Sequential synthesis of free-standing high quality bilayer graphene from recycled nickel foil

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ABSTRACT

The recycle and reuse of catalyst is an active research area motivated by the reduction of graphene production cost. Our process is derived from the conventional CVD method widely utilized for graphene synthesis. It allows the formation of uniform bilayer graphene by limiting the segregation of carbon. The relatively thick foil of Ni used as catalyst plays a crucial role in solubilizing and trapping large amount of carbon adatoms. The trapping mechanism is enhanced by the high-speed cooling subsequent to the growth stage. Segregation of carbon is then efficiently quenched and uniform bilayer graphene could be prepared. The separation process is also optimized thanks to a protective effect from the nickel carbide (Ni₃C) formed. We show that Ni₃C minimizes the catalyst lost due to the separation of graphene and it also facilitates the graphene separation process. The Ni foil could be recycled up to 6 times without significant variation in number of layers and perfectness in crystallinity of the obtained bilayer graphene. Besides, we discuss of the role playing by the roughness of the catalyst surface for bilayer graphene separation in our process.

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1. Introduction

Graphene is made up of a single or few layers of sp²-bonded carbon atoms arranged in a two-dimensional honeycomb structure [1]. Graphene is an attractive material due to its remarkable electronic properties. The recent advances in the synthesis of large-area graphene have opened up a post-silicon era. Among many methods ever reported, Chemical Vapor Deposition (CVD) and sublimation of SiC are currently the most favorable approaches for obtaining graphene in wafer-scale. CVD has attracted much more attentions than other methods attributing to its simpler synthesis process and easier in its subsequent separation of graphene from the substrate [2]. The transfer of graphene from its original substrate to the arbitrary substrate without deteriorating graphene crystallinity is a

challenging task. To date, the majority of researchers are still either using the wet-chemical etching or the mechanical exfoliation for separation of graphene from its substrate. Mechanical exfoliation would impose severe mechanical defects onto the basal plane of graphene. On the other hand, wet-chemical etching is more preferable as the process would cause fewer defects to the graphene sheets. However, the catalyst (substrate) will be consumed during the course of separation and it is impractical particularly when single crystal catalyst is used to grow graphene. Therefore, reuse and recycle of catalyst is necessary; but, due to the difficulty in the controlled etching of catalyst foil, the reports on the reuse of catalyst for synthesizing wafer-scale graphene are rarely found. Sophisticated approach, that utilizing electrolysis cell to delaminate the graphene from Cu and Pt foils was demonstrated recently [3,4]. Three cycles of repeated growth and separation of graphene over Cu foils were successfully carried out [3]. When Pt foils were used, the authors could repeatedly grow graphene on the same Pt foil over 100 times [4]. To preserve the graphene crystallinity, oxidative

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decoupling transfer which is an improved delamination process was also demonstrated [5]. However, all the aforementioned approaches are relatively complicated and involved multiple process steps.

Cu and Ni are the two common catalysts used for the growth of graphene through CVD. The formation of monolayer graphene is easier to be achieved with Cu as the Cu possesses lower carbon solubility. On the other hand, Ni has relatively higher carbon solubility as compared to that of Cu and the solubility of carbon into the bulk Ni at 900 °C is ca. 0.9 at% [6,7], meanwhile almost no carbon can “dissolve” into Cu [8]. During the cooling process after the growth of graphene, the carbon would segregate out from the Ni catalyst to form mainly multilayer graphene. Moreover, the bonding between Ni and graphene was calculated to be the mix of chemisorption and physisorption with high adhesion energy [9], making it hard to separate graphene using mechanical approach. On the other hand, the graphene formation mechanism over Ni catalyst is highly debatable. It was proposed that Ni₂C is formed in the CVD, which led to the formation of graphene on the surface of Ni [10–12]. However, this theory is not agreed by some researchers [13–15]. Meanwhile, the presence of other form of metastable carbide with the formula of Ni₃C is generally unnoticed. In this paper, we demonstrate for the first time to our knowledge a simple method to enable the recycle of Ni foils for repeated growth of wafer scale bilayer graphene, which is more difficult to grow as compared with monolayer graphene through applying rapid cooling after the CVD. We show that Ni₃C formed under a very rapid cooling stage plays the role as a protection layer for the Ni foils from excessive etching by etchants.

