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REVIEW ARTICLE

A brief overview on synthesis and applications of graphene and graphene-based nanomaterials

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ABSTRACT: Graphene is a remarkable material with great potential in many applications due to its chemical and physical properties. In this review we briefly present the recent research progress (2016–2018) in graphene and graphene-based nanomaterials synthesis and discuss the practical aspects of using the materials produced via these methods for different graphene-based applications.

KEYWORDS: graphene synthesis; nanomaterials; graphene-based applications

Contents

1 Introduction

Graphene, one of the carbon allotropes, has received increasing attention from the scientific community since the 2010 Nobel Prize for Physics accorded for "groundbreaking experiments regarding the two-dimensional (2D) material graphene". Since then the number of papers and patents related to graphene and graphene-based nanomaterials synthesis and applications gained a rapid increase and is still growing [1]. Graphene-based nanomaterials revealed unique features and there are highlighted new routes for the easy and proficient preparation of graphene-based nanocomposites with applications in various fields (Fig. 1) [2].

In the recent years many review works discussed the topics of synthesis and applications of graphene and graphene-based nanomaterials [2–6]. To cite just few recent works, Mohan et al. reviewed the latest outcomes in graphene production techniques, properties and their environmental applications, toxicity and safe handling protocols [7]. Wang et al. discussed the recent advances in the synthesis and drug delivery application of graphene-based nanomaterials [8]. The exfoliation of graphene by mechanical, chemical and thermal reduction and chemical vapor deposition (CVD) was also summarized [9]. Another recent review focuses on the most significant papers related to graphene-based electrochemical sensors for the determination of hazardous ions [10]. Wu et al. systematically

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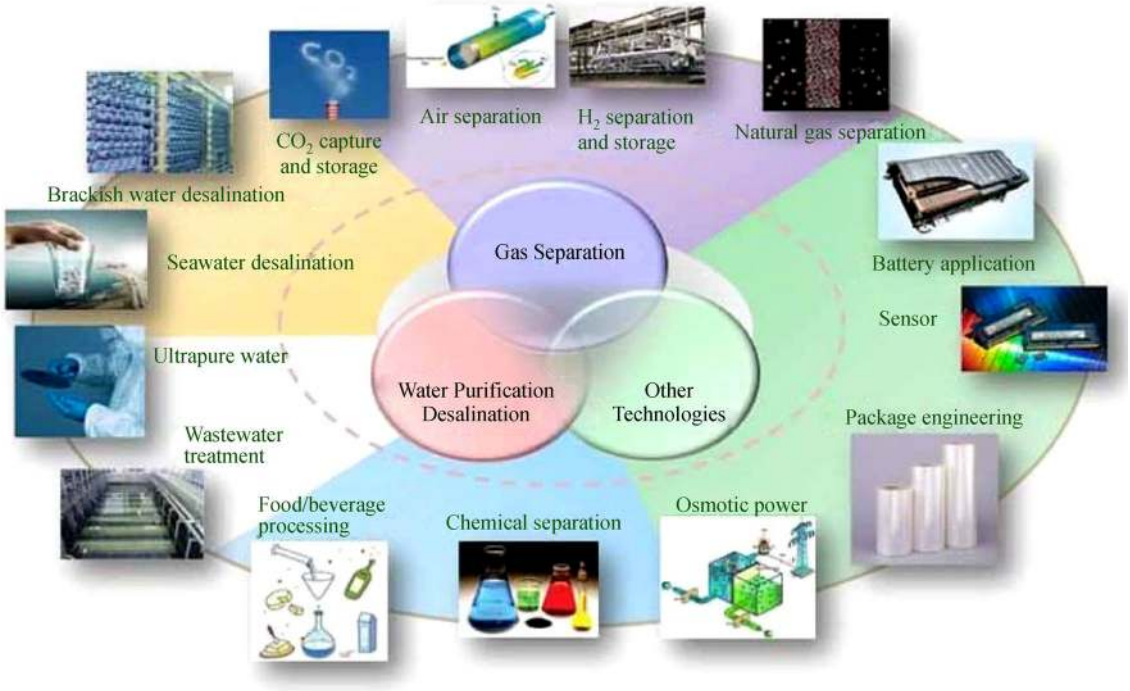

Fig. 1 An overview on the contribution of graphene to various applications and different sectors. Reproduced from Ref. [2] with permission of Elsevier.

