], which demonstrated that the diffusion of C atoms on the catalyst surface was the rate-determining step at low temperature. The effect of the plasma was to accelerate the decomposition of C_2H_2, and etch the amorphous carbon deposited on top of the Ni particles, thereby providing a steady supply of carbon atoms at the top surface of the Ni particles. Then carbon atoms adsorbed at the top surface of the Ni particles diffused along the surface, finally segregated at the bottom of the particles, forming graphitic planes. Later, researchers reported a low-temperature growth of SWNTs by water plasma CVD [85]. Water plasma strategy lowered the growth temperature to 450 °C, and SWNTs were purely and densely grown without MWNTs. The water plasma with a weak power (15 W) acted as an oxidant which removed carbonaceous impurities and disordered carbons, resulting in the growth of SWNTs with good crystallinity.

Besides CNTs, graphene was also successfully synthesized by PECVD at low temperature. For example, graphene was prepared by decomposing CH_4 at a Cu substrate with the temperature of 500 °C through PECVD [92]. Unfortunately, the active fragments produced by the plasma would make the graphene continue to grow on the as-formed graphene layer, resulting in the formation of multilayer graphene. At the same time, ion bombardment also influenced the growth of graphene and created defects in the obtained graphene. Therefore, it was necessary to add an etchant or adjust plasma initial point to improve the quality of graphene. Then, high-quality graphene films were synthesized by PECVD on Cu foil by using CH_4 and H_2 mixture at a low temperature of 600 °C (Fig. 6a) [86]. As can be seen in Fig. 6b, the intensity of the D band decreases with the increase of H_2 flow rate, indicating that H_2 as a reducing agent can etch excess carbon impurities to reduce the defects. In the meantime, the increased distance between the plasma and the substrate was effective to reduce the defect in graphene. Therefore, high-quality graphene film could be obtained under a high concentration of H_2. Recently, a forced convection (FC)-PECVD method for the synthesis of graphene has been reported, in which the distribution of reactive radicals reaching the surface of the substrate can be controlled by using a specially designed blown plasma source [87]. Monolayer graphene growing with few defects was achieved even at low temperature (<400 °C). In the PECVD system mentioned above, the gas passing through the gas inlet diffused in all directions in the vacuum chamber. In FC-PECVD system, the gas source introduced into the chamber was directly blown onto the Cu surface by the nozzle (Fig. 6c). The plasma and radicals were generated primarily in and around the nozzle by the electric fields of the microwaves, and then were forcibly transported to the Cu surface by the blowing gases. As shown in Fig. 6d, the intensity of D band was weak, which indicated the high quality of graphene. In this study, the ion-neutral collision occurred on the sheath region instead of the substrate, which avoided the effects of collisions on the preparation of graphene. This method overcomes the limitations of traditional PECVD and provides a new idea for further promoting the low-temperature synthesis of graphene.

The PECVD was also used to grow graphene at low temperature on the insulating substrate. The production of micrometer-scale graphene crystals was directly conducted on SiO_2/Si substrates by PECVD at the temperature as low as 400 °C [93]. The H_2 plasma was also used as an etchant to remove the defects generated at the edges and keep the edges atomically smooth and active during the whole process of graphene crystal growth (Fig. 6e). In this way, the synthesis of the catalyst-free centimeter-level continuous graphene film is expected to realize on various substrates, such as sapphire, highly oriented pyrolytic graphite and hexagonal boron nitride (h-BN). The wafer-scale uniform graphene films were also