2. Experiment section

Nickel (Ni) foil (99.9% purity, Sigma–Aldrich) with a thickness of ca. 125 µm and polycrystalline surface was cut into 10 mm × 10 mm and used as the catalyst to grow bilayer graphene. The graphene was synthesized by CVD and the detailed set-up was reported earlier [16,17]. The detail of the furnace setup and the strategy to enable the very rapid cooling is shown in [supporting information \(Fig. S1\)](#). Generally, the Ni foil was placed in a quartz boat and then located at the center of the furnace. The Ni foil was then heated from room temperature up to 900 °C with a heating rate of 10 °C/min. During the heating, high purity H₂ gas (99.999%) with a flowrate of 80 sccm was flowed into the quartz tube to reduce the oxide present on the Ni surface. As the desired temperature was obtained, high purity CH₄ (99.999%) was fed into the reactor at a flowrate of 20 sccm, the H₂ flowrate remaining the same. After 5 min of reaction, the quartz boat along with the Ni foil was displaced from the heating zone to ambient temperature zone for rapid cooling. The temperature of the Ni foil was cooled to 50 °C in roughly 10–15 of seconds; the average cooling rate for the Ni to room temperature (30 °C) was estimated to be higher than 900 °C min^{−1}. At the same time, CH₄ and H₂ gases were switched off and N₂ gas (99.999%) subsequently introduced into the quartz tube to quench the reaction.

Once the temperature cooled to room temperature, the graphene/Ni was taken out from the reactor for graphene separation process. 2 different etchants namely aqueous iron (III) nitrate and nitric acid with different concentrations, by diluting nitric acid (65%, Merck) and iron(III) nitrate nonahydrate (>99.95%, Sigma–Aldrich) were used. 4 edges of graphene/Ni foil were scrubbed with sand paper (800 mesh) to provide the opening for direct contact between Ni and the etchant. It was then floated on nitric acid and aqueous iron nitrate solution. After the graphene and Ni were separated, the iron nitrate and nitric acid were diluted with huge amount of DI water to minimize the contamination on the

graphene sheet. It was then transferred onto silicon/silicon oxide (1000 Å) wafer for characterization. Meanwhile, the remaining Ni foil can be easily removed from iron nitrate solution or nitric acid and rinsed with DI water. The surface of Ni was polished with sand paper to obtain a smooth surface and later placed into the reactor for the subsequent reaction. These steps were repeated until the Ni foil was too thin to be handled by hands or holes were observed.

High Resolution Transmission Electron Microscope (HRTEM) image of the graphene samples were taken by Tecnai 20 at 200 keV (Fei company). A Reinshaw inVia Raman Microscope with laser excitation of 633 nm was used for the point-based Raman spectroscopy. Meanwhile the Raman mapping was carried out by a Horiba LabRAM HR 800 micro-Raman spectrometer with the same laser. Atomic Force Microscopy (AFM) analysis was performed using a Park System XE-100. Meanwhile for the X-ray Diffraction (XRD) analysis, it was completed with INEL CPS120 with cobalt K-alpha X-ray for a scan range 2θ of 0–110°. XPS analysis was achieved in a conventional VSW apparatus equipped with a monochromatic Al source and a 150 mm hemispherical electron detector. The binding energies were calibrated with Ni 2p_{3/2} line at 852.3 eV. Core level spectra are recorded with an experimental resolution of 0.65 eV. Ni₃C compound in low amount in the samples was unstable under the X-ray beam. Therefore its detection without evolution was only possible at low incident power (240 Watts) for the sample before separation.

3. Results

A facile approach was proposed to transfer bilayer graphene from Ni foil. Firstly, the graphene/Ni substrate after CVD was scrubbed with sand paper at its 4 edges. The purpose is to expose Ni to the etchant during the separation stage. To prevent unnecessary contamination, we avoided coating of protective layer on the bilayer graphene. The sample was directly “floated” on the surface of the etchant solution (nitric acid). The nitric acid etched and intercalated between Ni foil and bilayer graphene started from the edge to the center ([Fig. 1\(a\)](#)). Graphene is highly hydrophobic, and thus it will not submerge into the nitric acid. On the other hand, the Ni foil with high density tends to sink. The sinking of the Ni foil in the solution provided a gentle force in tearing the graphene from the Ni foil. Eventually the bilayer graphene and Ni foil was totally separated ([Fig. 1\(b\)](#)), but the edges of bilayer graphene were slightly deteriorate. The concentration of nitric acid plays a very important role to preserve the Ni foil and also the graphene as well. A vigorous process would etch away quite large amount of surface layer of the Ni foil. If high concentration of acid is applied, it will etch away the whole Ni foil rapidly. At the same time, the hydrogen bubbles formed during the vigorous oxidation of Ni foil could subsequently break the bilayer graphene on top into small pieces. If the concentration of acid is too low, the separation process becomes very slow. The whole Ni foil especially at the edges exposed to acid at longer period would suffer damage and be unable to be reused as catalyst. From our study, nitric acid with concentration of 1.44 mol/L (6.5%) was a good compromise to preserve the Ni substrate. However, we could reuse the Ni foil only twice; after that, the Ni foil was too thin to be able to be handled by hand. The thickness of remaining nickel foil after the first separation was of 75 µm and after the polishing process only 52 µm left. The nickel foil was completely etched away during the second cycle. Furthermore, the overall uniformity of the grown bilayer graphene at the second cycle was not comparable with that obtained at the first cycle.

