# CVD Growth of Mono Layer Graphene: A Review

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*Abstract:* Nowadays, graphene, a single layer of $sp^2$-hybridized carbon atoms, has attracted enormous interest among scientists due to its unique physical, mechanical and electrical properties. Recently developed chemical vapor deposition technique has emerged as the most popular method for the scalable production of large-area and high-quality graphene for various applications. The key objective of this article is to provide a detailed and up to date review on the synthesis of large area monolayer graphene on different substrates via chemical vapor deposition method. Challenges and future perspective in this field are highlighted.

*Key words:* Graphene; monolayer; CVD; TEM; Raman.

## 1. Introduction

Graphene has extraordinary physical and electrical properties [1-2], so that it has attracted great interest in different scientific areas in the last years. While graphene is a nanomaterial with high electron mobility and elevated conductivity [3-5], it has been reported that bare graphene, graphene oxide or the combination with other semiconductor materials can be used as catalyst materials. However, for practical applications, a reproducible and large-scale production of graphene is of vital importance. Graphene can be prepared by mechanical exfoliation of graphite [6], epitaxial growth on SiC surfaces [7-9], reduction of graphene oxide [10-11], and chemical vapor deposition (CVD). Among these strategies, CVD has become the most promising approach because it is inexpensive, transferrable and it has the ability to produce high quality and large-area graphene films [12-13]. CVD graphene was first reported in 2008 and 2009, using Ni and Cu as substrates [13-14], which was then followed by an explosion of research activities. To date, many problems still remain, hampering the further development of graphene in fundamental research and practical application. This review article summarizes the main techniques used for the synthesis of large area graphene by CVD methods. Recent important advances in controllable synthesis of large-area monolayer, wafer-scale single crystal, bilayer and multilayer graphene on metal and insulating substrates are presented. Finally, problems and future perspectives are discussed.

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## 2. CVD growth of large area monolayer graphene on Cu foil

The growth of graphene using copper as the catalyst substrate is the most popular method for preparing large-area, high quality monolayer graphene [15]. The growth mechanism on Cu surface is a surface adsorption process owing to the low solubility of C atoms in Cu, offering a path to grow monolayer graphene based on selflimiting process [16].

Since Li *et al.* firstly produced uniform monolayer film on Cu foils by low pressure CVD (LPCVD) in 2009 [17], Cu has been viewed as an ideal substrate. In their experiment, graphene was prepared on Cu substrate for 30 min at temperatures up to 1000 C by CVD using a mixture of methane and hydrogen. Several characterizations analysis methods including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy has confirmed that more than 95% of the area was covered with monolayer graphene with high quality (Fig. 1 a–b). However, graphene prepared by this CVD method is typically polycrystalline [18]. The defect along the grain boundaries would strongly depress the crystalline quality [19]. Therefore, one main challenge for the production of large area monolayer graphene with high quality is to synthesize single crystal monolayer graphene. One way is to lower the nucleation density. The factors effecting graphene nucleation on a Cu catalyst by CVD include the flow rate of hydrocarbon [20], the hydrocarbon/hydrogen ratio [21], the growth temperature [22], the pressure of the system [23], and the pretreatment of Cu substrate [24]. The resulting domain size of graphene achieved on Cu foil varies with different CVD conditions. Seeding is another strategy to control the nucleation density. Pre-patterned polymethyl methacrylate (PMMA) [25], exfoliated graphite [26] or graphene oxide (G-O) flakes [27] have been used as preferred nucleation sites on Cu foil. As shown in Fig. 2, Li et al. have successfully synthesized graphene with domain sizes vary from a few microns to hundreds of microns by introducing different concentration of G-O solution used to deposit the G-O flakes onto the Cu foil under the same growth parameters [28].
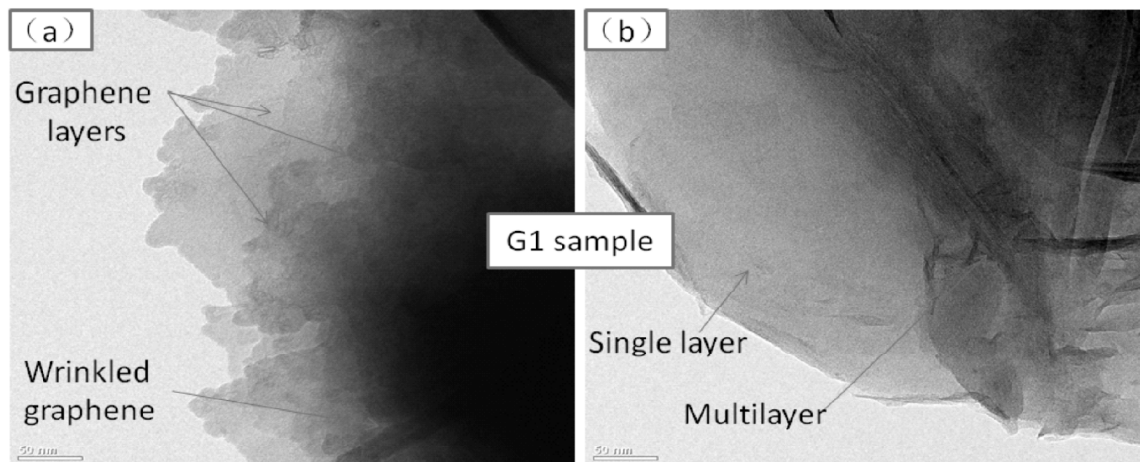