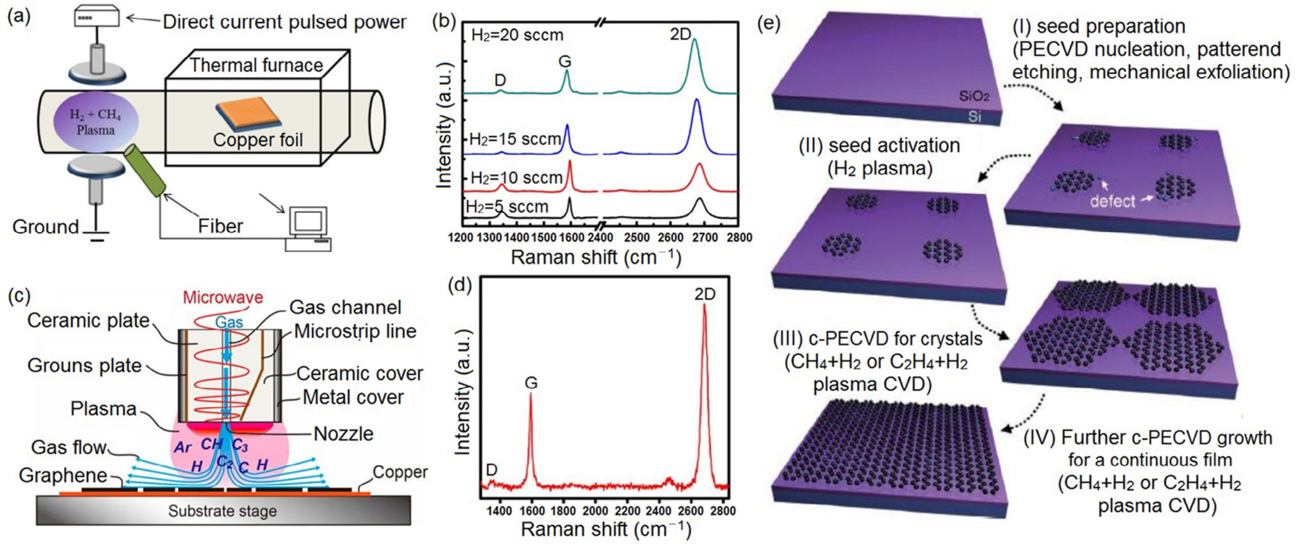


Fig. 6. (Color online) Plasma assisted growth of graphene at low temperature. (a) Schematic illustration of plasma-assisted thermal CVD system. (b) Raman spectra of the as-obtained graphene films transferred onto SiO_2/Si substrate. (c) Schematic illustration of the mechanisms of FC-PECVD using a blowing-type microwave-excited plasma. (d) Raman spectrum for the as-obtained graphene film transferred onto SiO_2/Si substrate. (e) Schematic illustration of the PECVD procedure of graphene growth on SiO_2/Si. Reproduced with permission from (a, b) Ref. [86], Copyright 2013 Springer; (c, d) Ref. [87], Copyright 2019 ACS; (e) Ref. [93], Copyright 2013 Wiley.

directly synthesized on SiO_2 substrates at a low temperature of around 550 °C, using a remote PECVD system with CH_4 as the carbon source [94]. The nanographene islands with high coverage exhibited exponential tunneling behavior. At the same time, the nanographene islands with low coverage exhibited linear conduction behavior of metal. Moreover, N-doped graphene films were prepared on SiO_2/Si substrate at 435–650 °C by using C_2H_2 as the carbon source in PECVD [95]. The NH_3 plasma was used as both N and H source, which generated N-containing species for the substitutional incorporation of N atoms into the graphene lattice and produced active H atoms to remove the edge defects. Reducing the temperature by plasma enhancement provides a feasible way to directly grow graphene on the dielectric substrate of electronic circuits. However, some defects and grain boundaries of graphene caused by plasma cannot be completely avoided, which limits its application in the high-performance electrical devices.

5. Summary and outlook

The low-temperature synthesis of high-quality sp^2 carbon nanomaterials (graphene and CNTs) has attracted extensive attentions in recent years. In this review, we have discussed recent advances in the low-temperature synthesis approaches, including selecting precursors with high reactivity, adjusting the component and physical state of catalysts and offering additional energy for the pre-decomposition of precursors. Table 1 summarizes these strategies and the specific growth parameters of low-temperature synthesis in the mentioned studies. Graphene and CNTs can be obtained at 200–400 °C by using precursors with low decomposition energy for radical coupling reactions, for example, carbon halides. Although the growth temperature is greatly reduced, the use of carbon halide precursor may cause the doping of halogen atoms and the forming of structural defects. At the same time, the choice of precursor containing aromatic structure or carbon chain skeleton structure can also produce graphene and CNTs at low temperature. The surface-mediated synthesis is one of the most promising methods toward low-temperature growth of GNRs, which can precisely control the length, width and edge structure. Unfortunately, the low conversion rate and low yield limit its large-scale industrial application. Precursors with carbon chain skeletons like MOFs can be used to prepare sp^2 carbon nanomaterials in large quantities, increasing their applications in energy storage and conversion. The combination of catalysts with different carbon solubility and catalytic activity is also an effective strategy to lower the activation energy of the reaction, thus reducing the growth temperature. High-quality and large-area graphene film can be obtained, which facilitates its applications in electronic devices. In addition, the use of liquid metal catalysts helps to solve problems including breakage and wrinkles during the transfer process by an innovative sliding transfer method, and ensures the high quality of graphene in the whole growth and transfer process [96]. Except for the thermal energy, the introduction of additional energy can effectively pre-decompose the carbon source, such as microwave energy, plasma energy and electric field energy. Based on this way, the temperature at the growth region is reduced below 500 °C without the strict requirement of the growth substrate. As the temperature decreases, sp^2 carbon nanomaterials are expected to be synthesized on any substrate by PECVD method without the limitation of the temperature tolerance, such as insulating substrate or polymer film, improving compatibility with silicon-based modern electronics and flexible electronics.