Considering that the etching capability of iron nitrate solution is relatively weaker compared with nitric acid, we further explore the possibility of recycling of Ni foil if iron nitrate solution was applied for bilayer graphene separation. [Fig. 2\(a\)](#) shows the process of

Fig. 1. Separation of bilayer graphene from Ni foil by nitric acid. (a) Intercalation and etching of Ni foil at the beginning of the process. (b) Completely separated bilayer graphene from Ni foil that is submerged into nitric acid. The separated graphene is in the white box. (A colour version of this figure can be viewed online.)

Fig. 2. (a) The progress of the bilayer graphene separation from Ni foil after the graphene/Ni floated onto iron(III) nitrate solution. The separated graphene is in the white box. (b) Image of six bilayer graphenes that transferred to silicon wafer with 1000 Å oxide obtained from their respective cycles. The white boxes are indicating the locations of graphene on respective silicon substrate. (c) HRTEM image for bilayer graphene separated under the sixth cycle. (A colour version of this figure can be viewed online.)

graphene separation from Ni foil under the interaction of iron nitrate. The observed behavior was different than that shown for the separation through nitric acid (Fig. 1). From Fig. 2(a), a “white zone” started to appear at the edge of the foil between bilayer graphene and Ni; it resulted from the intercalation and partial etching by iron nitrate solution. The strong interaction between bilayer graphene and Ni was obviously broken and the “white zone” was enlarged with time and eventually it covered all the Ni foil. Meanwhile, the weight of Ni applied a gentle force to tear the graphene from Ni foil during it sinking. The same phenomenon was observed regardless of how many cycles the Ni foil was used for CVD and the subsequent bilayer graphene separation. From our current study, we managed to recycle the Ni foil up to 6 times and the graphene samples were shown in Fig. 2(b). Under characterization of HRTEM, we found that the graphene synthesized under sixth 6th cycles was mostly bilayers (Fig. 2(c)). Meanwhile, HRTEM images were taken at other random spots in the sample, and all giving 2 parallel straight lines characteristic, which is typical observation for bilayer graphene (Fig. S2(a–c)). Meanwhile, regarding the use of iron nitrate, the concentration of 0.50 mol/L was the most efficient for the

separation. Further increase of the concentration of iron nitrate solution did not give any significant enhancement for the process and a lower concentration (0.25 mol/L) did not favor the intercalation mechanism even after several days.

From Raman spectroscopy analysis, three primary peaks at $ca.$ 1350 cm^{-1} , $ca.$ 1600 cm^{-1} and $ca.$ 2680 cm^{-1} indicates D-band, G-band and 2D-band respectively. Fig. 3(a) containing all 6 Raman spectra of graphene under 6 cycles of separation, it is clear that the peaks for D-band are very weak as compared to G-band, indicating the high crystallinity perfectness of the graphene [18]. For all 6 spectra, the ratio of I_{2D}/I_G is in the range of 0.979–1.352, meanwhile the full width half maximum (fwhm) in the range of 40–50 cm^{-1} , within the range for bilayer graphene [19–21]. To further verify the uniformity of the graphene, Raman mapping was carried out at the graphene grown under the sixth cycle (Fig. 3(b) and (c)). The fwhm in the range of 43–46 cm^{-1} , while the ratio of I_{2D}/I_G is in the range of 1.03–1.35, suggesting the present of uniform bilayer graphene, in agreement with the observation obtained by HRTEM (Fig. 2(c)), irrespective to the number of time that the catalyst has been recycled. Sheet resistance of the bilayer graphene was also tested

Fig. 3. (a) Raman spectra for six bilayer graphene samples after separation from Ni foil and transfer onto a silicon/silicon oxide wafer. Raman maps of (b) $fwhm_{2D}$ and (c) I_{2D}/I_G of the bilayer graphene grown under the sixth cycle. (A colour version of this figure can be viewed online.)

with a four-point collinear probe method (refer to [supporting materials Fig. S3](#)). The sheet resistance was around 774 Ohm/sq which is comparable with the values reported in previous report for stacked bilayer graphene [22]. One to notice, the graphene obtained after different cycles of reaction and separation, the crystallinity and the number of graphene layers are consistent.