**Figure 1:** TEM images of CVD growth graphene (3minute reaction time) (a) 50nm (b) 50 nm
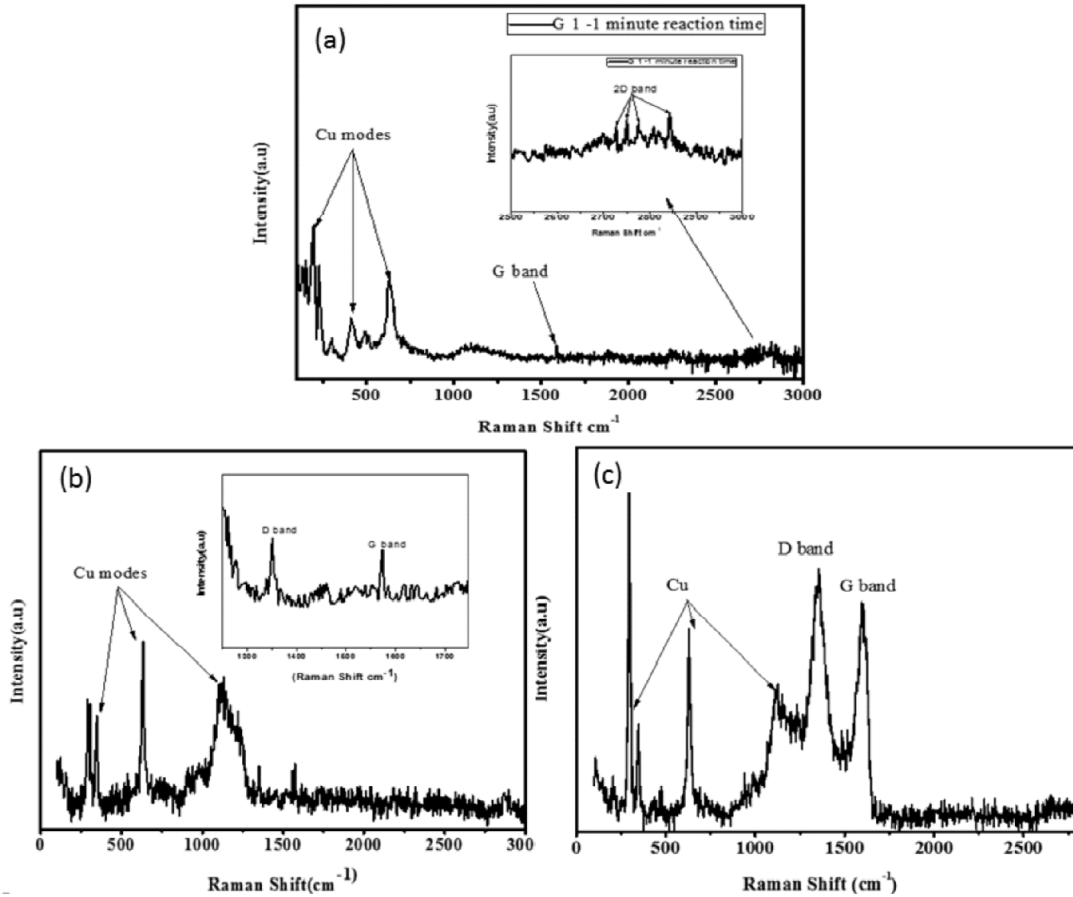
**Figure 2:** Raman spectra of as-prepared samples: (a): 1min reaction time; (b): 3min reaction time; (c): 3min reaction time

