

Effects of copper, nickel, and its alloy as catalysts for graphene growth via chemical vapor deposition method: A review

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Abstract

Enormous characteristics exhibited by two-dimensional carbon-based nanomaterial, graphene attract current researchers in integrating this advanced material into the development of next-generation electronic, optoelectronic, photonic, and photovoltaic devices. The ultimate aim was to synthesis a single layer of graphene with large-size domain with less defect formation. The solid state of the graphene promises ultra-high performance in the devices due to ultra-high electron mobility. Within a decade, previous researchers have narrowed down their studies by applying different types of metal species as catalyst substrate in chemical vapor deposition method. The crucial part was to determine the characteristics of carbon precipitation and diffusion onto the metal surfaces. Each metal-based catalyst and its alloy revealed different behavior according to its carbon solubility and intrinsic properties. Until now, copper, nickel, and its alloy combination provide tremendous finding in the synthesization of graphene. Currently, researchers are still exploring the ideal parameters related to feeding gases, growth temperatures, and working pressures which are essential to each catalyst metals characteristic such as copper, nickel, and its alloy.

Keywords: Copper, nickel, alloy, graphene, chemical vapor deposition

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INTRODUCTION

Generally, in the chemical vapor deposition (CVD) process, transition metal catalysts such as nickel (Ni), copper (Cu), ruthenium (Ru), palladium (Pd), platinum (Pt), iridium (Ir), cobalt (Co), gold (Au) and rhodium (Rh) play vital roles by fabricating graphene in two-dimensional (2D) form, decomposing the carbon precursor, expediting the carbon diffusion process, and recovering the defect graphene (Seah *et al.*, 2014; Wu *et al.*, 2016; Liu *et al.*, 2011; Wang *et al.*, 2013). The growth of graphene on various transition metal surfaces and their alloys has been broadly explored and distinct growth behaviors were fundamentally observed in detail (Sutter *et al.*, 2008; Li *et al.*, 2009; Li *et al.*, 2010; Li *et al.*, 2009; Gao *et al.*, 2010; Diaye *et al.*, 2008; Sutter *et al.*, 2009; Kwon *et al.*, 2010; Sicot *et al.*, 2010; Gao *et al.*, 2011). The process starts with the nucleation of graphene nuclei, in which resulting in the formation of graphene domains with certain level of thickness. Thus, it is important to review and determine the effect of catalyst metal species as it involved in the diffusion of the carbon besides the formation of the layer graphene. There is also a vast of exploration when it comes to excessive carbon decomposition, hence the result would varied accordingly. Fig. 1 shows the schematic diagram of basic CVD setup.

Seah *et al.* (2014) claimed that transition metal substrate not only works as a catalyst to lower the energy barrier of the reaction but also determines the graphene deposition mechanism. Metal-assisted thermal CVD is considered to be a prominent method for fabricating large area of graphene with high uniformity and low defects. Besides, this method

could engage with the utilization variety of transition metals as catalysts.

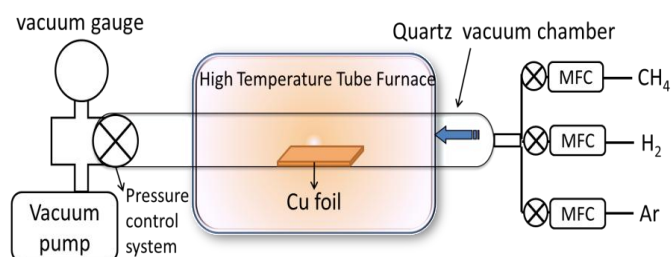


Fig. 1 Schematic diagram of the CVD (Kumar and Lee, 2013).

Atmospheric CVD method consist of carbonaceous gaseous species that reacted at high temperatures (750 – 1100 °C) in the presence of metal thin films or foils, which react as catalyst in the decomposition of the carbon precursor and in the nucleation of the carbon atoms into graphene. The growth mechanism of graphene is influenced by several factors, which are the carbon solubility limit in the metal, its crystal structure, lattice parameter, and thermodynamic parameters such as the temperature and pressure of the CVD system (Bhaviripudi *et al.*, 2010). To our knowledge, the variation of graphene's growth mechanism would be strongly contributed to the carbon solubility in the metals. Cu metal has very low carbon solubility (< 0.001 atomic %) usually shows limited graphene growth on the surface of the catalyst. In contrast, Ni

and Co metal which have intermediate-high carbon solubility (> 0.1 atomic %) describing graphene growth via combination of carbon atoms diffusion into the metal surface at the growth temperature and precipitation of carbon atoms to the surface of metal upon the cooling process (Li *et al.*, 2009; Kim *et al.*, 2009; Reina *et al.*, 2009). So far, transition metals such as Cu and Ni are the most commonly used metals as catalysts for the graphene synthesized using CVD method (Lee and Lee, 2010; Bharadwaj *et al.*, 2014; Ma *et al.*, 2015; Dardona *et al.*, 2016). Moreover, these catalysts have advantage in reducing the pyrolysis reaction temperature of simple alkane gases from 1400 °C to lower than 1000 °C.