reviewed the developments in Raman spectroscopy of graphene-based materials from both fundamental research and practical perspectives [11]. A detailed summary of the different applications of graphene-based nanomaterials in drug delivery, nucleic acid delivery, phototherapy, bio-imaging and theranostics was provided by Roy and Jaiswal [12]. The recent research progresses on the synthesis of nanoporous graphene materials and their applications in different areas were considered [13]. Phiri et al. discussed about the synthesis methods of graphene (particularly from graphite) and some properties and applications in polymer composites [14]. The theoretical insights of graphene growth on various metal surfaces were recently reviewed [15]. Another article provides a comprehensive review of ever-expanding application of graphene nanomaterials with different inorganic and organic materials in drug delivery and theranostics. The preparation methods of nanomaterials were detailed and biological and physico-chemical characteristics of biomedical relevance were discussed [16]. A comprehensive summary of graphene-based nanomaterials characteristics, synthesis and applications as well as of their *in vitro* and *in vivo* evaluation in medicine was presented [17].

In this review, we summarized the recent development (2016–2018) on the graphene and graphene-based nanomaterials preparation methods and the uses of these materials for different applications (sensors, electronic devices, supercapacitors, dye adsorbents, composites, transparent conductive films). However, due to the extremely large number of publications it was not possible to cover all of these articles and so we made a selection of the most recent articles in each of the relevant sections based on their accessibility.

2 Recent progress of graphene and graphene-based nanomaterials synthesis

It is desirable that the synthesis of graphene and graphene-based materials to be controlled in such way as to confer properties for specific applications. As is known, the synthesis of graphene can be accomplished by two main approaches, the bottom-up and the top-down, respectively. Bottom-up methods comprise the synthesis of graphene from alternative carbon sources while top-down approaches involve the separation of stacked graphite layers to yield single graphene sheets (Fig. 2) [18–19].

One of the major challenges in commercializing graphene is how to produce high-quality material in a reproducible manner, on a large scale and at low cost. Although this still continues to be a considerable challenge, a number of different routes to synthesize graphene have

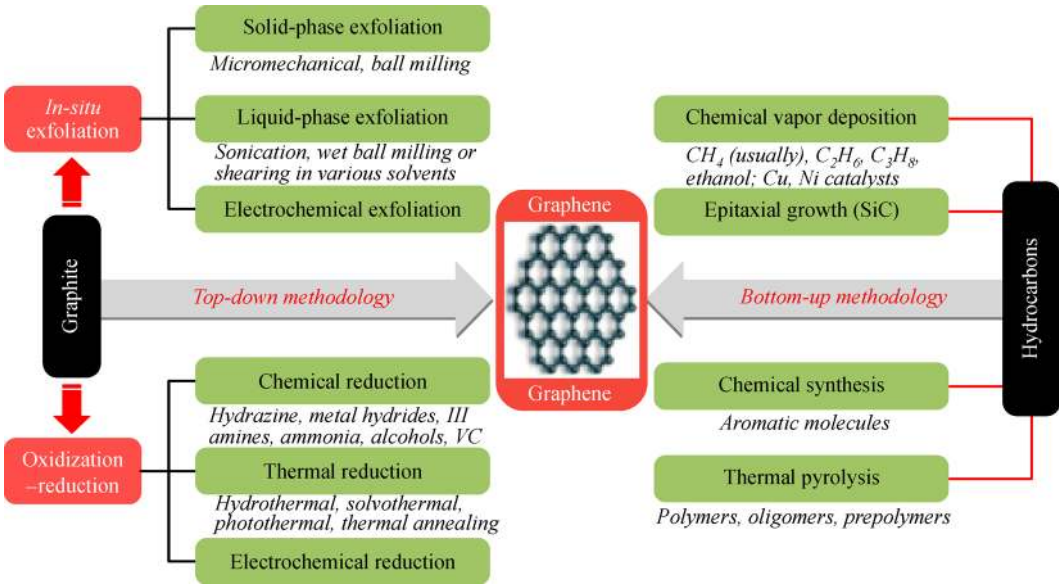

Fig. 2 Schematic representation for graphene synthesis through top-down and bottom-up approaches. Reproduced from Ref. [18] with permission of Elsevier.

been developed over recent years (2016–2018) as discussed below.