To grow single crystal graphene with millimeter size, different configurations of the Cu substrate such as Cu tube [29] or Cu enclosure [30], which maintains a smooth copper surface by suppressing evaporative loss of Cu during high temperature LPCVD, were applied during CVD growth of graphene (Fig. 3a and b). Wu *et al.* reports hexagonal-shaped single crystal graphene domain of 1.2 mm in size on polished Cu by choosing polystyrene as the carbon source because of its relative weak C-H bonds and low decomposition temperature [31]. Zhou et al. reports the synthesis of single crystal graphene of 5 mm in size by maintaining a catalytic inactive $Cu_2O$ layer during the initialnucleation stage [32]. Hao *et al.* synthesized centimeter-scale single-crystal graphene grains by exposing Cu enclosure to oxygen before introducing methane [33], as shown in Fig. 3c and d. Oxygen on the Cu surface could reduce the graphene nucleation density by passivating Cu surface active sites. This has been the largest single crystal graphene monolayer achieved on Cu foil reported up todate.
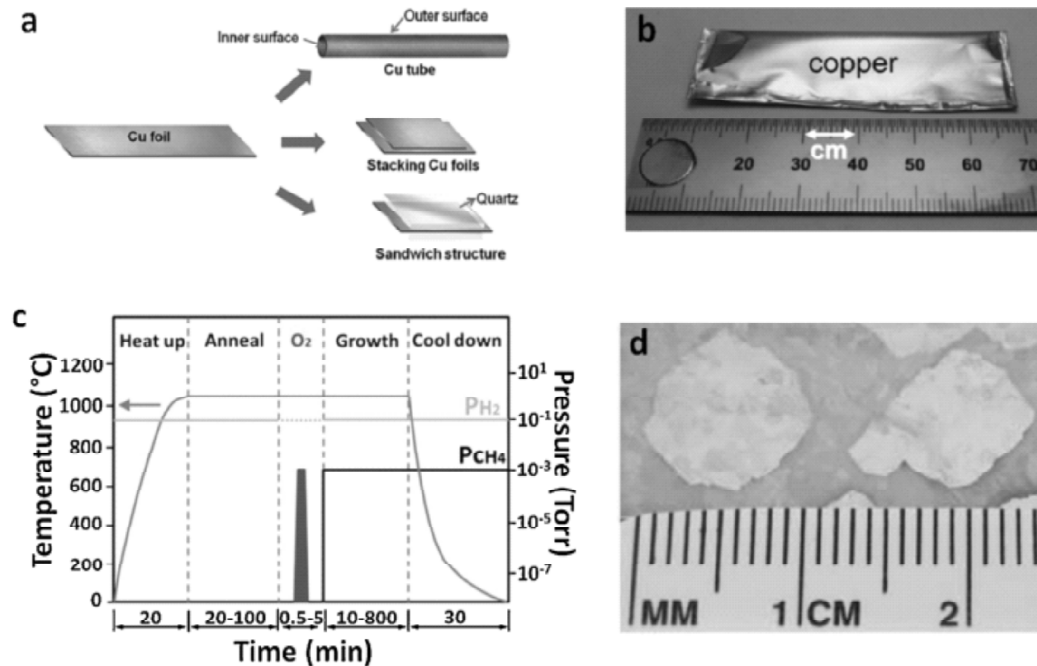
**Figure 3:** (a) Cu tube, stackedCu foils, and Cu foil between twoquartz slides, prior tographenegrowth. (b) Copper foil enclosureprior toinsertion in the furnace. (c) Schematic of a typical CVD graphene growth process that includes $O_2$ exposure. (d) Optical image of low-density graphene domains on Cu exposed to $O_2$. Adapted with permission from Ref. [34-36]. (a): ã 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (b): ã American Chemical Society; (c and d): ã 2013 American Association for the Advancement of Science.