In this review, the potentials of Cu, Ni, and its alloy combination are explored, specifically on its significant effect on graphene growth using CVD method. The discussion is derived from scanning electron microscope (SEM), optical microscope, Raman spectroscopy, atomic force microscopy (AFM), x-ray diffraction (XRD), and transmission electron microscopy (TEM) characterization in order to gain knowledge on domain sizes, defects, layers, and nucleation densities. The interaction and atomic arrangement due to carbon solubility of Cu and Ni are also studied as complementary findings to previous research.

COPPER CATALYST

Cu is the most trending transition metal catalyst employed in the CVD in the form of polycrystalline thin film to acquire single-layer graphene. Generally, Cu catalyst brings high stability in synthesizing single-layer graphene which is significantly cheap compared to other pure metal elements. Moreover, Cu catalyst also provides vast catalytic reaction on the synthesized graphene according to application demand. Otakar *et al.* (2014) reported that there was significant effect of copper lattice instead of grain boundaries to the growth mechanism of graphene on the working pressure and temperature. Cu is soft, malleable, ductile metal with very high thermal and electrical conductivity. Exposed surface of pure copper has a reddish-orange colour. Cu is naturally grown in very fine polycrystalline form, which has greater tensile strength than monocrystalline forms as reported by Smith and Javad (2010).

Cu catalyst has relatively low carbon solubility compare to Ni, which is 0.04 % at reaction temperature 1084 °C (Mattevi *et al.*, 2011). The growth mechanism of graphene only occurred on the surface of copper catalyst or a few nanometers below the surface due to very low carbon solubility (Bhaviripudi *et al.*, 2010). The kinetic behavior of Cu which were intensively studied significantly boosts the current advancement of Cu catalyst in CVD system (Joyce and Bradley, 1963; Eversteyn and Severin, 1970; Claassen and Bloem, 1981; Kamins, 1988; Tao, 1993).

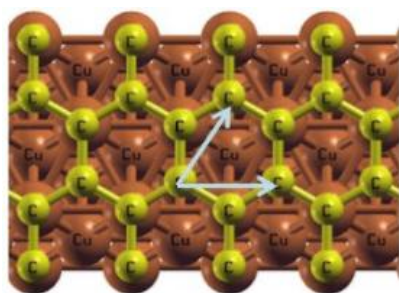


Fig. 2 The atomic deposition of carbon atoms (hexagonal) on Cu crystalline (Mohsin *et al.*, 2016).

Fig. 3(a) shows the optical microscope image of graphene (bright region) grown on Cu foil (dark region) supported by Raman spectra in Fig. 3(b). Due to low carbon solubility properties of Cu, the deposition of carbon atoms commonly ended as monolayer graphene varying to the growth reaction temperature. The size of graphene crystal domains would greatly affect the quality of synthesized graphene. The domains size typically effected by the grain boundaries of Cu. Li *et al.* (2011) explained that low nucleation density of carbon atoms on Cu, propped by suitable growth parameter of CVD system and proper surface treatment of Cu were the vital points to produce single layer graphene.

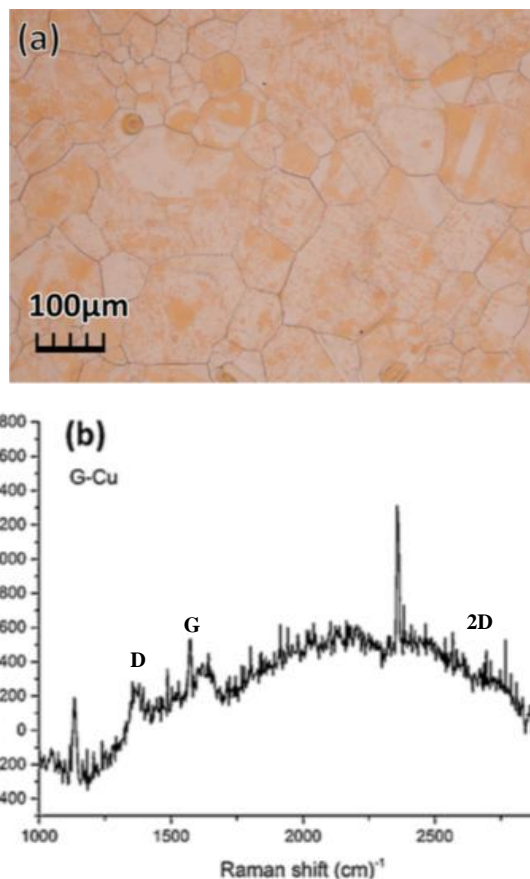


Fig. 3 (a) Optical microscope image of graphene on Cu surface and its alloy (b) Raman spectroscopy (Karamat *et al.*, 2016)