2.1 Top-down synthesis

2.1.1 Liquid-phase exfoliation

Liquid-phase exfoliation of graphite generally implicates wet chemical dispersion followed by sonication induced exfoliation in appropriate solvents in the absence or the presence of surfactants. It was developed [20] a new nanoparticle assisted liquid-phase exfoliation method of graphite to graphene sheets. The method is based on the use of magnetic Fe_3O_4 nanoparticles as "particle wedge" to ease the delamination of graphitic layers (Fig. 3). It was concluded that exfoliation using particle wedges would be an applicable technique in order to reduce ultrasonication time and suppress structural defects arising from long-term sonication.

Recently it was reported an effective and green method for large scale synthesis of few layered graphene from graphite in pure water without any use of chemicals or surfactants [21]. The principle of this strategy consists in the facile liquid exfoliation route with the assistance of vapor pretreatment for the preparation of edge hydroxylated graphene. After synthesis, they used the water dispersed graphene to obtain an ultrathin conductive film made of graphene nanoplatelets only. The typical atomic force microscopy (AFM) images indicated that the thickness of nanoplateles were about 2.24, 0.52 and 1.76 nm, which corresponds to six-layer, single-layer, and four-layer graphene. The statistical analysis of over 100 flakes displayed that $>25\%$ of the graphene nanoplatelets are single layer (<1 nm in thickness) with a lateral size ranging from 0.5 to 2.5 μm. The method opened the way for the cost effective and environmentally friendly production of graphene-based materials with significant potential for real-life applications.

The authors of another study [22] have demonstrated a high-yield method to produce defect free few-layer graphene by exfoliation of graphite in a chemically modified degradable water-soluble polymer modified by cholamine assisted by physical sonication. They obtained high-quality graphene with a production rate of 6 $g \cdot h^{-1}$. The transmission electron microscopy (TEM) images of the exfoliated graphene reveal that the graphene sheets are transparent under the electron beam, suggesting a very small thickness of the graphene sheets, which was also confirmed by AFM analysis.

The liquid-phase exfoliation technique was applied to produce one- to four-layer graphene from flaky graphite using various solvents and surfactants. By depositing the exfoliated flakes on arbitrary substrates the authors obtained half-centimeter-size graphene films which can be useful for electronic and photonic applications [23].

The galvanostatic electrochemical assisted liquid-phase exfoliation of graphite using constant current setup was developed to synthesize few layer graphene [24]. Also, the

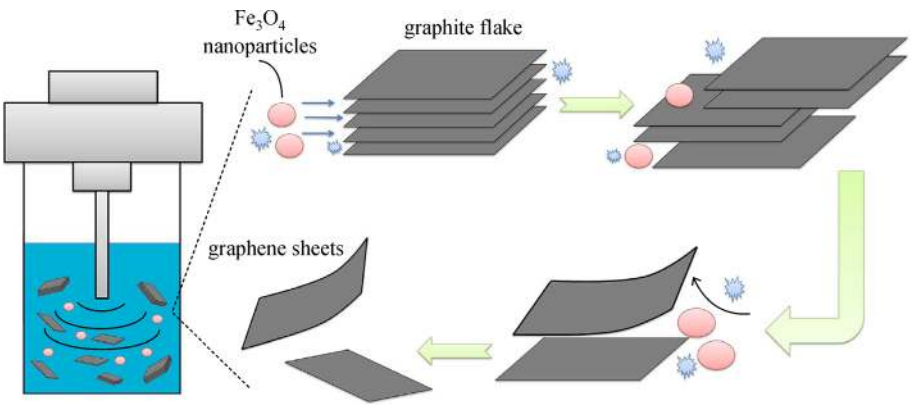

Fig. 3 Schematic illustration of the nanoparticle-assisted liquid-phase exfoliation method. Reproduced from Ref. [20] with permission of Elsevier.

authors studied liquid phase exfoliation of graphene dispersion with stabilizer and concluded that the addition of stabilizers like diethanolamine created extra defects and increased the thickness.

A continuous, semi-industrial sonication procedure for the production of graphene sheets in aqueous media was presented [25]. They characterized the product both in the supernatant and in the precipitate and observed that, above a certain critical specific energy, all graphite flakes were exfoliated into graphene sheets. It was demonstrated that sonication is a valid and scalable method for producing defect-free graphene from graphite and that the graphene production rate increases with volume.

