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Single- and few-layer graphene growth on stainless steel substrates by direct thermal chemical vapor deposition

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Abstract

Increasing interest in graphene research in basic sciences and applications emphasizes the need for an economical means of synthesizing it. We report a method for the synthesis of graphene on commercially available stainless steel foils using direct thermal chemical vapor deposition. Our method of synthesis and the use of relatively cheap precursors such as ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) as a source of carbon and SS 304 as the substrate proved to be economically viable. The presence of single- and few-layer graphene was confirmed using confocal Raman microscopy/spectroscopy. X-ray photoelectron spectroscopic measurements were further used to establish the influence of various elemental species present in stainless steel on graphene growth. The role of cooling rate on surface migration of certain chemical species (oxides of Fe, Cr and Mn) that promote or hinder the growth of graphene is probed. Such analysis of the chemical species present on the surface can be promising for graphene based catalytic research.

 Online supplementary data available from stacks.iop.org/Nano/22/165701/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the most rapidly expanding disciplines of contemporary research is the science of graphene. Graphene is a flat single-layer of sp^2 bonded carbon atoms that are tightly packed into a two-dimensional (2D) honeycomb lattice, which is the basic building block for graphitic materials of all other dimensionalities, and traditionally used to describe the properties of such structures [1]. Though realized only in 2004, graphene research took the central stage within a short span of time, owing to its exotic physical properties [2]. Graphene has been proven to be a promising material for various applications. Recently, for example, 100 GHz transistors based on epitaxial graphene [3], hybrid materials with graphene enabled bandgap engineering [4], nanomats for next-generation catalysis and sensing [5], nanomeshes to

circumvent the problem of the zero bandgap which hampers its effective usage in electronics [6], heat conductor as well as heat removal quilts in high-power electronics [7], etc were demonstrated.

The earliest studies used graphene exfoliated mechanically using a Scotch Tape method from highly oriented pyrolytic graphite. Although the yield is very poor for this method, the quality of obtained graphene is high [8]. The influence of graphene, however, is yet to be felt in the commercial market, owing to the lack of mass production methods for the fabrication of high-quality, large-area graphene in usable quantities. Except for thermal chemical vapor deposition (CVD), most of the methods developed for the production of graphene are proven to be ill suited for the commercial-scale production, some being cumbersome and expensive while others result in poor or uneven quality of graphene [9]. Various substrates for growing graphene have been used in the recent past and some of these involve the use of an active metallic layer [9, 10]. Most notably, single- and bi-layer graphene

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coverage of up to 87% area on nickel films [11] and ~95% area single-layer coverage on copper foils [12] were reported. Analogous synthesis methods have been attempted in the case of carbon nanotubes (CNTs) and other nano-graphitic materials [13–15]. Alcohol based synthesis on catalytically active surfaces is a common synthesis strategy for making organized CNT assemblies [13].

A rapid growth of graphene on simple substrates, such as stainless steel (SS), without elaborate synthetic controls will help in the growth of graphene research. Although graphene synthesis on SS304 substrates has been reported, using microwave plasma CVD and the radio-frequency plasma enhanced CVD method, the carbon source remains CH_4 [14–16]. We have developed a thermal CVD method for the synthesis of graphene from single- to few-layers over large surface area using alcohol precursor (ethanol), which in comparison to CH_4 is economically cheap, and easy to handle and store. The custom-built horizontal split tube furnace allows us to cool the substrate by opening the furnace. Synthesis was achieved within ~10 min after flushing the setup. The grown material was characterized by confocal Raman microscopy/spectroscopy and x-ray photoelectron spectroscopy. Studies reveal that graphene growth is enhanced in specific regions and is retarded in others, depending on the surface chemical composition. This understanding may lead to the development of new catalytic surfaces for uniform graphene growth.

2. Experimental details

2.1. Sample preparation

A schematic of the CVD setup used for the synthesis of graphene is shown in figure 1. A 1 m long (35 mm ID) quartz tube, horizontally placed inside a hot wall, split tube furnace (designed locally and capable of reaching 1100°C), serves as the CVD reactor. The horizontal split tube furnace allows rapid cooling, simply by opening it. The substrate for graphene growth was 0.1 mm thick foil of SS304, cut into a size of $\sim 1\text{ cm} \times 1\text{ cm}$, which was supported on an alumina base plate. The reaction chamber was flushed using hydrogen (99.9% purity) at a pressure of little above 1 atm for 1 h to create a reducing environment. The same flow rate was used throughout the experiment. The SS304 substrates were used as received. Under H_2 flow, the temperature of the chamber was increased to the growth temperature, at a heating rate of $\sim 20^\circ\text{C min}^{-1}$. At the growth temperature, vapors of spectroscopic purity ethanol (EtOH, Changshu Yungyaun Chemical, (AR) 99.9% purity) carried by the H_2 flow were introduced into the quartz tube. After 10 min of reaction time, the furnace was cooled to room temperature, under H_2 flow, with various cooling rates from 40 to $200^\circ\text{C min}^{-1}$. The experiment was also repeated for various growth temperatures and reaction times. The prepared samples were removed from the quartz tube and used directly for various spectroscopic and microscopic measurements.

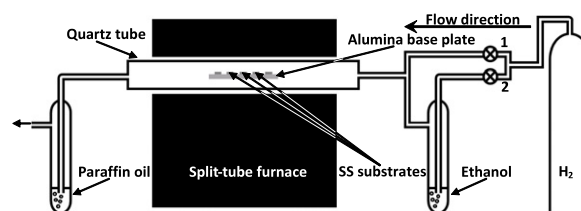


Figure 1. Schematic of the assembled CVD setup used for the synthesis of graphene. The outlet trap containing paraffin oil acts as a seal to prevent air from entering into the reaction tube.