The remaining Ni foil after underwent the separation process with both etchant are shown in [Fig. S4](#). The surface of Ni foil after the separation using nitric acid is obviously different from the original Ni foil and that after the separation induced by iron nitrate solution. The surface of Ni foil became rough after in contact with nitric acid, especially at the edge of foil, due to the longer period exposed in acid and the formation of an oxidized layer. On the contrary, the surface of the Ni foil is seen like undamaged after being exposed to iron nitrate. [Fig. 4](#) shows the AFM surface morphology of the Ni foil surface before and after the separation process. The surface of Ni foil after separation using iron nitrate was highly preserved, no severe damage are evidenced ([Fig. 4\(b\)](#)), except a few small holes of around 1 μm . For Ni foil exposed to nitric acid ([Fig. 4\(c\)](#)), the observed surface was highly uneven with a lot of protrusions. The surface flatness of Ni foil is important for success of graphene transfer. Under calculation with the software, XEI come along with AFM, the surface roughness were 46.20 nm, 176.27 nm, 883.00 nm and 90.28 nm respectively for [Fig. 4\(a–d\)](#). If an

untreated Ni foil from separation process is directly used for the growth of following graphene, the separated graphene is highly contaminated with un-removed Ni particles observable by optical microscopy ([Fig. S5](#)). To minimize the contaminating Ni particles on the separated graphene and reduce the roughness of Ni foil, the surface of the Ni foil was polished with sand paper prior to graphene growth ([Fig. 4\(d\)](#)). The surface roughness was highly reduced after polishing (from 883.00 nm to 90.28 nm), so that more uniform and cleaner bilayer graphene could be obtained after subsequent CVD.

XRD pattern of the surface of nickel foil after graphene growth, and subsequent separation using iron nitrate solution or nitric acid are shown in [Fig. 5](#) (insert). As expected, the diffraction peaks with high intensity at $2\theta = 52.1^\circ$, 60.9° , 91.5° and 114.0° assigned to (111), (200), (220) and (311) reflection of the super-lattice of Ni (fcc). If the range of 40° – 52° was magnified ([Fig. 5](#)), less pronounced intensity peaks at $ca. 2\theta = 46.3^\circ$ and 49.1° which can be assigned to (110) and (006) peaks of rhombohedral Ni_3C . They are well noticeable on the three shown patterns, especially for the substrate just after the CVD deposit and that after separation using the iron nitrate solution. A weaker diffraction peak is also visible for the sample after separation by nitric acid in agreement with the strong character of that etchant.

Ni_3C was also evidenced by XPS. The recorded C1s core level

Fig. 4. AFM images for the (a) nickel foil before the CVD reaction, (b) the remaining nickel foil after CVD and the graphene separated with iron nitrate solution, (c) nickel foil after CVD and the graphene separated through nitric acid and (d) the nickel foil obtained from separation process and polished with sand paper (800 mesh). The dimensions for all the images are $15\ \mu\text{m} \times 15\ \mu\text{m}$. (A colour version of this figure can be viewed online.)

Fig. 5. XRD pattern of nickel foil after CVD (red), after the CVD and graphene separation using iron nitrate solution (blue) and after CVD and the graphene separation by nitric acid (black). (A colour version of this figure can be viewed online.)

displays two contributions, one at low binding energy around 283.8 eV (arrow in Fig. 6) appearing as a shoulder of the main line at 284.4 eV with a full width at half maximum (FWHM) of 0.8 eV, not far from the 0.65 eV of experimental resolution. The main line is attributed to graphitic carbon, here probably from the grown bilayer graphene. The low energy line can be assigned to nickel carbide with a binding energy in good agreement with the literature [23–25].

Fig. 6. C1s XPS spectra of the nickel foil after the CVD reaction; the arrow showing Ni_3C contribution.