2.1.2 Electrochemical exfoliation

Electrochemical exfoliation of graphite into graphene consists in using carbon sources (graphite or highly oriented pyrolytic graphite rods, graphite foils) as electrodes in an aqueous or non-aqueous electrolyte solution.

Recently, we reported a simple, cost-effective electrochemical approach to produce graphene by electrochemical exfoliation of graphite rods in acidic electrolytes [26]. The size of graphene flakes and the exfoliation/oxidation level were studied by varying the electrochemical parameters (e.g. applied bias, electrolyte concentration). In scanning electron microscopy (SEM) images (Fig. 4) one can see the thin and crumpled nanosheets which are randomly arranged and overlapped with each other.

Also, we prepared graphene nanosheets through one-step exfoliation of a graphite rod and subsequently attached gold nanoparticles to the graphene surface. The obtained material was then employed to modify a glassy carbon electrode and the electrochemical behavior of hydroquinone in the presence and absence of interfering species was studied [27].

Munuera et al. investigated an easy method for the preparation of ready-to-use and low oxygen content graphene material based on electrochemical delamination of graphite in aqueous medium using sodium halides as the electrolyte [28]. The halide-derived graphenes were tested as dye adsorbents, adsorbents for oils and non-polar organic solvents and as electrodes for supercapacitors and displayed comparable or even better performances than that of other types of graphene.

Hossain and Wang prepared graphene by electrochemical exfoliation of graphite rods in $(NH_4)_2SO_4$ solutions, at the temperature from 25 to 95 °C with and without the

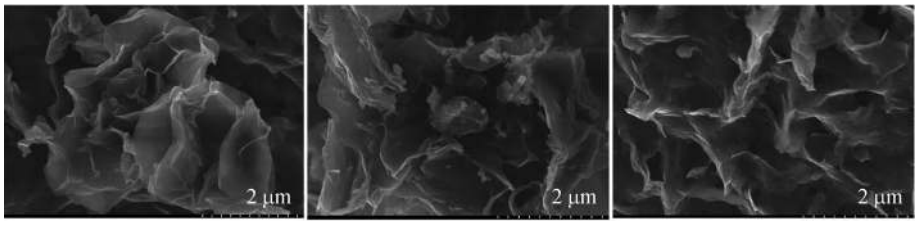

Fig. 4 SEM images of electrochemically exfoliated graphene. Reproduced from Ref. [26] with permission of the Royal Society of Chemistry.

addition of H_2O_2 [29]. Using this procedure they produced low defect, double layer or overlap of two single-layer graphene (Fig. 5).

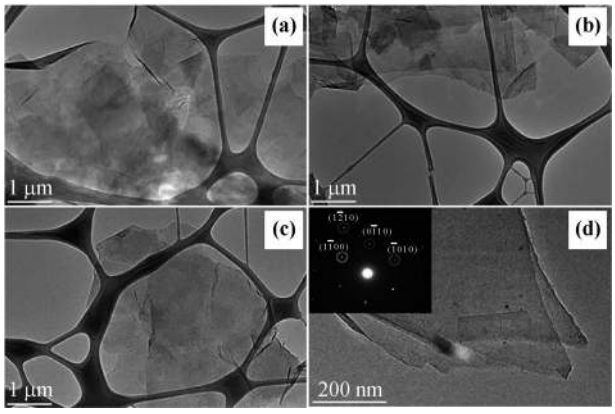

Fig. 5 TEM images of exfoliated graphenes synthesized using electrochemical exfoliation **(a)** at 50 °C without the addition of H_2O_2, **(b)** at 50 °C with the addition of 5 mL H_2O_2, **(c)** at 50 °C with the addition of 10 mL H_2O_2, and **(d)** at 95 °C with the addition of 10 mL H_2O_2 (inset showing the corresponding selected area electron diffraction pattern). Reproduced from Ref. [29] with permission of Elsevier.

Their research demonstrated the essential role of both temperature and H_2O_2 addition in producing high-quality graphene, which is significant for future applications.

A facile electrochemical exfoliation process was used for the synthesis of graphene from graphite anode in 0.1 mol·L^{-1} solution potassium sulphate. The analysis confirmed the synthesis of graphene nanosheets which were then used for making flexible paper supercapacitors [30].