Significant findings on graphene domain size have been observed by Bhaviripudi *et al.* (2010) by synthesizing graphene on copper foil under atmospheric pressure CVD method. The size of nonuniform small domains were varied depending on hydrogen gas composition in the total gas flow (Fig. 4A-D). Similar results obtained by Li *et al.* (2009) using low pressure CVD showed that graphene domain sizes were not only relying on Cu catalyst during the synthesis process. Moreover, Bhaviripudi *et al.* (2010) verified that monolayer graphene domain size is capable of reaching up to 96% of the total area of the Cu surface by lowering the methane gas concentration in the total gas flow (Fig. 4E-H). At low concentration, methane as the source of carbons had been through unchainable C-bond process at very low rate by hydrogen composition. Hence, the incoming carbons precipitation and diffusion onto Cu surface were limited and suppressed the nucleation density of graphene, which lead to formation of large-scale graphene domain. This growth parameter setup also revealed suitable way to reduce grain boundary of graphene by controlling the growth rate of carbon. The results supported by the Raman D peak, which was significantly lower suggesting that it consists of high quality graphene.

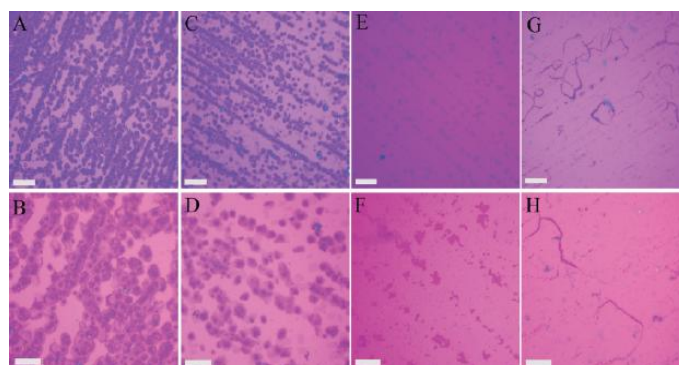


Fig. 4 Optical microscope images of graphene on Cu at different methane gas composition (Bhaviripudi *et al.*, 2010)

Another interesting discovery on the manipulation of Cu catalyst was applying etching pit process in generating defects on graphene network towards membrane and filter applications. Kidambi *et al.* (2017) shared their work by exposing Cu to iron chloride (FeCl_3) and ammonium persulfate (APS) in different concentration before dissolving it into deionized (DI) water. The size of the etching pits and chemical reaction gradually increased in time causing higher concentration of Cu^{2+} in solution (Fig. 5), also confirmed by Georgiadou and Alkire (1993), Bryce and Berk (1995). However, the average etch pits densities were reduced from 0.0225 to 0.0098 pits/ μm^2 due to merging process of nearby pits which lead to the decreasing pits densities (Kidambi *et al.*, 2017).

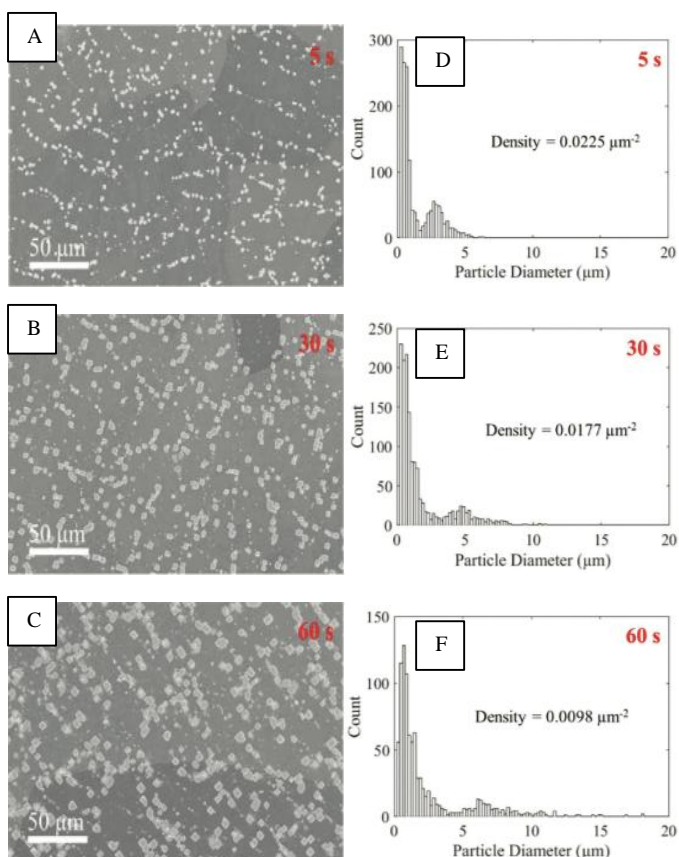


Fig. 5 SEM images showing the etch pits formed after FeCl_3 , 0.1 M in DI water for (A) 5 s, (B) 30 s, (C) 60 s and corresponding size distributions (D) 5 s, (E) 30 s, (F) 60 s (Kidambi *et al.*, 2017).