With the significant progress of CVD graphene on copper foils, the great challenge is the scaled production of large-area graphene for commercial applications. Conventional CVD systems makes convection and radiation heat transfer between the heating sources using hot-wall reactors. One energy-efficient way to achieve CVD heating process is using an inductive heating cold wall reactor (Fig. 4a), where the radio frequency field directly heats the Cu substrate for rapid temperature ramp up/down. This CVD process, can be used to prepare large area graphene in a much faster way as compared to the conventional CVD system with hotwall reactor [37]. Kim et at. directly contacted the Cu foil with a heating source to give fast heat transfer by conduction, which was named rapid heating CVD (RHCVD), leading to the pretreatment and annealing process of Cu be accomplished in a shorter time [38], as shown in Fig. 4b. Such heating method makes larger Cu grains which benefit the graphene growth with large scale and high quality.

## 3. Mechanism of chemical vapor deposition of graphene

High temperature decomposition of various hydrocarbon sources by CVD method to produce thin, graphitic layers on transition metal surfaces and metal carbides have been studied for over 70 years [40]. The growth process involves the thermal decomposition of a hydrocarbon source on a heated substrate. Depending on the substrate, the process
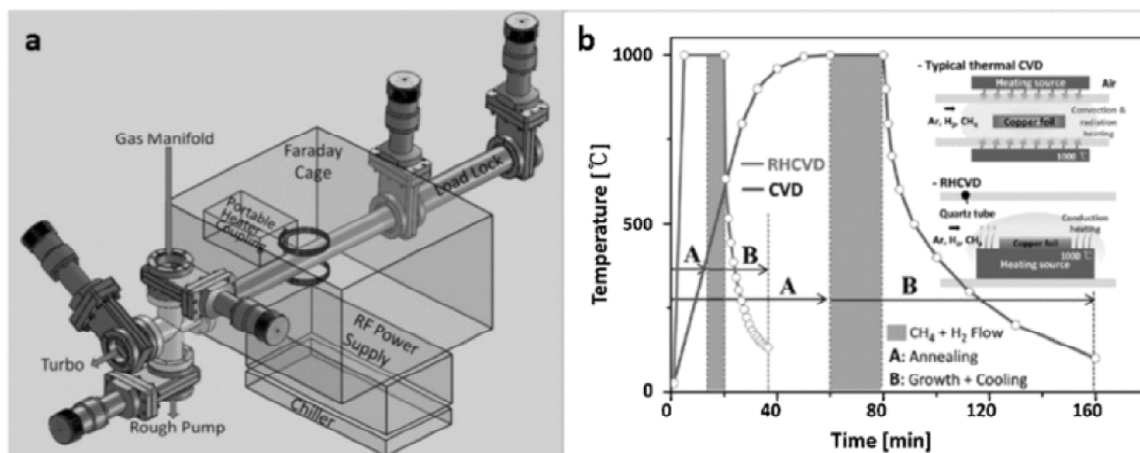
**Figure 4:** (a) Apparatus design of a cold-wall reactor based on RF magnetic inductive heating. (b) The graphene growth diagram of a conventional thermal CVD and a rapid heating CVD respectively.Adapted with permission from Ref. [39]. (a): ã 2013 American Chemical Society;(b): ã 2014 The Royal Society of Chemistry.

can be catalytically enhanced. Transition metals are the most widely used substrates in graphene synthesis. During the reaction, the metal substrate not only works as a catalyst to lower the energy barrier of the reaction, but also determines the graphene deposition mechanism. Table 1 lists out the solubility of carbon in various metal substrates and the corresponding growth mechanism. In the case of metals having high carbon solubility (such as Ni and Fe), the carbon will diffuse/dissolve into the heated substrate according to the solubility of carbon. As the substrate cools, the dissolved carbon will segregate to the surface to form graphene sheets [41-43]. This "segregation" process is depicted clearly in Fig. 5a [44]. On the other hand, for metals with low carbon solubility (such as Cu), carbon atoms will nucleate and laterally expand around the nucleus to form graphene domains with decomposition of hydrocarbon catalyzed by the substrates at high temperature. The growth process will terminate when the substrates are fully covered by the graphene layer, which is usually referred as a "self-limited surface deposition" growth

mechanism (Fig. 5b) [45]. Recently, it has been observed that the self-limiting growth process could be broken on Cu and few layer graphene can be produced under special growth conditions, such as CVD growth under atmosphere pressure [46], a very slow cooling rate [47] as well as a high methane concentrations [48].