A novel electrochemical exfoliation mode to efficiently prepare graphene sheets with potential applications in transparent conductive films was achieved [31]. Concentrated sodium hydroxide solution was used as electrolyte and the graphite electrode was coated with paraffin in order to keep the electrochemical exfoliation in confined space. The experiments were conducted at a low voltage (3 V) so as to prepare graphene with decreased amounts of defects and increased yield.

A high-yield method for producing low-defect graphene nanosheets by electrochemical exfoliation of graphene from natural graphite electrode in the presence of sulfate ions under constant voltage and constant current models was developed (Fig. 6) [32].

Based on the experimental results, their approach may constitute an industrial scalable processing method for producing high-yield and low-defect graphene products.

By contrast with the above mentioned works, the direct

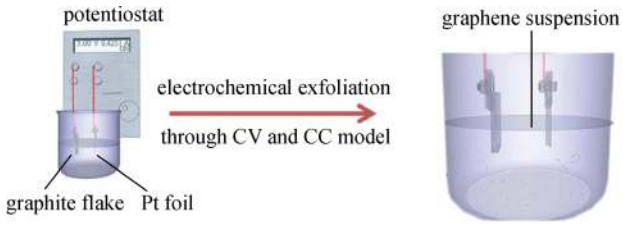

Fig. 6 The schematic diagram of electrochemically exfoliating graphene from graphite electrode under constant voltage and constant current models with the temperature range of 300–333 K. Reproduced from Ref. [32] with permission of the Royal Society of Chemistry.

electrochemical reaction between graphite powder and metallic Li in 1 mol·L^{-1} lithium hexafluorophosphate/propylene carbonate electrolyte was used to continuously exfoliate graphite with a high yield of 80% without any consumption of electric energy [33]. The SEM and TEM images (Fig. 7) suggest that the non-electrified electrochemical exfoliation method can produce few-layer

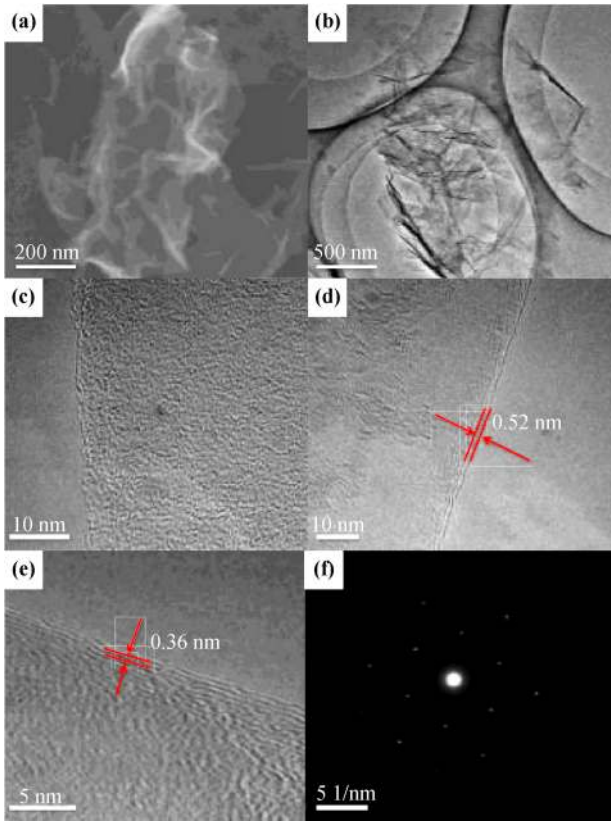

Fig. 7 Morphological observation on the non-electrified electrochemical exfoliated graphene: **(a)** SEM and **(b)** TEM images; HRTEM images of **(c)** single layer, **(d)** bi-layer and **(e)** four-layer; **(f)** SAED pattern of bilayer graphene. Reproduced from Ref. [33] with permission of Elsevier.

graphene nanosheets with high quality similar as typical electrochemical exfoliation route.

2.1.3 Chemical reduction of graphene oxide

The chemical reduction of graphene oxide (GO) is an efficient method to produce graphene with respect to costs and large-scale production. A disadvantage of this method is the fact that the reduced graphene sheets tends to agglomerate. Furthermore, the chemical reduction process usually employs toxic reducing agents, such as hydrazine or sodium borohydride, which are harmful to the environment. The use of green reducing agents over toxic chemicals has currently become one of the appealing topics in the graphene field [34–36].

Table 1 presents a series of different green reducing agents recently used in the graphene oxide reduction process [37–48].