4. Discussion

4.1. Graphene separation mechanism and cleanness of grown graphene

We have shown that as the surface of the Ni foil is relatively smooth, intercalation and mild etching by iron nitrate solution would be easier to take place between graphene and Ni foil surface.

The soft separation process is partly responsible for the graphene cleanliness (Fig. 7(a)). As nickel surface was exposed to nitric acid, the surface became highly uneven and full of protrusions resulted by the edge of grains of Ni (Fig. 4(c)). The conventional polycrystalline Ni foil is composed of numerous grains that are closely bounded. As reported by Zhang et al. [26], graphitic carbon could be accumulated in between the grains during the graphene growth stage. The presence of graphitic carbon probably weakens the interactions between the Ni grains and assists that way etchant to intercalate between the grains. This phenomenon is emphasized as nitric acid was utilized as etchant. The strong etching property of nitric acid attacks the surface of the Ni foil vigorously. Besides that, graphene usually mitigates the surface morphology of the catalyst. If an individual grain is over exposed, the interaction with neighboring grain is weakened leading to encapsulation of Ni grains by graphitic layers. Graphene is indeed known to strongly interact with Ni due to hybridization between π orbitals of graphene and d_{z^2} states Ni [27,28]. The spacing between graphene and Ni surface is thus reduced and was calculated as low as 2.11 Å [29]. It was reported that the π -band structure of graphene could not be found in the first two layers [30]. In that case, interaction between protruded grains and the foil is expected to be highly reduced. The graphitic layer prevents the encapsulated particles from being etched and results in high Ni residue on the transferred graphene (Fig. 7(b)). Encapsulated Ni particles were widely observed under HRTEM for graphene grown from Ni foil with rough surface (Fig. S6). We have shown that Ni residue on graphene could be minimized by a simple polishing process applied to the Ni foil using sand paper. The cleanliness of the transferred graphene could be preserved as Ni was smoothed under mild polishing conditions. It enabled the graphene separation to occur as illustrated in Fig. 7(a) and preserved the uniformity of bilayer graphene under various cycles.

4.2. Protecting effect of nickel substrate by nickel carbide

As already mentioned, acid and aqueous iron solution are widely used for the separation of graphene from both Ni or Cu substrate and normally, the substrates are etched away completely [31–33]. Indeed, if pure metal foil is placed into the etchant solution, it is rapidly solubilized even with weak concentrations. Interestingly, in our study, the etching rate of Ni was significantly reduced which allowed the Ni foil to be reused several times. Ni_3C is known to offer good protection against corrosion. Ni_3C was already reported in several patents for its use as an insulating layer covering Ni in order to inhibit oxidation and other chemical reactions [34–36]. Hence, Ni_3C probably plays a crucial role to enable the reuse of Ni foil. From the Ni–C phase diagram, the concentration of the diluted carbon adatom in the bulk Ni is as low as 0.9 at% at 900 °C. Under our CVD conditions, the amount of formed Ni_3C is thereby expected to be small. The presence of small amount of Ni_3C was also reported to be formed during [37] and after [38] the CVD reaction. However, in most of the studies, Ni_3C was unfortunately unnoticed. We believe

that the evidenced Ni_3C present at the surface of our Ni foil after CVD could act as a shield to protect Ni foil from being fully etched by iron nitrate solution. It allowed the minimum loss of Ni foil during the separation process and permitted the reused of Ni foil for later CVD. But from Fig. 4(b), some etch pits observed on the surface of Ni foil, with the depth of around 1 μm , show that the Ni_3C layer is not uniform on the nickel surface. That could provide weak points for the etchant attack. Meanwhile if stronger etchant like nitric acid was used, this non-uniformed and thin Ni_3C could not preserve the perfectness of surface of Ni foil anymore. The presence of Ni_3C is vital to inhibit the excessive etching of the Ni foil by mild etchant. Several conditions are required for the formation of sufficient Ni_3C . It will be elaborated in subsequent section.