Despite the low carbon solubility in Cu, several researchers have observed the segregation growth mechanism occurred on Cu enclosure, where carbon species penetrate from one side of the Cu foil to the other side, and then forms the second layer or multilayer graphene underneath the top first layer [49-50]. This mechanism is denoted as the "penetration" growth mode (Fig. 5c) [51], which favors the production of large scale graphene bilayer or multilayer, more details will be discussed later.

Besides the metal substrates, graphene synthesis on insulating substrate has been studied on several different substrates [51-52]. The growth mechanism of graphene on non-metal surfaces usually involves the surface adsorption, nucleation and coalescence. Without catalytic effect, multilayer graphene could be deposited on the insulating substrates. However, higher decomposition temperature is usually required on insulating substrates than on metal substrates such as Cu or Ni for graphene with high quality. Fig. 5d depicts the growth graphene on sapphire using methane under 1450 °C [53].

## 4. Remarkable application of CVD technique

The semiconductor index device (pipe) has been considered to coat with CVD method. After CVD coating the material was found to be a remarkable heat sink source because of large area graphene attachment. This describes the importance of our new method to produce low temperature CVD graphene for device application. Knowing the benefits of large area graphene composites several studies has been devoted to these composites nanostructures [39-40]. In addition, after coating with graphene, the electrical resistance of the semiconduct pipe changed in a certain range (30mΩ-50mΩ), and we can check the
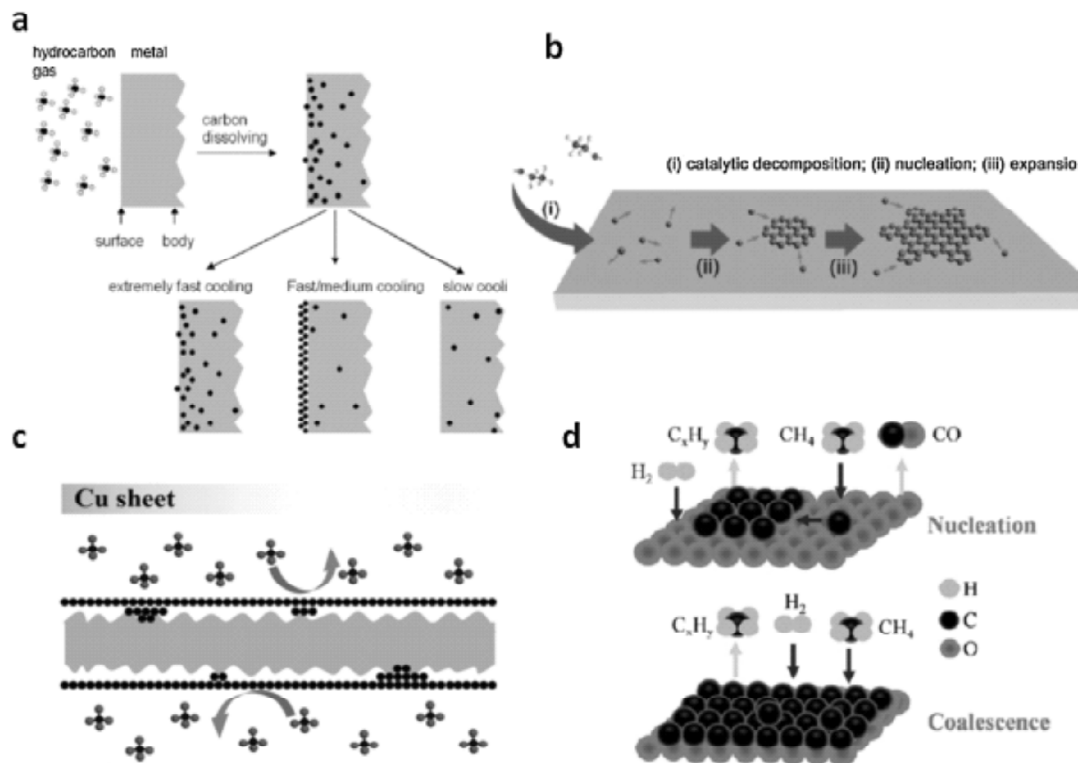


**Figure 5**: Schematics of CVD graphene grown on (a) metals with high carbon solubility, (b) Cu foil, (c) Cu enclosure, and (d) sapphire. Adapted with permission from Ref. [54-58]. (a): ã 2008 American Institute of Physics; (b): ã 2013 American Chemical Society; (c): ã 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; (d): ã 2012 American Chemical Society