All of the reducing agents have proven to be environmentally friendly and the products obtained are highly dispersible and biocompatible and, hence, useful in one way or another.

2.2 Bottom-up synthesis

The bottom-up synthesis includes epitaxial method, CVD, thermal pyrolysis [49] and chemical synthesis from aromatic molecules.

2.2.1 Epitaxial method

The thermal decomposition of SiC is a promising method to prepare high-quality graphene and the epitaxial graphene obtained by this way can be applied to graphene-based electrical devices directly without transferring. Qin et al. studied the polarized Raman spectra of non-exfoliated monolayer and bilayer epitaxial graphene on 4H-SiC substrates. Their results indicated that the G band of epitaxial graphene showed non-polarization, while the 2D band showed strong polarization dependency [50].

A new method to produce uniform epitaxial graphene on C-face 6H-SiC substrates with a sputtered SiC film by annealing temperatures ranging from 1400 to 1900 °C under Ar atmosphere was investigated. Bi-layer graphene of about 95% in a 75 μm × 75 μm square were observed using Raman mapping and a low energy electron microscopy. Their conclusion was that this novel method is very promising for manufacturing analog high frequency devices [51].

Another research study [52] presents a new approach for the transfer-free graphene growth directly on cemented carbide. The authors explain the mechanism of chemical processes behind, especially underlying the structural, chemical and morphological aspects of the graphene layer formation. This paper opens new horizons towards further enhanced industrial applications of the cemented carbides. They used the currently existing engineering material and scientific data to develop a sustainable new aspect of cemented carbides without any need of depositing metal oxide layer to control carbon diffusion.

2.2.2 CVD synthesis

CVD is a complex method that requires precise control of synthesis parameters (temperature, pressure, deposition time, type of precursors) [53]. However, it still remains an attractive method for preparation of high-quality graphene. Table 2 summarizes some recent studies of graphene preparation by different CVD techniques [54–65].

Table 1 Few of green reducing agents recently used in the GO reduction process [37–48]

Reducing agent of GO	Temperature of reduction/°C	Time of reduction/h	c(GO solution) /(mg·mL^{-1})	Ref.
Uric acid	90	1	1	[37]
Tea leaves extract	90	1	0.5	[38]
Ascorbic acid	95	1	0.5	[39]
Polydopamine	60	2	6	[40]
Annona squamosa leaf extract	100	12	0.4	[41]
Vancomycin	60	24	0.1	[42]
Alanine	85	24	0.05	[43]
Melissa officinalis extract	RT	12	0.5	[44]
Crude polysaccharide solution of *Pleurotus flabellatus*	RT	48	2	[45]
Lycium barbarum extract	95	24	1	[46]
Caffeic acid	95	24	1	[47]
Artemisinin	95	24	1	[48]

Table 2 Synthesis parameters and graphene quality for some CVD-synthesized graphenes [54–65]

Synthetic method	Substrate/Precursor	T/°C	Graphene product	Ref.
CVD	Cu/($H_2 + CH_4$)	1070	graphene single crystals	[54]
CVD	electrolytic Cu (technical grade)/ N_2 (90%):H_2 (10%), C_2H_2	1000	good quality graphene	[55]
CVD	Cu/CH_4	1060	polycrystalline monolayer graphene	[56]
CVD with induction heating	(AuCu + MgO or AgCu + MgO)/ CH_4	1000	high quality graphene decorated with bimetallic nanoparticles (AuCu and AgCu)	[57]
CVD	(Ni or Cu)/CH_4	1050 (Cu), 980 (Ni)	high quality graphene	[58]
Inductively-coupled plasma CVD	Cu/($CH_4 + H_2$ + Ar plasma)	300	AB-stacked bilayer graphene films	[59]
ALC[a)] CVD	(Cu or NiCu)/CH_4	1050 (Cu), 1100 (NiCu)	continuous single crystal monolayer graphene	[60]
CVD	PET and glass/10 nm thick Ti layers	150	defect-free graphene	[61]
CVD	Cu/CH_4	1000	single-layer graphene	[62]
CVD	Cu/CH_4	1030	large and high-quality graphene films with single crystallinity	[63]
CVD	Cu/CH_4	1000	high-quality graphene	[64]
Plasma enhanced CVD	1,2-dichlorobenzene/CH_4	without any active heating	graphene nanostripes	[65]

a) ALC: advancing local control of the precursor concentrations.