However, in order to make further advances in the practical applications, there are still many challenges to be faced with. At the low temperature, the arrangement and incorporation of precursors may be disordered and limited by their geometric structure, resulting in the inevitable formation of structural defects. In the meantime, precursors cannot be decomposed completely at low temperature, leading to the formation of disordered hydrocarbon structures on the surface of obtained materials. Furthermore, the diffusion of carbon atom is also limited at low temperature, which also contributes to a large defect density. Therefore, the as-synthesized sp^2 carbon nanomaterials at low temperature are likely to exhibit poor crystallinity and uniformity. Thence, further effort can be focused on seeking for suitable precursor with a specific structure and a low decomposition energy. Precisely controlling the reaction path is also a promising direction for low-temperature synthesis. It has been reported that room-temperature growth of graphene can be achieved based on the Ni substrate with excellent carbon solubility, while the yielded graphene shows poor uniformity [97]. Therefore, a promising effort goal can be achieved with

Table 1
Strategies for the low-temperature synthesis of sp^2 carbon nanomaterials.

Synthesis strategy	Synthesis strategy	Synthesis method	Synthesis temperature (°C)	Carbon source	Catalyst or substrate	Product	Refs.
Carbon source selection with high reactivity	Carbon source with active halogen group	Liquid phase reaction	200	C_2Cl_4	Fe/Au	MWCNTs	[32]
		Liquid phase reaction	350	C_6Cl_6	Co/Ni	MWCNTs	[30]
		Supercritical fluid reaction	175	CCl_4	Fe	MWCNTs	[31]
		CVD	220–250	C_6Br_6	Cu(1 1 1)	Monolayer graphene	[33]
	Carbon source with primitive aromatic structure	CVD	300	C_6H_6	Cu	Monolayer graphene	[37]
		CVD	300–600	$C_{10}H_8$	Cu	Monolayer graphene	[38]
		CVD	400–600	$C_{16}H_{10}$, $C_{34}H_{24}$	Cu	Monolayer graphene	[40]
		CVD	400	$C_{18}H_{14}$	Cu	Monolayer graphene	[31]
		CVD	300	C_6H_6, $C_{18}H_{14}$	Cu	Monolayer graphene	[32]
		Liquid phase reaction	80	Benzonaphthosilole and $C_{14}H_{10}$	–	GNRs	[44]
		Surface-assisted reaction	400–440	$C_{28}H_{16}Br_2$, $C_{42}H_{26}Br_2$	Au(1 1 1)	GNRs	[42]
		Surface-assisted reaction	201.85–351.85	$C_{22}H_{10}Br_2$	Au(1 1 1)	GNRs	[45]
		Surface-assisted reaction	400	$C_{28}H_{16}Br_2$	Au(1 1 1)	GNRs	[46]
	Carbon source with carbon chain skeleton	CVD	400–800	PMMA and PS	Cu	Monolayer graphene	[37]
		CVD	180–400	PMMA, C_6H_5Cl	Cu	Graphene	[53]
		Pyrolysis	430	ZIF-67	Co	CNTs	[58]
Catalyst design to reduce the energy barrier of the reaction	Composition design of catalyst	CVD	600	C_2H_2	Cu-Ni	Monolayer graphene	[72]
		CVD	450	C_2H_2	Au-Ni	Monolayer graphene	[73]
		CVD	750	CH_4	Cu-Co	Monolayer graphene	[74]
		RF-PECVD	400	C_2H_4	Pd-Co	Few-layer graphene	[75]
	Physical state design of catalyst	CVD	800	CH_4	Ga-Cu	Monolayer graphene	[78]
		CVD	600	CH_4	Ga-Ni	Monolayer graphene	[79]
		CVD	200	CBr_4	Ga	Nanographene	[80]
		CVD	50–100	CH_4	Ga	Monolayer graphene	[81]
Non-thermal energy supply for the pyrolysis activation of the precursor	Microwave assistance	Microwave CVD	550–650	C_2H_2	Ferrocene	Aligned CNTs	[88]
		Microwave CVD	600	Cellulose	Ni	CNTs	[82]
	Plasma assistance	PECVD	<666	C_2H_2	Ni	Aligned CNTs	[28]
		dc PECVD	120	C_2H_2	Ni	Vertically aligned CNTs	[89]
		Water plasma CVD	450	CH_4	Fe	SWNTs	[85]
		PECVD	500	CH_4	Cu	Graphene	[92]
		PECVD	600	CH_4	Cu	Graphene	[86]
		FC-PECVD	<400	CH_4	Cu	Monolayer graphene	[87]
		PECVD	400	CH_4	SiO_2/Si or sapphire	Graphene	[93]
		Remote PECVD	550	CH_4	SiO_2	Nanographene	[94]
		PECVD	435–650	C_2H_2 and NH_3	SiO_2/Si, Al_2O_3, h-BN, mica, HOPG	N-doped graphene	[95]