Recently, numerous researchers have reported the oxidation process of graphene grown on the Cu foil surface (Zhou *et al.*, 2013; Gan and Luo, 2013; Hao *et al.*, 2013; Miseikis *et al.*, 2015; Li *et al.*, 2015; Chen *et al.*, 2015; Suzuki *et al.*, 2015). Ding *et al.* (2016) revealed that the nucleation density of as grown graphene was significantly decreased with the presence of oxygen. Fig. 6 showed significant discovery reported by Ago *et al.* (2017) by AFM surface profiles, XRD analysis, and Raman spectroscopy characterization on the pristine and pre-oxidized samples of Cu foil. According to Fig. 6A, it is observed that the trend of the different height profile, in which reflecting the increased surface roughness after oxidation process. The height increment was most probably due to formation of oxide layer on the Cu foil. On XRD analysis, Cu (200) crystalline lattice structure peak appeared with high intensity for both samples. Ago *et al.* (2017) suggesting the predominance of (100) crystalline grains parallel to the copper surface. However, a very weak Cu_2O (111) peak was observed only on the pre-oxidized sample, signifying that the sample was exposed to oxygen. This result clarified that there was additional oxygen concentration appeared after oxidation process which also confirmed by from the Raman spectroscopy analysis. Similar results from Solache-Carranco *et al.* (2008) also agreed on the presence of

Cu_2O peak after the oxidation, which proving that the oxide layer was mainly consist of Cu_2O .

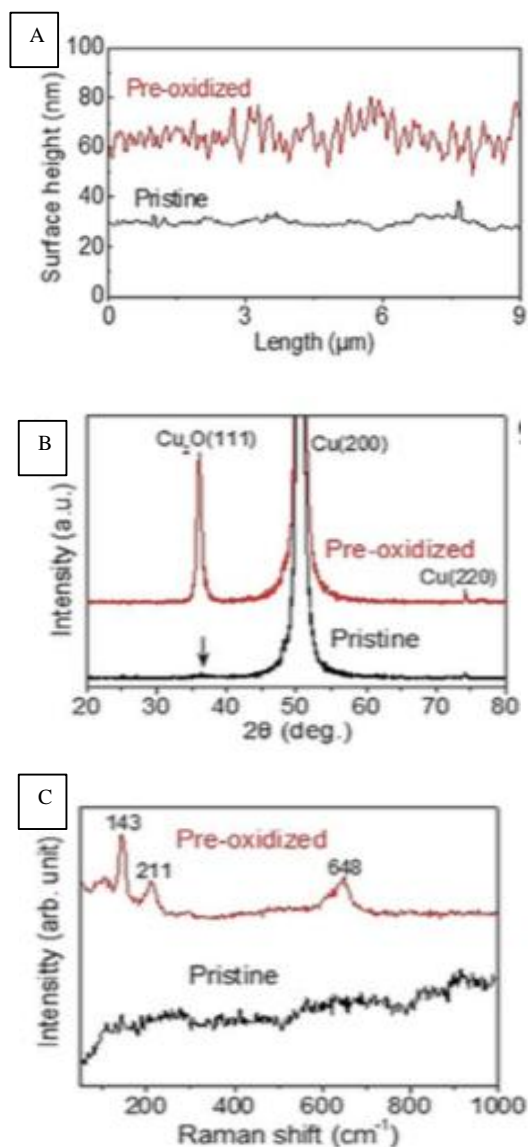


Fig. 6 Analysis results of pristine and pre-oxidized Cu foils on (A) surface height profiles, (B) XRD analysis, and (C) Raman spectroscopy analysis (Ago *et al.*, 2017).

NICKEL CATALYST

Ni is the common metal catalyst that typically used to synthesis a few layers of graphene. Aside from Cu catalyst, Ni catalyst have low reaction temperature, which is $< 900^\circ\text{C}$, significantly promoted towards low synthesis temperature of graphene. To our knowledge, the carbon solubility for Ni was reported at 0.37 % with reaction temperature 750°C (Yang *et al.*, 1990). Hence, Ni catalyst became one of the most trending metal catalyst for graphene in the electronic devices application field. However, the carbon solubility would increase up to 2.93 % with growth temperature around 1326°C (Mattevi *et al.*, 2011). Similar results were reported by Zhang *et al.* (2017) when the reaction temperature increased more than 1000°C to provide sufficient carbon source on the Ni thin film to synthesis graphene in CVD. Weatherup *et al.* (2012) reported that nickel has good reactivity towards thermal decomposition of hydrocarbons. This statement has been verified by Futko *et al.* (2016) demonstrating that decomposition of acetylene using Ni catalyst employed in CVD. There were a few reports focused on dispersion of metal particles in nickelocene precursor which act as vaporous catalyst to enhance the decomposition of carbon sources and increase the synthesis rate of graphene, simultaneously. Li *et al.* (2017)

stated that vaporous catalyst technique was capable in improving the synthesis rate by almost one magnitude and effectively lowering the energy barrier for fabricating graphene in comparison with benzoic acid-precursor method.