2.2.3 Chemical synthesis from aromatic molecules

The promising results of the ongoing chemical synthesis of graphene materials have already settled the direction of future research goals. Materials scientists and chemists are investigating new solutions for the synthesis of defect-free graphene with customized properties.

Moreno et al. reported a bottom-up method to synthesize nanoporous graphene formed in separate steps [66]. First, they synthesized graphene nanoribbons using the surface-assisted Ullmann coupling of aromatic dihalide monomers into polymer chains and the cyclodehydrogenative aromatization of the intermediate polymeric chains into graphene nanoribbons (Fig. 8). The final step interconnects the graphene nanoribbons laterally by a highly selective dehydrogenative cross-coupling leading to nanoporous graphene which can be transferred to suitable substrates so its functionalities to be exploited.

An innovative, single-pot synthesis for chemically producing graphene/polyaniline nanocomposites was presented. Both graphene and polyaniline were chemically synthesized from benzene and aniline in a one-pot reaction. After characterization, the films with different polyaniline/graphene ratios were applied as the active layer in supercapacitors [67].

It was demonstrated that alkyne benzannulation promoted by Bronsted acid is a practical method for the bottom-up synthesis of graphene nanoribbons [68].

Using butadiyne-containing monomers initially converted to polydiacetylenes via topochemical polymerization and subsequent aromatization of the isolated polydiacetylenes at temperatures between 150 and 300 °C were obtained graphene nanoribbons with an average width of ~1.36 nm and an optical band gap of 1.4 eV [69].

3 Conclusion and outlook

It is impossible to discuss in a brief review all the aspects of graphene. In this article we have reviewed few of the recent advances in the field of graphene and graphene-based nanomaterials synthesis and applications. Several top-down approaches for graphene exfoliation have been considered such as liquid phase exfoliation, electrochemical exfoliation and chemical reduction of graphene oxide. Also, we discussed some of the bottom-up synthesis of graphene: epitaxial method, CVD and chemical synthesis from aromatic molecules. Overall, it can be seen from the discussion, that the progress which was made to date is absolutely remarkable. However, it is evident that still remains the need for an economical and viable large scale

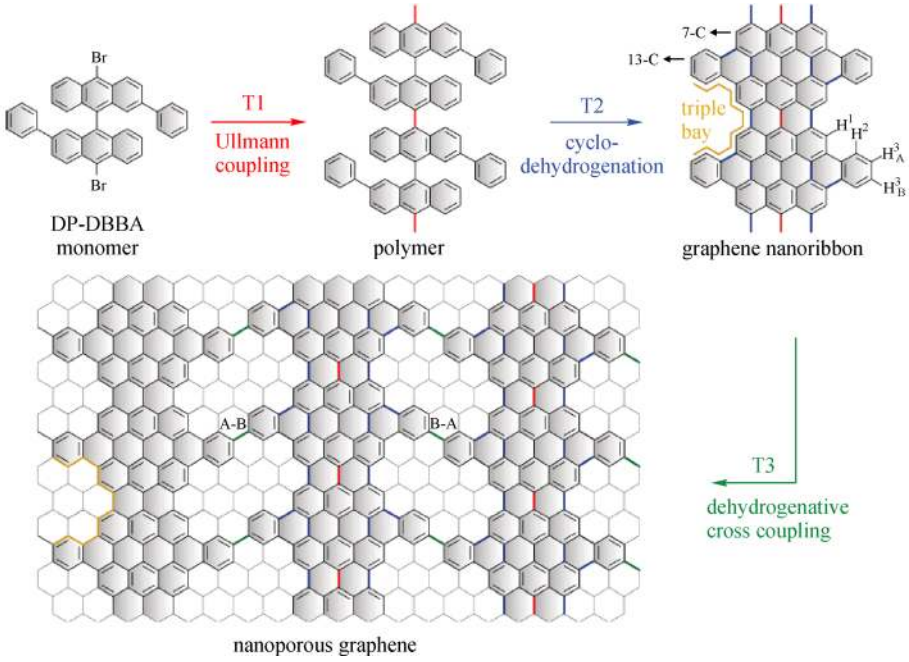

Fig. 8 Schematic illustration of the synthetic hierarchical path for the generation of nanoporous graphene. Reproduced from Ref. [66] with permission of American Association for the Advancement of Science.

production method for high quality graphene which also to be environmentally friendly.

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