4.3. Graphene layer control by fast temperature quenching and formation of Ni_3C

It is widely accepted that graphene formation follows a bulk-mediated growth mechanism [2,39], whereas the concentration of carbon solubilized in nickel is relatively high compared with other catalyst. During the CVD process, the methane gas is catalytically decomposed at the surface of Ni foil and the carbon adatoms dissolve into bulk Ni (Fig. 8(a)). The nucleation process of graphene starts as the carbon concentration has achieved or above a threshold, especially during the cooling process (Fig. 8(b)). Referring to Ni–C phase diagram, the carbon solubility in bulk Ni decreases with descending temperature, the excess of carbon would segregate from Ni upon cooling. Fe, Co and Ni are among transition metals that are known to easily form carbides after expose to elevated temperature with carbon source [40]. The presence of Ni_3C is however rarely reported in the area of the Ni-catalysed CVD for the graphene synthesis. Presence of Ni_3C is commonly reported at the surface of core-shell Ni– Ni_3C nanoparticles in the carbon nanotube (CNT) samples [41–43]. The growth conditions of CNTs and graphene differ especially regarding the control of dissolved carbon adatom into the bulk metal catalyst. Large amount of dissolved carbon adatom is favorable to increase the yield of CNT formation. Meanwhile, for graphene synthesis, the dissolved carbon is commonly lowered either through vacuum CVD [44], utilizing low ratio of carbon precursor to dilution gas, with very thin nickel film as catalyst [45] or introduce inhibitor in the system [15]. Under these conditions, carbon atoms could segregate and precipitate at the surface of Ni with the optimum level and lead to formation of monolayer or bilayer graphene which has the higher research value. Conversely, in our CVD process, the ratio of carbon precursor to dilution gas is 0.25, which is much higher as compared to those usually reported for the growth of monolayer or bilayer graphene, for example 0.02 [44] or 0.04 [26]. Under our high carbon precursor concentration, the number of graphene layers was minimized to 2 by the very fast cooling we used. In comparison to other reported works with fast rates in the range of 10–600 C min^{-1} [13,26,45,46], our average cooling rate is much higher ($>900 \text{ C min}^{-1}$). Fast cooling facilitates the quenching

Fig. 7. Schematic illustrating interaction and etching mechanism during the separation of graphene with (a) smooth surface and (b) corrugated surface. The particles indicating the Ni grains, black line represents the graphene layer and the arrows show interacting paths. (A colour version of this figure can be viewed online.)

Fig. 8. Schematic diagram of graphene and Ni_3C formation. (a) At elevated temperature, methane decomposes at the surface and carbon adatoms dissolve into Ni foil. (b) Graphene formation by segregation of carbon from Ni above a threshold during the cooling process. (c) Very rapid cooling: inhibition of carbon diffusion to the surface of Ni. Red circles indicating hydrogen, meanwhile black circle represent carbon atoms. (A colour version of this figure can be viewed online.)

process and reduces the amount of carbon atoms segregated, only carbon situated near the surface had enough time to segregate and form graphene. Meanwhile, diffusion of carbon atoms in the middle of the Ni foil is highly inhibited. They would eventually form Ni_3C , as evidenced by XRD and XPS (Figs. 5 and 6). Moreover, the thickness of the used Ni foil is quite elevated ($125\ \mu\text{m}$ instead of standard nanometer scale of thickness); leading to increase the amount of carbon atoms dissolved in nickel. At the same time, the longer diffusion path for the carbon adatoms certainly assists the trapping of carbon inside the Ni foil (Fig. 8(c)). This is the reason why presence of Ni_3C is more obvious for iron nitrate treated Ni foil (blue) compared with the spectra before graphene separation (red) in Fig. 5. The etching of surface metallic Ni favors exposition of Ni_3C to the surface. The fast cooling of Ni foil is the key step to create the necessary conditions for formation of Ni_3C and control of the number of layers of the grown graphene. It subsequently facilitates the reuse of catalyst if the right etchant is used for graphene separation. If the catalyst was cooled naturally along with the furnace, which took around 6 h, only multilayer graphene was obtained and the unable to carry out the reuse of catalyst. Most of the time, the Ni foils were fully etched away.

5. Summary

We have developed a very rapid cooling process for high-quality uniform bilayer graphene grown by Ni-catalyzed CVD growth. The proposed mechanism involves (i) bilayer graphene segregation quenching process, (ii) diffusion inhibition of the carbon dissolved inside the Ni foil and (iii) formation of Ni_3C responsible for graphene cleanliness and catalyst reuse. The presence of Ni_3C combined with the use of iron nitrate as soft etchant for the graphene separation enables the Ni foil to be reused again up to 6 cycles without causing huge deviation on the quality and uniformity of bilayer graphene. Ni_3C is indeed able to limit the etching effect of the Ni foil. We have also shown that the surface smoothness of Ni foil before CVD is crucial to ensure efficient separation of the grown graphene. A corrugated surface results in encapsulation of Ni grains on the graphene layer and makes the separation incomplete.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2015.09.073>.

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