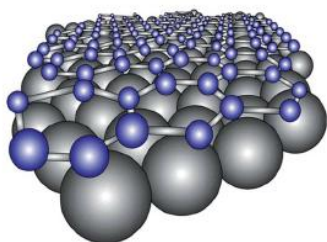


Fig. 7 The atomic arrangement of carbon atoms on the nickel crystalline (Peng *et al.*, 2013)

Apart from nickelocene precursor, methane is also relatively stable in synthesizing a few layers' graphene. Tian *et al.* (2017) reported that combination of Ni catalyst and methane in CVD method produced the vertically aligned graphene nanoflowers up to 10 μm with petals formed from two to seven layers of graphene. The fabricated graphene nanoflowers exhibited very rapid photodegradation of phenol, which exposed high catalytic activity properties that can only acquire from the Ni catalyst. These graphene nanoflowers were believed to have potential as photoelectrocatalysts for environmental remedial applications. In further studies, graphene nanoflowers were deposited using direct current (DC) arc plasma jet CVD with decomposition of Ni(NO₃)₂ (Ge *et al.*, 2015). The reaction temperature was fixed at 800 °C, which the optimum temperature for dissolved carbon to precipitate out and crystallized in the form of graphene centers. In this work, the Ni catalyst particles were dispersed uniformly through plasma on the graphene sheets simultaneously with methane decomposition. Huang *et al.* (2014) introduced an alternative for the Ni particles dispersion on graphene assisted with NiAl₂O₄ film, as shown in Fig. 8.

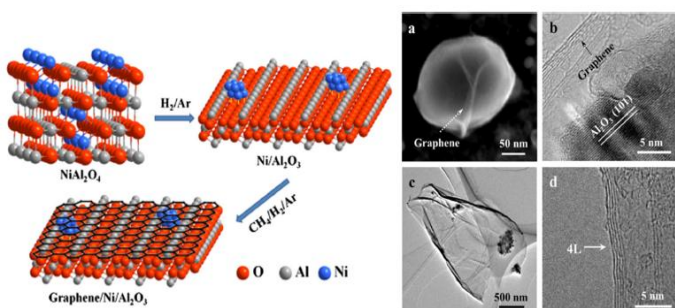


Fig. 8 Schematic diagram of graphene prepared using NiAl₂O₄ with uniform dispersion Ni particles on graphene for photoelectrocatalyst application. (a) SEM image of graphene growth on Ni particles, (b) HRTEM image of graphene direct growth on Al₂O₃, (c) and (d) TEM and HRTEM images of the freestanding graphene sheets (Huang *et al.*, 2014).

Ni particles play important functions to attract carbon atoms and accelerating the nucleation of graphene layers covered on Al₂O₃ film. The new formation of graphene domain has highly active edges to accept free carbon atoms which were decomposed from methane and gradually grow without the assistance of catalysts. Wang *et al.* (2017) stated that continuous graphene films exhibit tremendous electrical-transport properties with a sheet resistance smaller than 18.5 Ω/m.

Some of the earlier report discovered that liquid Ni-based metal catalyst that having small crystal lattice is good to produce high quality graphene (Zeng *et al.*, 2014; Ding *et al.*, 2013). Nanda *et al.* (2009) have utilized ultrathin metal film (20 – 130 nm in thickness) heated at slightly lower than its melting temperature to obtain micro-scale single crystal. Based on previous Nanda *et al.* (2009) work, Zhang *et al.* (2017) managed to fabricate micro-scale crystal lattice through CVD method with variation of the thickness at elevated temperature around

1000 °C (Fig. 9), which is significantly lower than the actual Ni melting point, 1460 °C.

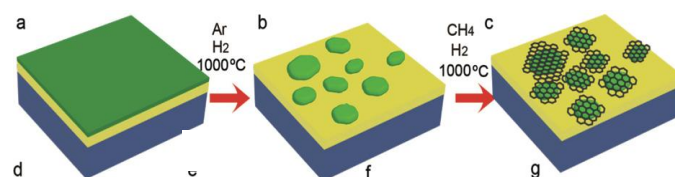


Fig. 9 Schematics diagram showing the microscale single crystal metallic thin film in CVD process: a) deposition of a Ni thin film on the top of a silicon substrate; b) formation of microscale thin film; and c) synthesis of graphene on the Ni microscale thin film (Zhang *et al.*, 2017).

Fig. 10 shows Raman spectra corresponding to the various Ni thin film thickness. It was observed that the graphene properties grown on 20 – 75 nm thin film thickness exhibited single layer characteristic, where the I_G/I_{2D} value was lower than 0.5. As the thin film thickness exceed more than 105 nm, the I_G/I_{2D} values were increased more than 0.5, which indicated that there was an additional layer of graphene. At Ni foil thickness (300 nm), multilayers graphene was detected with slightly shifted and broader 2D peak intensity.