the accurate control of the carbon precipitation toward the surface. Liquid metal, as an emerging candidate, also exhibits enormous potential in the synthesis of sp^2 carbon nanomaterials at low temperature. It can be used as the “container” of carbon precursors due to the abundant vacancies in its bulk. It has been reported that the phase transition of liquid metal helps to facilitate the self-limited growth of graphene on the surface. Once presetting decomposed carbon atoms in the liquid metal bulk, the uniform layer graphene may be obtained via the liquid metal catalyst. In spite of the quality and uniformity maintenance in the growth process, the in-growth or post-growth impairment of sp^2 carbon nanomaterials can also work well for achieving the goal. Recently, a few reports have shown that the introduction of CO_2, water vapor and static electricity can help with the removal of amorphous carbon on the surface of sp^2 carbon nanomaterials [98–100]. Another challenge or opportunity is a better understanding of growth mechanism of sp^2 carbon nanomaterials at low temperature. Emerging *in-situ* characterization techniques, such as *in-situ* TEM, *in-situ* scanning tunneling microscopy (STM) and *in-situ* Raman spectroscopy, can be used to explore the elementary reaction processes at a relatively low temperature. The establishment of the growth mechanism can enrich the fundamental research of graphene and CNTs and promote the growth parameter design for obtaining high-quality materials at the low temperature.

In addition to sp^2 carbon nanomaterials, the low-temperature synthesis of other nanomaterials, especially for the various emerging 2D materials, is also urgently to be developed. For example, 2D transition metal chalcogenides (TMDs) exhibit a variety of electronic properties, ranging from semiconducting to superconducting due to their abundant elemental composition and crystal structure. The rich experience in the low-temperature synthesis of sp^2 carbon nanomaterials can be implanted into the synthesis of TMDs and other 2D materials. It is favorable for lowering the growth temperature to choose appropriate precursors with low melting point and high chemical reactivity with chalcogen source. The pre-activation of the precursors assisted by the plasma and microwave is also promising for the low-temperature synthesis. The low-temperature growth of high-quality nanomaterials in a controllable way has achieved many progresses toward the industrial application. We believe such a timely review will inject new blood for the future industrial production of nanomaterials and thus promote their applications in the various fields.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21673161), the Sino-German Center for Research Promotion (1400), and the Postdoctoral Innovation Talent Support Program of China (BX20180224).

Author contributions

Lei Fu conceived the review topic; Yu Ding charted the figures; Yu Ding wrote the original draft in consultation with all the other authors; Mengqi Zeng and Lei Fu reviewed and edited the draft.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2019.10.009.