**Table I**
**Carbon solubility and the growth mechanism on typical metals for CVD graphene**

| Metal (bulk) | Carbon solubility at 1000 °C (at.%) [38] | Primary growth mechanism |
|---|---|---|
| Cu | 0.04 | Surface deposition [20–42]/penetration [31,32] |
| Co | 3.41 | Segregation [43] |
| Pt | 1.76 | Segregation [44–47]/surface deposition [48,49] |
| Ni | 2.03 | Segregation [50–55]/surface deposition [56] |
| Pd | 5.98 | Segregation [57,58] |
| Fe | 7.89 | Segregation [56] |
| Ge | 0.00 | Surface deposition [36,37] |

inner part by scratching its surface. In light of the above experimental results our work is novel, one step low temperature techniques to produce monolayer graphene structure. The use of a separator between Cu foil and catalyst materials is consider being very important to reduce the interaction between Cu and metallic catalyst materials.
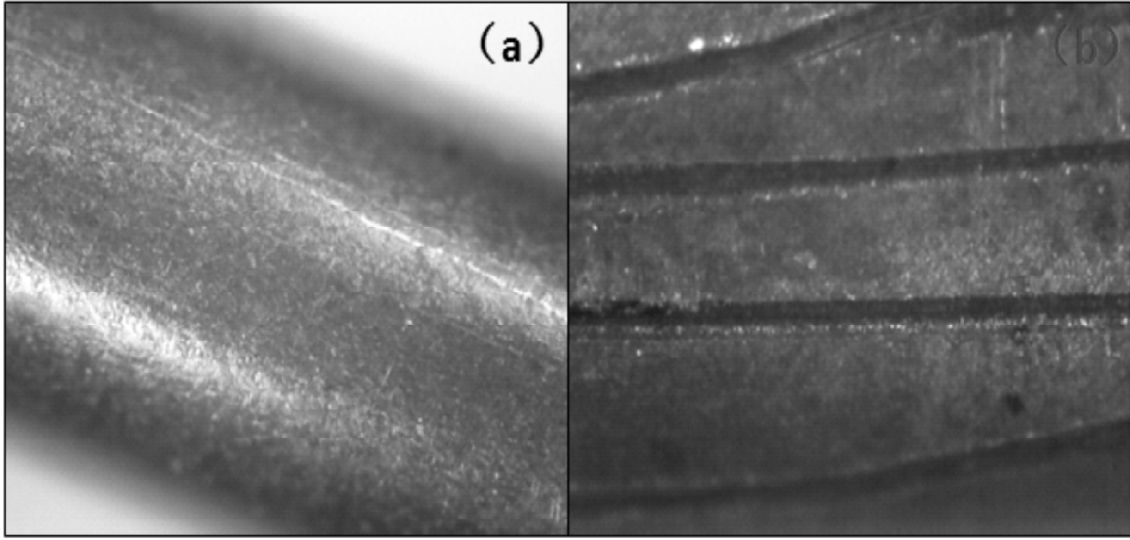


**Figure 6:** Coating of monolayer graphene on semiconductor index device using our CVD technique (a): After graphene coating; (b): After scratch with knife

## 5. Conclusions and perspective

In this article, we have summarized the fundamental mechanism of CVD graphene on different substrates including metals and insulting materials. We have reviewed the different growth manner and the latest techniques for producing large area monolayer on Cu foil substrates. In spite of the significant progress, there are still a number of important and interesting challenges that must be overcome for the practical applications of CVD graphene. (i) Synthesis of wafer scale single crystalline monolayer and bilayer graphene. (ii) Precise control of graphene layers has not been achieved yet. The synthesis of perfect

bilayer or tri-layer graphene with controllable stacking order is required for both fundamental research as well as electronic and photonic devices application. (iii) Direct growth of high quality graphene with controllable thickness on insulating substrates. To overcome the limitations of substrate etching and the damage arise from the post-transfer process, direct synthesis of graphene on dielectric substrate is strongly required for transparent conducting electrode application. It is imperative to develop more effective transfer technique which could provide less or even no further damage to the graphene itself. Rapid progress has been already made and the worldwide efforts have been devoted in the synthesis and application of graphene. We believe significant breakthrough in the field of graphene will come soon in the near future.

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