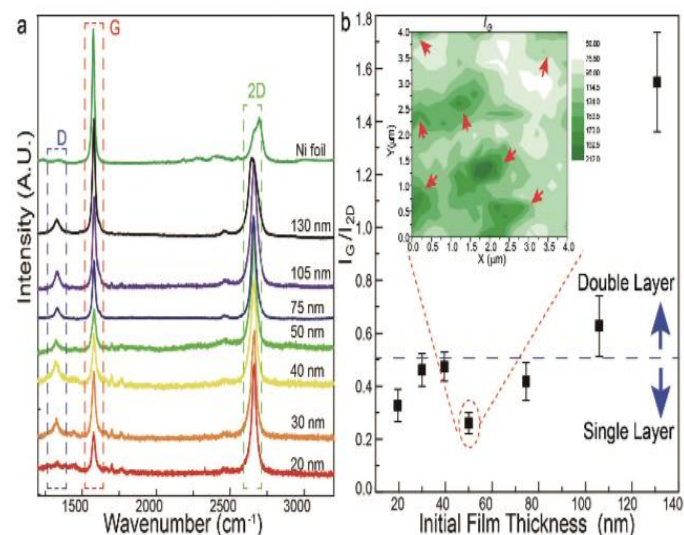


Fig. 10 (a) Raman spectra corresponding to graphene grown in CVD method on the variation thickness of Ni thin films at 20, 30, 40, 50, 75, 105, 130 nm, and a 300 nm thick Ni foil, respectively (b) I_G/I_{2D} versus the initial Ni film thickness calculated from (a) with mapping of G peak intensity (for film thickness, 50 nm). Red arrows denote possible Ni droplet sites (Zhang *et al.*, 2017).

This is one of the best explanation why it is so difficult to synthesis single layer graphene on Ni-based catalyst using CVD method which principally due to the grain boundaries in the Ni thin film. Generally, the common thickness of Ni thin films would attract extremely high diffusions rate of carbon atoms which end up in forming multilayers graphene. In addition, the prepared graphene was exposed to atomic fringes due to the deformation which will be occurred during the transfer process. Moreover, Cuxart *et al.* (2017) observed variation of graphene defects which synthesized on Ni foil using PECVD as shown in Fig. 11.

The color version of SEM images for sample 1 and 5 (as depicted in Fig. 12) show improvement on homogeneous graphene coverage with defect concentration reduced, which are in accordance with the findings captured in Raman spectra in Fig. 11. The bright region area in Fig. 12 revealed defects concentration, whereas the darker region area indicated a distinct homogenous multilayers graphene. However, the multilayers graphene growth was varying throughout the whole sample.

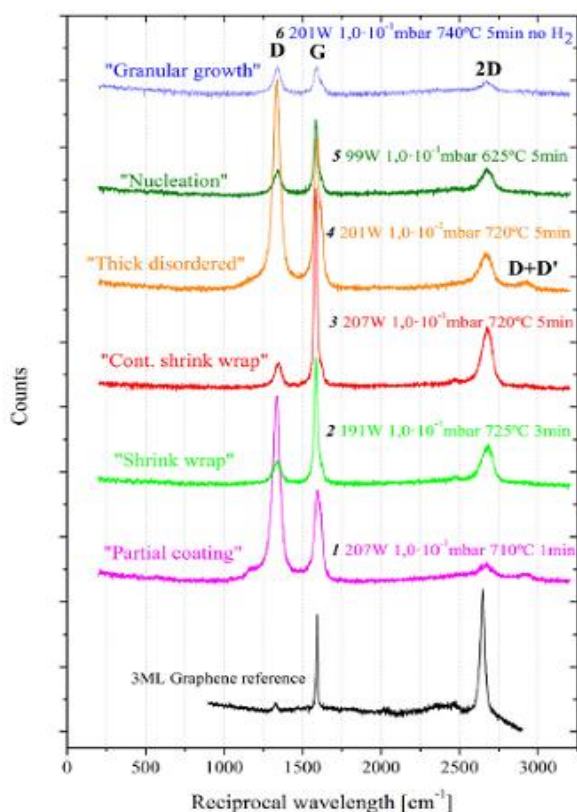


Fig. 11 Raman spectroscopy analysis on the variation of graphene's defects grown on Ni foil (Cuxart *et al.*, 2017).

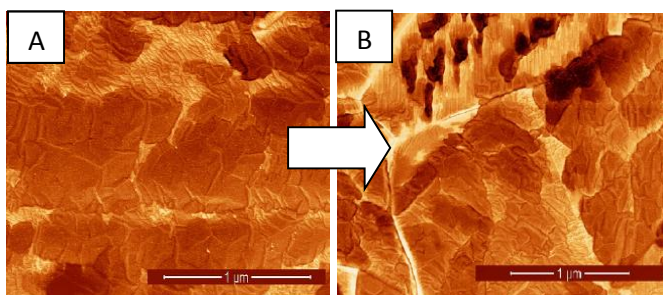


Fig. 12 Colour version of SEM images of (A) sample 1 and (B) sample 5 grown on Ni foil (Cuxart *et al.*, 2017).