References

[1] Novoselov KS, Fal-ko VI, Colombo L, et al. A roadmap for graphene. Nature 2012;490:192–200.
[2] De Volder MF, Tawfick SH, Baughman RH, et al. Carbon nanotubes: present and future commercial applications. Science 2013;339:535–9.
[3] Yang Z, Ren J, Zhang Z, et al. Recent advancement of nanostructured carbon for energy applications. Chem Rev 2015;115:5159–223.
[4] Georgakilas V, Perman JA, Tucek J, et al. Broad family of carbon nanoallotropes: classification, chemistry, and applications of fullerenes, carbon dots, nanotubes, graphene, nanodiamonds, and combined superstructures. Chem Rev 2015;115:4744–822.
[5] Geim AK, Novoselov KS. The rise of graphene. Nat Mater 2007;6:183–91.
[6] Taylor R, Walton DRM. The chemistry of fullerenes. Nature 1993;363:685–93.
[7] Nakamura E, Isobe H. Functionalized fullerenes in water. The first 10 years of their chemistry, biology, and nanoscience. Acc Chem Res 2003;36:807–15.
[8] Echegoyen L, Echegoyen LE. Electrochemistry of fullerenes and their derivatives. Acc Chem Res 1998;31:593–601.
[9] Tasis D, Tagmatarchis N, Bianco A, et al. Chemistry of carbon nanotubes. Chem Rev 2006;106:1105–36.
[10] Dai H. Carbon nanotubes: synthesis, integration, and properties. Acc Chem Res 2002;35:1035–44.
[11] Wang X, Chen L, Wang L, et al. Synthesis of novel nanomaterials and their application in efficient removal of radionuclides. Sci China Chem 2019;62:933–67.
[12] Lee C, Wei X, Kysar JW, et al. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008;321:385–8.
[13] Sander JT, Michel HD, Dai H, et al. Individual single-wall carbon nanotubes as quantum wires. Nature 1999;386:474–7.
[14] Bonaccorso F, Sun Z, Hasan T, et al. Graphene photonics and optoelectronics. Nat Photonics 2010;4:611–22.
[15] Shigeki K, Andrea B, Enrico G, et al. Superlubricity of graphene nanoribbons on gold surfaces. Science 2016;351:957–61.
[16] Liu Y, François G, Zheng Q. The high-speed sliding friction of graphene and novel routes to persistent superlubricity. Sci Rep 2014;4:4875.
[17] Kim K, Zhao Y, Jang H, et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature 2009;457:706–10.
[18] Raccichini R, Varzi A, Passerini S, et al. The role of graphene for electrochemical energy storage. Nat Mater 2015;14:271–9.
[19] Son J, Son M, Moon K, et al. Sub-10 nm graphene nanoribbon array field-effect transistors fabricated by block copolymer lithography. Adv Mater 2013;25:4723–8.
[20] Stankovich S, Dikin DA, Dommett GHB, et al. Graphene-based composite materials. Nature 2006;442:282–6.
[21] Ebbesen TW, Ajayan PM. Large-scale synthesis of carbon nanotubes. Nature 1992;358:220–2.
[22] Thess A, Lee R, Nikolaev P, et al. Crystalline ropes of metallic carbon nanotubes. Science 1996;273:483–7.
[23] Amelinckx S, Zhang X, Bernaerts D, et al. A formation mechanism for catalytically grown helix-shaped graphite nanotubes. Science 1994;265:635–9.
[24] Emtsev KV, Bostwick A, Horn K, et al. Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. Nat Mater 2009;8:203–7.
[25] Li X, Cai W, An J, et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. Science 2009;324:1312–4.
[26] Cheung CL, Kurtz A, Park H, et al. Diameter-controlled synthesis of carbon nanotubes. J Phys Chem B 2002;106:2429–33.
[27] Kong J, Cassell AM, Dai H. Chemical vapor deposition of methane for single-walled carbon nanotubes. Chem Phys Lett 1998;292:567–74.
[28] Ren Z, Huang Z, Xu J, et al. Synthesis of large arrays of well-aligned carbon nanotubes on glass. Science 1998;282:1105–7.
[29] Nandamuri G, Roumimov S, Solanki R. Chemical vapor deposition of graphene films. Nanotechnology 2010;21:145604.
[30] Jiang Y, Wu Y, Zhang S, et al. A catalytic-assembly solvothermal route to multiwall carbon nanotubes at a moderate temperature. J Am Chem Soc 2000;122:123834–5.
[31] Vohs JK, Brege JJ, Raymond JE, et al. Low-temperature growth of carbon nanotubes from the catalytic decomposition of carbon tetrachloride. J Am Chem Soc 2004;126:9936–7.
[32] Wang X, Lu J, Xie Y, et al. A novel route to multiwalled carbon nanotubes and carbon nanorods at low temperature. J Phys Chem B 2002;106:933–7.
[33] Jiang L, Niu T, Lu X, et al. Low-temperature, bottom-up synthesis of graphene via a radical-coupling reaction. J Am Chem Soc 2013;135:9050–4.
[34] Gharagozloo-Hubmann K, Müller NS, Giersig M, et al. Requirement on aromatic precursor for graphene formation. J Phys Chem C 2016;120:9821–5.
[35] Choi J, Li Z, Cui P, et al. Drastic reduction in the growth temperature of graphene on copper via enhanced London dispersion force. Sci Rep 2013;3:1925.
[36] Jeong SH, Ko J, Park J, et al. A sonochemical route to single-walled carbon nanotubes under ambient. J Am Chem Soc 2004;126:15982–3.
[37] Li Z, Wu P, Wang C, et al. Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources. ACS Nano 2011;5:3385–90.
[38] Wu T, Ding G, Shen H, et al. Continuous graphene films synthesized at low temperatures by introducing coronene as nucleation seeds. Nanoscale 2013;5:5456–61.
[39] Reed D, Kass S. Experimental determination of the α and β C-H bond dissociation energies in naphthalene. J Mass Spectrom 2000;35:534–9.
[40] Lee E, Lee H, Jo S, et al. Heterogeneous solid carbon source-assisted growth of high-quality graphene via CVD at low temperatures. Adv Funct Mater 2016;26:562–8.

