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Synthesis of Single-layer Graphene: A Review of Recent Development

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Abstract

Since graphene has been successfully synthesized in year 2004, graphene has become the highlight of the research study in the material science field because of its peculiar properties and attracted a large amount of research for its application. The extraordinary properties of graphene show some promising applications such as optical electronics, photovoltaic systems, composites and others. However, it is found that the production of single layer graphene for commercial application still under research for improvement of its quality, size and amount. It has been reported that single-layer graphene can be synthesized using several methods, but the most promising method to synthesize high quality single-layer graphene is chemical vapour deposition (CVD). In this review, current development of the synthesis of single layer graphene and its future prospects is presented and discussed.

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Keywords: graphene; chemical vapour deposition; transition metal

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1. Introduction

In 2004, two scientists, Andre Geim and Konstantin Novoselov have successfully synthesized graphene which was thought as a concept material that was not able to be produced in large quantity[1]. However, some synthesis techniques were reported after few years of the discovery of graphene and attracted many scientists to do more research about it[2,3]. Therefore, numerous reports were published in the following years from the synthesis to application of graphene[4,5]. In addition, graphene oxide and reduced graphene oxide have been studied extensively[6-8].

Graphene, this wonder material comprises a monolayer of hexagonal arranged sp^2 hybridized carbon atoms[9]. Despite of being the thinnest material known, graphene possesses remarkable high mechanical and electrical properties. For instance, it has very high carrier mobility and quantum hall effect at room temperature[1]. The states of conduction electrons in graphene fulfills the Dirac equation and the conduction electrons are called massless Dirac particles[10]. Since graphene could displays excellent optical transparency to a wide range wavelength of light, various optoelectronic devices utilize graphene as its transparent electrodes[11]. There are more graphene properties can be explored to exploit the full potential of graphene for various application[12]. This review article presents the current development of synthesis of monolayer graphene using chemical vapour deposition (CVD).

Nomenclature

PMMA	poly (methyl methacrylate)	**$C_{13}H_{10}$**	fluorene	**Ni**	nikel
Cu	copper	**$C_{12}H_{22}O_{11}$**	sucrose	**Cu-Ni**	copper-nickel
CH_4	methane	**Pt**	platinum		
CVD	chemical vapour deposition	**Co**	cobalt		

2. Recent development of synthesis

2.1. Carbon precursors

In the synthesis of single-layer graphene, various types of precursors can be used including solid, liquid and gas precursors. Hydrocarbon gas precursors are the popular carbon source because of its higher purity[13] as compared to liquid and solid. However, in recent years, liquid precursors are also attracting the interest of researchers[14,15]. The main reason is the availability and comparably cheaper than the hydrocarbon gas precursors.

Methane (CH_4) gas is one of the common gaseous precursors to grow graphene films. Lewis and coworkers demonstrated that single-layer graphene can be synthesized using diluted CH_4 gas[16]. They found that the produced graphene films consisted of monolayer and few layers individual graphene. However, no significant multilayer or bulk graphite was observed in the produced graphene films. In addition, Chen et al.[17] also showed that monolayer graphene sheets with high quality and crystallinity can be synthesized using CH_4 gas as precursor.

Besides gaseous, synthesis of graphene using solid carbon sources was demonstrated. Synthesis of graphene was first started when camphor was used to produce graphene[18]. Even though it was not successful, but it provided a path to synthesize graphene films using solid carbon precursors. Few years later, poly (methyl methacrylate) (PMMA) was used to grow graphene as reported by Sun and coworkers[19]. PMMA was coated on copper (Cu) metal before the Cu substrate was taken into the CVD furnace. A temperature of as low as 800˚C was needed to grow high quality monolayer graphene as identified by Raman spectroscopy. In addition, Sun et al.[19] used other types of solid carbon precursors including fluorene ($C_{13}H_{10}$) and sucrose ($C_{12}H_{22}O_{11}$) to synthesize graphene. The results showed that monolayer graphene sheets were synthesized by using Cu substrate when the same growth conditions as PMMA-derived graphene were used[19]. Fig. 1. shows the effect of H_2 flow rates on the number of graphene layers and the comparison of quality of graphene derived from sucrose, fluorene and PMMA. Furthermore, polystyrene was also used as the carbon precursor because of the lower decomposition energy are needed due to comparably weak bonding between atom carbon and hydrogen[20,21]. By using polystyrene, monolayer graphene film was successfully produced[20,21]. Therefore, various types of solid precursors can be used to synthesize graphene using CVD.