Aiming towards large scale of graphene fabrication, Lee *et al.* (2012) tempted to successfully fabricated more than 1 mg of graphene through CVD method using mixture of 40 mg of Ni nanoparticles and polymethyl methacrylate (PMMA) as solid carbon source. Fig. 13 indicated that aggregation of as-grown graphene was not observed after Ni removal most probably due to formation of graphene wrinkles (Fig. 13B). This can be explained by the differential of thermal expansion coefficients between Ni and graphene (Kim *et al.*, 2009). Moreover, graphene wrinkles have potential to enhance mechanical properties and possible to induce its chemical activity based on density functional theory (Boukhalov and Katsnelson, 2009).

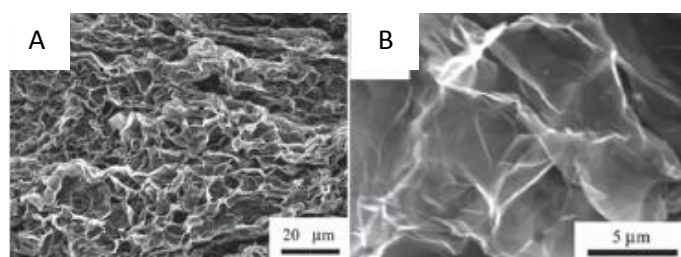


Fig. 13. SEM images of graphene after Ni removal (A) overview image and (B) high magnification SEM image of graphene wrinkles (Lee *et al.*, 2012).

Similar findings about graphene thermal properties which directly effect by the wrinkles size were observed by Du *et al.* (2008) and Chen *et al.* (2010) with different CVD subsequently at higher reaction time and lower the cooling rate. Ghaemi *et al.* (2017) clarified that the width and thickness of the graphene flakes would also increase respectively following to the mentioned parameters. This caused the graphene flakes to enlarge into graphene sheets without contamination thus suitable to cytotoxicity studies using human cells.

ALLOY-BASED CATALYST

Recently, many researchers are inspired to design new binary alloys to improve and grasp precise control of graphene layers' fabrication. One of the key factors to acquire high quality of graphene layers is by directional dissolution of carbon atoms into the atomic transition metals followed by the non-equilibrium diffusion process. Hence, transition metals with high carbon solubility such as Ni and Co are always be considered to synthesize graphene. However, the non-equilibrium diffusion process somehow contributed a drawback on dragging the excessive carbon atoms, which later critically affect the homogeneous graphene layers' formation. Concerning on this problem, Reina *et al.* (2009) proposed to utilize slow cooling process on metal thin films in CVD method effectively to suppress excessive carbon precipitation. Iwasaki *et al.* (2011) demonstrated a successful technique to synthesis free defects single layer graphene supported by Raman I_{2D}/I_G value range 0.4 – 0.5 (Fig. 14b) using Ni – Mo binary alloy. Yang *et al.* (2015) also believed that binary alloy technique would limited the carbon diffusion in CVD method.

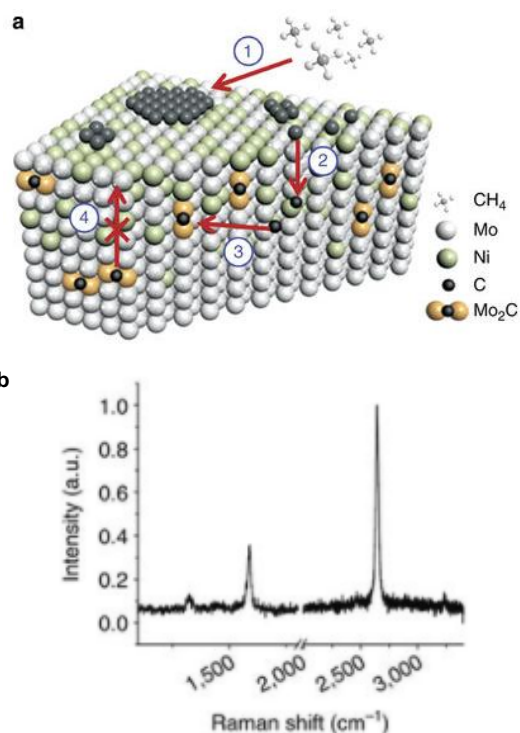


Fig. 14 (a) Schematic drawing of a designed binary alloy for single layer graphene growth in CVD method by suppressing carbon diffusion that was demonstrated by Ni – Mo binary alloy model and (b) Raman spectra of single layer graphene grown on Ni – Mo alloy (Dai *et al.*, 2011).

Similar work has been done by Papon *et al.* (2016) in investigating the effect of Cu – Ni binary alloy in the formation of N-doped bilayer graphene. Fig. 15(a) shows SEM images indicating that the synthesized graphene contains bright and dark regions with non-uniform layers. Consistent image was also observed after the graphene transferred on SiO₂/Si substrate as mention in Fig. 15(b). Raman spectra shows the intensity of G and 2D peaks in spot 1, the value is almost 1, which reflected to bilayer formation. At spot 2, the G, and 2D peaks were captured at 1570 cm⁻¹ and 2692 cm⁻¹, respectively (Papon *et al.*, 2016). The ratio between I_G and I_{2D} indicated multilayers formation.