[41] Yang X, Dou X, Rouhanipour A, et al. Two-dimensional graphene nanoribbons. J Am Chem Soc 2008;130:4216–7.

[42] Yang W, Lucotti A, Tommasini M, et al. Bottom-up synthesis of Soluble and narrow graphene nanoribbons using alkyne benzannulations. J Am Chem Soc 2016;138:9137–44.

[43] Narita A, Feng X, Hernandez Y, et al. Synthesis of structurally well-defined and liquid-phase-processable graphene nanoribbons. Nat Chem 2014;6:126–32.

[44] Yano Y, Mitoma N, Matsushima K, et al. Living annulative π-extension polymerization for graphene nanoribbon synthesis. Nature 2019;571:387–92.

[45] Ruffieux P, Wang S, Yang B, et al. On-surface synthesis of graphene nanoribbons with zigzag edge topology. Nature 2016;531:489–92.

[46] Cai J, Ruffieux P, Jaafar R, et al. Atomically precise bottom-up fabrication of graphene nanoribbons. Nature 2010;466:470–3.

[47] Talirz L, Sode H, Dumslaff T, et al. On-surface synthesis and characterization of 9-atom wide armchair graphene nanoribbons. ACS Nano 2017;11:1380–8.

[48] Basagni A, Sedona F, Pignedoli CA, et al. Molecules-oligomers-nanowires-graphene nanoribbons: a bottom-up stepwise on-surface covalent synthesis preserving long-range order. J Am Chem Soc 2015;137:1802–8.

[49] Moreno C, Vilas-Varela M, Kretz B, et al. Bottom-up synthesis ofmultifunctional nanoporous graphene. Science 2018;360:199–203.

[50] Han W, Kawakami RK, Gmitra M, et al. Graphene spintronics. Nat Nanotechnol 2014;9:794–807.

[51] Sun Z, Yan Z, Yao J, et al. Growth of graphene from solid carbon sources. Nature 2010;468:549–52.

[52] Zhu M, Du Z, Yin Z, et al. Low-temperature in situ growth of graphene on metallic substrates and its application in anticorrosion. ACS Appl Mater Interfaces 2016;8:502–10.

[53] Sulaiman K, Ali AY, Elkington D, et al. Matrix assisted low temperature growth of graphene. Carbon 2016;107:325–31.

[54] Zeng W, Li S, Chow W. Review on chemical reactions of burning Poly(methyl methacrylate) PMMA. J Fire Sci 2002;20:401–33.

[55] Luo YR. Comprehensive handbook of chemical bond energies. Boca Raton, FL: CRC Press; 2007. p. 9.

[56] Pachfule P, Shinde D, Majumder M, et al. Fabrication of carbon nanorods and graphene nanoribbons from a metal-organic framework. Nat Chem 2016;8:718–24.

[57] Xia B, Yan Y, Li N, et al. A metal-organic framework-derived bifunctional oxygen electrocatalyst. Nat Energy 2016;1:15006.

[58] Meng J, Niu C, Xu L, et al. General oriented formation of carbon nanotubes from metal-organic frameworks. J Am Chem Soc 2017;139:8212–21.

[59] Ma L, Wang R, Li Y, et al. Apically Co-nanoparticles-wrapped nitrogen-doped carbon nanotubes from a single-source MOF for efficient oxygen reduction. J Mater Chem A 2018;6:24071–7.