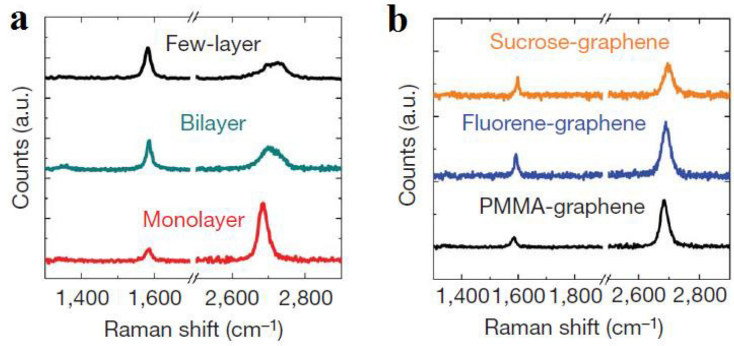

Fig. 1. (a) Raman Spectra of PMMA-derived graphene samples synthesized using different flow rates of H_2, (b) Comparison of Raman Spectra of graphene derived from sucrose, fluorene and PMMA. (Reproduced with permission from Sun et al.[19])

Besides gases and solid precursors, liquid carbon precursor such as hexane has been used to synthesize graphene sheets by Y. Yao's group[14]. It was proposed that a surface-catalyzed process and followed by a template growth occurred during the CVD graphene growth. Template growth is the extensive carbon sheets growth onto the existing graphene layer[22]. Therefore, the template growth should be suppressed in order to obtain thinner graphene layers. Later on in year 2011, Guermoune's group[13] used different alcohols as liquid carbon sources to synthesize high quality single-layer graphene. They compared the amount and quality of monolayer graphene sheets that produced using ethanol, propanol, methanol, and methane gas at growth temperature and time of 850˚C and 5 minutes, respectively. The Raman results showed that the quality of graphene films that synthesized using alcohol precursors are comparable to the quality of graphene that produced using CH_4. Similarly, in another experiment done by Campos et al.[15], the use of two different kinds of alcohols namely 2-phenylethanol and ethanol to grow single layer graphene were reported. They found that the single layer graphene that produced using ethanol were of better in terms of coverage, layer continuity and need shorter time for synthesis than that of 2-phenylethanol. Besides, larger surface area of single-layer graphene as compared to graphene flakes was synthesized from ethanol. A low-temperature growth is more feasible for industrial applications, because it is more convenient and less costly. Decomposition of liquid precursor at lower reaction temperature to produce graphene was demonstrated by Li et al.[21]. The synthesis of monolayer graphene flakes with good quality was achieved at growth temperature as low as 300˚C when using benzene as liquid precursor. As compared to the graphene grew at temperature of 500˚C, the monolayer graphene flakes were comparably smaller.

2.2 Catalysts

Transition metals have been used to synthesize high quality carbon nanotubes and graphene. There are a lot of metal catalysts including Platinum (Pt)[23], Cobalt (Co)[24], Nickel (Ni)[25-27], Copper (Cu)[28] and others.

Platinum (Pt) has been used as catalyst to grow graphene by CVD, although the wrinkles graphene film was produced. It is reported that the low carbon solubility of Pt that induce to the formation of monolayer graphene on Pt[23]. Cobalt (Co) is one of the popular transition metal that has been used to grow uniform single-layer graphene. Graphene film with predefined orientation was produced by Hiroki and coworkers[24] and hence, this graphene film can be applied in graphene engineering. The success of graphene film synthesized on Co does inspire scientists to synthesize single-layer graphene using different types of metal catalysts.

Nickel is another transition metal that is widely used as metal catalyst in synthesis of graphene[29]. Nickel possesses high carbon solubility that causes the difficulty to control the number of graphene layer. Thus, in more cases, instead of single-layer graphene, a mixture of single-layer graphene and multilayer graphene were formed[25]. Fig. 2. shows the schematic diagrams of graphene growth mechanisms on single-crystalline and polycrystalline nickel surface demonstrated by Zhang et al.[27]. The comparison of graphene growth on different crystal structure of nickel by CVD was made and the results showed that polycrystalline nickel leads to a higher percentage of multilayer graphene