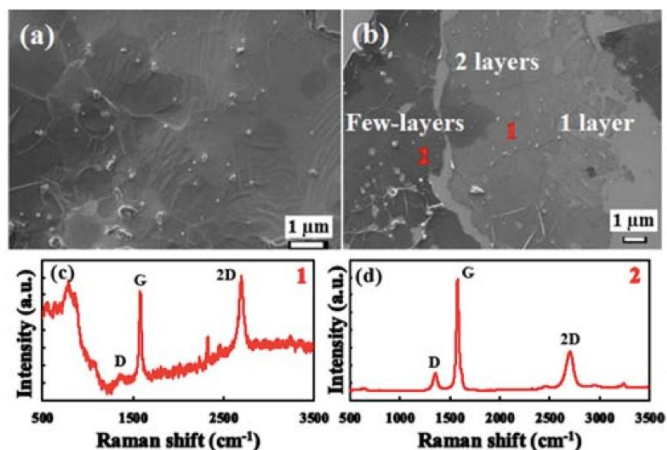


Fig. 15 SEM images of (a) synthesized graphene on Cu – Ni substrate and (b) as prepared graphene transferred on SiO₂/Si, (c and d) Raman spectra at positions 1 and 2, respectively (Papon *et al.*, 2016).

Recently, Takesaki *et al.* (2016) reported similar findings on Cu – Ni binary alloy. The formation of bilayers and multilayers graphene on Cu – Ni binary alloy were believed contribute by the growth temperature constant with Ni composition (Takesaki *et al.*, (2016). The increment of growth temperature would simultaneously create more uniform bilayers graphene and improved the crystallinity of Cu – Ni binary alloy.

In other fascinating work, Ding *et al.* (2013) improved graphene layer's thickness and domains quality by adding a portion of Cu, Silver (Ag), and Ni into the Indium (In) and Tin (Sn) liquids to form a mixture of liquid metals alloy catalyst. The Raman spectra of graphene grown on the substrates consisting of different low-melting-point metals (In and Sn) and alloys (Sn – Ni, Sn – Cu, and Sn – Ag – Cu) are shown in Fig. 16. The continuous of single and bilayers graphene can be achieved on In and In-Cu substrates with a low D peak in Raman spectra, whereas on Sn and Sn – Ag – Cu substrates the grown-graphene shows significant defects. On the Sn – Ni alloy substrates, very thick graphite was detected however no D peak in the Raman spectra. These preliminary results indicated that Ag, In, and Sn liquids have good catalytic ability to synthesis graphene, and it is possible to synthesis high quality graphene on these metals alloy liquids at high growth temperature assisted with systematical optimization (Ding *et al.*, 2013).

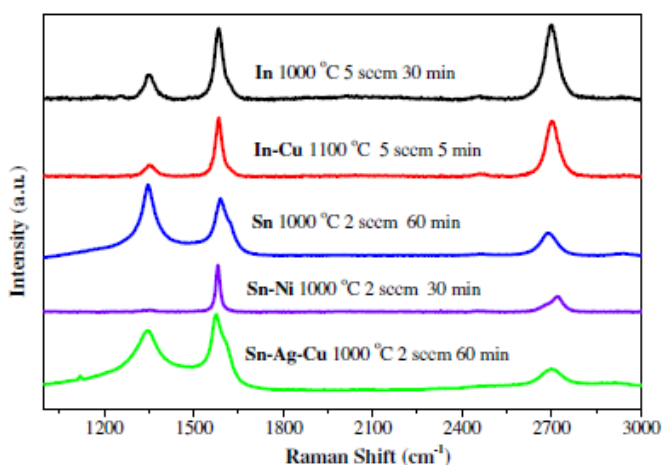


Fig. 16 Raman spectrum analysis of the graphene grown on different low-melting-point metals (In and Sn) and alloys (Sn – Ni, Sn – Cu and Sn – Ag – Cu). The CVD system was H₂-free, with only 200 sccm argon (Ar) (Ding *et al.*, 2013).

CONCLUSION

In this review, it is believed that the carbon solubility of Cu and Ni were huge contributing factor in graphene growth. The usage of Cu, Ni,

and other alloy combinations played an important role as catalysts for the decomposition of hydrocarbon. The growth mechanism of CVD process provides enormous variation of the graphene, in which suit with the application requirement. In summary, the reaction temperature needed to synthesize graphene using Cu was relatively high compared to binary alloy or Ni. However, it is easier to gain single layer of graphene using Cu due to its low carbon solubility. To this date, many researchers preferred to growth single layer of graphene because of its interesting characteristic of zero electron mobility, in which meets future nanodevice fabrication. As of Ni, its grain boundary characteristic would attract more carbons and accelerate nucleation of graphene. As a result, the multilayer of graphene is formed. In comparison with alloy, there is massive composition of alloy that would provide solution for the formation of graphene layer. It is because the utilization alloy-based catalyst is not only relying on diffusion of the carbon. In fact, its non-equilibrium state of alloy also playing vital role to obtain, either single or multilayer of graphene.

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