[60] Li X, Cai W, Colombo L, et al. Evolution of graphene growth on Ni and Cu by carbon isotope labeling. Nano Lett 2009;9:4268–72.

[61] Zeng M, Wang L, Liu J, et al. Self-assembly of graphene single crystals with uniform size and orientation: the first 2D super-ordered structure. J Am Chem Soc 2016;138:7812–5.

[62] Li W, Xie S, Qian L, et al. Large-scale synthesis of aligned carbon nanotubes. Science 1996;274:1701–3.

[63] Takagi D, Homma Y, Hibino H, et al. Single-walled carbon nanotube growth from highly activated metal nanoparticles. Nano Lett 2006;6:2642–5.

[64] Bethune DS, Kiang CH, de Vries MS, et al. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. Nature 1993;363:605–7.

[65] Ago H, Ito Y, Mizuta N, et al. Epitaxial chemical vapor deposition growth of single-layer graphene over cobalt film crystallized on sapphire. ACS Nano 2010;4:7407–14.

[66] Maruyama T, Kondo H, Ghosh R, et al. Single-walled carbon nanotube synthesis using Pt catalysts under low ethanol pressure via cold-wall chemical vapor deposition in high vacuum. Carbon 2016;96:6–13.

[67] Cushing GW, Johánek V, Navin JK, et al. Graphene growth on Pt(111) by ethylene chemical vapor deposition at surface temperatures near 1000 K. J Phys Chem C 2015;119:4759–68.

[68] Li X, Magnuson CW, Venugopal A, et al. Large-area graphene single crystals grown by low-pressure chemical vapor deposition of methane on copper. J Am Chem Soc 2011;133:2816–9.

[69] Liu X, Fu L, Liu N, et al. Segregation growth of graphene on Cu-Ni alloy for precise layer control. J Phys Chem C 2011;115:11976–82.

[70] Fu Z, Zhang Y, Yang Z. Growth mechanism and controllable synthesis of graphene on Cu-Ni alloy surface in the initial growth stages. Phys Lett A 2015;379:1361–5.

[71] Chen S, Cai W, Piner RD, et al. Synthesis and characterization of large-area graphene and graphite films on commercial Cu-Ni alloy foils. Nano Lett 2011;11:3519–25.

[72] Woo Y, Seo D, Yeon D, et al. Low temperature growth of complete monolayer graphene films on Ni-doped copper and gold catalysts by a self-limiting surface reaction. Carbon 2013;64:315–23.

[73] Weatherup RS, Bayer BC, Blume R, et al. In situ characterization of alloy catalysts for low-temperature graphene growth. Nano Lett 2011;11:4154–60.

[74] Sugime H, D'Arsie L, Esconjauregui S, et al. Low temperature growth of fully covered single-layer graphene using a CoCu catalyst. Nanoscale 2017;9:14467–75.

[75] Kim E, Shin H, Yoon S, et al. Low-temperature graphene growth using epochal catalyst of PdCo alloy. Appl Phys Lett 2011;99:223102.

[76] Savadogo O, Lee K, Oishi K, et al. New palladium alloys catalyst for the oxygen reduction reaction in an acid medium. Electrochem Commun 2004;6:105–9.

[77] Lee K, Savadogo O, Ishihara A, et al. Methanol-tolerant oxygen reduction electrocatalysts based on Pd-3D transition metal alloys for direct methanol fuel cells. J Electrochem Soc 2006;153:A20–4.

[78] Wang J, Chen L, Wu N, et al. Uniform graphene on liquid metal by chemical vapour deposition at reduced temperature. Carbon 2016;96:799–804.

[79] Chen L, Kong Z, Yue S, et al. Growth of uniform monolayer graphene using iron-group metals via the formation of an antiperovskite layer. Chem Mater 2015;27:8230–6.

[80] Wang S, Gong Q, Li Y, et al. A novel semiconductor compatible path for nano-graphene synthesis using CBr 4 precursor and Ga catalyst. Sci Rep 2014;4:4653.

[81] Fujita JI, Hiyama T, Hirukawa A, et al. Near room temperature chemical vapor deposition of graphene with diluted methane and molten gallium catalyst. Sci Rep 2017;7:12371.

[82] Omoriyekomwan JE, Tahmasebi A, Zhang J, et al. Mechanistic study on direct synthesis of carbon nanotubes from cellulose by means of microwave pyrolysis. Energy Convers Manage 2019;192:88–99.