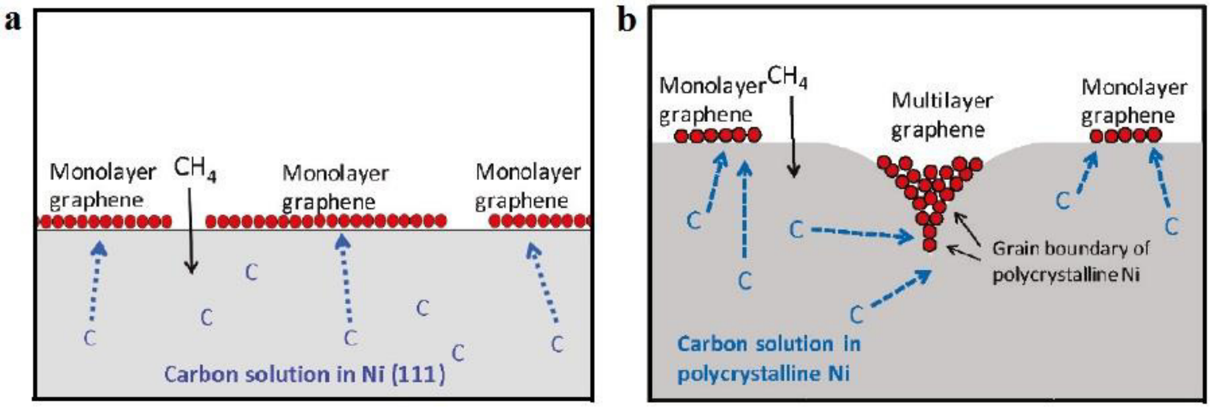

Fig. 2. Schematic diagrams of graphene growth mechanisms on single crystalline and polycrystalline Nickel surface. (Reproduced with permission from Zhang et al.[15])

due to the presence of grain boundaries. These grain boundaries can be the nucleation sites for multilayer graphene growth. In contrast, larger sheet of monolayer or bilayer graphene was grown on a single-crystalline nickel as compared to polycrystalline nickel. In addition, Reina et al. also demonstrated that mostly one or two layers of graphene were grown on the polycrystalline nickel using atmospheric CVD[26]. By controlling the methane concentration and the cooling rate during graphene growth, the thickness uniformity and the region of one- and two-layer graphene can be improved significantly.

Copper (Cu) is the most promising metal catalyst to grow single-layer graphene instead of multilayer graphene due to its low carbon solubility[30]. A mechanism which known as self-limiting process was proposed for the growth of graphene on Cu[28]. It was reported that high-quality and uniform of single-layer graphene films were grown successfully on Cu catalyst[28]. Thus, single-layer graphene can be grown preferably on Cu foils. In addition, thin copper foils are inexpensive and transferring process can easily be achieved because of the availability of Cu etching solvents.

Nickel was not as popular as copper due to the difficulty in controlling the number of graphene layer but once it was doped with another type of transition metal, the metal alloy could perform better. Liu's group[31] demonstrated that the synthesis of graphene on copper-nickel (Cu-Ni) alloys is an ideal system where the carbon solubility can be controlled by adjusting the atomic fraction of Ni in Cu. Therefore, Cu-Ni alloy was used to produce monolayer and multilayer graphene using CVD with methane gas as precursor as shown by Chen et al.[32]. It was found that the thickness and quality of the graphene films that obtained using Cu-Ni alloy foil could be controlled by varying the deposition temperatures and cooling rates. The produced monolayer graphene on Cu-Ni alloy was much better of uniformity than that graphene grown on polycrystalline Ni.

Up to date, copper is the most preferable transition metal to synthesize graphene at controllable layer because of its lowest carbon solubility as compared to nickel, iron, ruthenium, iridium, platinum and others.

2.3 Pressure

In an attempt to use low pressure of CVD, graphene film with uniform monolayer and low defects density was successfully produced[33]. However, when atmospheric pressure CVD was used to grow graphene film, not uniform and mixture of mono and multilayer graphene film were synthesized[34]. However, by reducing the methane concentration in the gas mixture, monolayer graphene film can be produced. Another factor that can affects the graphene growth quite significantly is the pressure of hydrocarbon. This is obvious as the pressure of hydrocarbon can directly determine the concentration of carbon species that are eventually grown on the catalyst surface. Therefore, low carbon precursor concentration was preferred to be used in growing single layer graphene[35]. In the study, low methane concentration induced the growth of single-layer graphene films where exceeding 95% of the sample area was occupied by graphene films. In addition, Regmi et al. also demonstrated that low concentration of methane can synthesized single-layer graphene films without any bilayer and multilayer flakes being observed[36]. Thus, it indicated that the quality and the cleanliness of graphene films can be improved by utilizing low pressure of carbon precursor and applying lower of the methane-to-hydrogen ratio.

3 Future prospects

Graphene as a new type of nanomaterial still has many challenges such as synthesis, characterization, application and others. The extraordinary properties of high purity pristine graphene synthesized by exfoliating graphite using scotch tape is a small scale method which does not fulfil demand of any large scale device production. Therefore, CVD and epitaxially methods have been used as alternative methods to grow single, bilayer and few-layer graphene. Recent reports demonstrated the scalability using CVD to synthesize graphene on wafer and facile transfer of graphene for following device production, has made a breakthrough in semiconductor industries by offering novel opportunities to scientists and engineers. For large scale synthesis, reduced graphene oxide has been produced in the chemical exfoliation from graphite into graphene oxide and subsequently reduced by thermal and chemical methods into reduced graphene oxide which is a lower cost synthesis route. However, the electrical and mechanical properties of samples were degraded by the chemical and thermal modification. Thus, controlled modification of graphite, graphene oxide and reduced graphene oxide is very important to protect the material properties in expanding the applications of graphene-based materials.

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