[83] Zhang J, Tahmasebi A, Omoriyekomwan JE, et al. Production of carbon nanotubes on bio-char at low temperature via microwave-assisted CVD using Ni catalyst. Diam Relat Mater 2019;91:98–106.

[84] Boskovic BO, Stolojan V, Khan RU, et al. Large-area synthesis of carbon nanofibres at room temperature. Nat Mater 2002;1:165–8.

[85] Min Y, Bae E, Oh B, et al. Low-temperature growth of single-walled carbon nanotubes by water plasma chemical vapor deposition. J Am Chem Soc 2005;127:12498–9.

[86] Chan S, Chen S, Lin W, et al. Low-temperature synthesis of graphene on Cu using plasma-assisted thermal chemical vapor deposition. Nanoscale Res Lett 2013;8:285.

[87] Kim J, Sakakita H, Itagaki H. Low-temperature graphene growth by forced convection of plasma-excited radicals. Nano Lett 2019;19:739–46.

[88] Fu D, Ma Q, Zeng X, et al. Synthesis and magnetic properties of aligned carbon nanotubes by microwave-assisted pyrolysis of acetylene. Phys E 2013;54:185–90.

[89] Hofmann S, Ducati C, Robertson J, et al. Low-temperature growth of carbon nanotubes by plasma-enhanced chemical vapor deposition. Appl Phys Lett 2003;83:135–7.

[90] Ducati C, Alexandrou I, Chhowalla M, et al. Temperature selective growth of carbon nanotubes by chemical vapor deposition. J Appl Phys 2002;92:3299–303.

[91] Mojica J, Levenson L. Bulk-to-surface precipitation and surface diffusion of carbon on polycrystalline nickel. Surf Sci 1976;59:447–60.

[92] Terasaw T, Saiki K. Growth of graphene on Cu by plasma enhanced chemical vapor deposition. Carbon 2012;50:869–74.

[93] Wei D, Lu Y, Han C, et al. Critical crystal growth of graphene on dielectric substrates at low temperature for electronic devices. Angew Chem Int Ed 2013;52:14121–6.

[94] Yang W, He C, Zhang L, et al. Growth, characterization, and properties of nanographene. Small 2012;8:1429–35.

[95] Wei D, Peng L, Li M, et al. Low temperature critical growth of high quality nitrogen doped graphene on dielectrics by plasma-enhanced chemical vapor deposition. ACS Nano 2015;9:164–71.

[96] Lu W, Zeng M, Li X, et al. Controllable sliding transfer of wafer-size graphene. Adv Sci 2016;3:1600006.

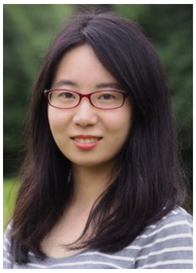
[97] Kwak J, Chu J, Choi J-K, et al. Near room-temperature synthesis of transfer-free graphene films. Nat Commun 2012;3:645.

[98] Zhang J, Jia K, Lin L, et al. Large-area synthesis of super-clean graphene via selective etching of amorphous carbon by carbon dioxide. Angew Chem Int Ed 2019;9:14446–51.

[99] Hata K, Futaba D, Mizuno K, et al. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. Science 2004;306:1362–4.

[100] Wei D, Peng L, Li M, et al. Thickness controlled water vapors assisted growth of multilayer graphene by ambient pressure chemical vapor deposition. J Phys Chem C 2015;119:3079–89.

Yu Ding received her B.S. degree from College of Chemistry and Materials Science, Northwestern University in 2018 and continued her studies as a Master's degree candidate under the supervision of Prof. Lei Fu at the Laboratory of Advanced Nanomaterials (LAN) of Wuhan University. Her current research is focused on the synthesis and applications of two-dimensional materials.



Mengqi Zeng received her Ph.D. degree from the College of Chemistry and Molecular Science, Wuhan University. In 2018, she joined Wuhan University as an Associate Professor. Her current research is focused on the controllable synthesis and self-assembly of two-dimensional materials.

Lei Fu received his B.S. degree in Chemistry from Wuhan University in 2001, and Ph.D. degree from the Institute of Chemistry, Chinese Academy of Sciences in 2006. After that, he worked as a Director's Postdoctoral Fellow at the Los Alamos National Laboratory, Los Alamos, NM (2006–2007). Thereafter, he became an Associate Professor at Peking University. In 2012, he joined Wuhan University as a Full Professor. His current interests of research relate to the controlled growth and novel property exploration of 2D atomic layer thin crystals.