2.2. Instrumentation

Confocal Raman measurements were performed with a WiTec GmbH Alpha-SNOM CRM 200 instrument having a 532 nm Nd:YAG laser as the excitation source. The excitation laser was focused using a $100\times$ objective, and the signal was collected in a backscattering geometry and sent to the spectrometer through a multimode fiber. The effective scan range of the spectrometer was $0\text{--}9000\text{ cm}^{-1}$ (which amounts to a wavelength maximum of 1020.70 nm for 532 nm excitation), with the detection efficiency falling above 750 nm. A super-notch filter placed in the path of the signal effectively cuts off the excitation radiation. The signals were then dispersed using a grating of $150\text{ grooves mm}^{-1}$ and the dispersed light intensity was measured by a Peltier-cooled charge coupled device (CCD). Raman imaging was performed using the same grating, with an integration time of 100 ms. Single-spot spectra were also acquired with larger integration times. For improved resolution and to ascertain the peak positions, a $1800\text{ grooves mm}^{-1}$ grating was used while acquiring single-spot spectra. The intensities of the desired portion of the spectra, collected over all of the pixels, were compared by Scan CTRL Spectroscopy Plus Version 1.32 software, to construct color-coded images. Also, the images corresponding to various features of graphene, namely D, G and 2D, were filtered from the image using WiTec Project 3.2.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an Omicron Nanotechnology ESCA Probe system with monochromatic $\text{Al K}\alpha$ x-rays (energy of 1486.6 eV). The x-ray power applied was 300 W. The survey spectra were collected at constant analyzer energy (CAE) of 50 eV and the detailed regions were collected at a CAE of 20 eV and were averaged 15 times. Measurements were performed at a base pressure of 10^{-9} mbar. The parent SS304 substrates alone were sputtered with Ar^+ ions (argon ions) at a base pressure of 10^{-6} mbar, to remove the oxide layers and other impurities from the surface of the sample prior to the XPS measurement.

Scanning electron microscopic (SEM) images and energy dispersive analysis of x-ray (EDAX) studies were carried out using an FEI QUANTA-200 ESEM with an EDAX system.

3. Results and discussion

Raman spectroscopy is established as the most accurate and easy tool to characterize graphene [2, 10–12], the number of layers and the presence of defects (quality), especially when

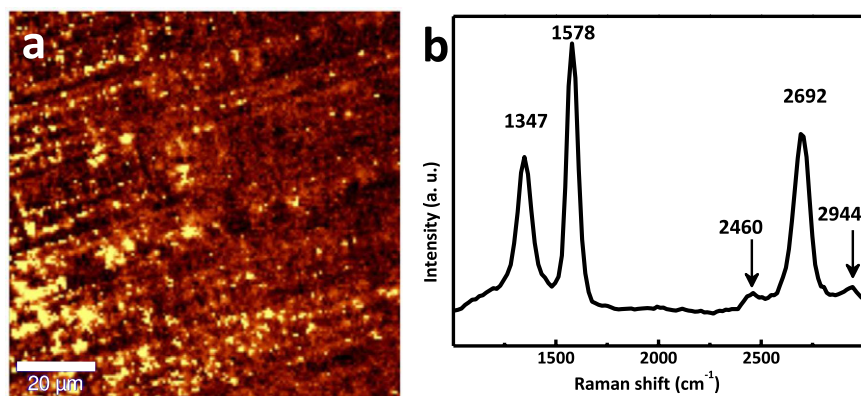


Figure 2. (a) Raman images corresponding to the graphene features (filtered for the 1300–2750 cm^{-1} range) from an area of $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ for a growth temperature, reaction time and cooling rate of 850°C , 10 min and $100^\circ\text{C min}^{-1}$, and (b) the corresponding average Raman spectrum from the 40 000 spectra, each of them corresponding to a pixel of the image.

the number of layers is less than 5 [17]. Figure 2(a) is the Raman image from an area of $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ from the grown graphene sample for a growth temperature, reaction time and cooling rate of 850°C , 10 min and $100^\circ\text{C min}^{-1}$, respectively. Figure 2(b), an average Raman spectrum of the prepared sample, shows the three most intense features at ~ 1347 , ~ 1578 and $\sim 2692\text{ cm}^{-1}$. These are identified as the Raman fingerprints of graphene, namely of D, G and 2D (or known historically as G') peaks. The G peak is from the first-order Raman scattering process and is attributed to the doubly degenerate in-plane longitudinal optic (iLO) and in-plane transverse optic (iTO) phonon modes (E_{2g} symmetry) of sp^2 hybrid carbons at the Γ -point, whereas the D and 2D bands result from second-order Raman processes. The D peak originates from a second-order process involving one iTO phonon and a defect at the K-point, and the 2D band is an overtone of the D peak involving two iTO phonons [18]. In addition, the D band is silent for infinite layers but becomes Raman active for a few layers with a substantial number of defects [18]. Thus, the presence of the D peak ($\sim 1347\text{ cm}^{-1}$) suggests that the formed graphene is disordered and has inherent defects in it. These defects may include vacancies and strained hexagonal/non-hexagonal (pentagon or heptagon) distortions that lead to the non-uniformity, corrugation and twisting of the layers, as shown in electron microscopic images (supplementary information, figures S1 and S2 available at stacks.iop.org/Nano/22/165701/mmedia). The low intensity peak at $\sim 2460\text{ cm}^{-1}$, known as G^* , is due to the intervalley double resonant Raman process similar to that of the 2D band but involving one LO and one iTO phonon [18]. Another weak feature at $\sim 2944\text{ cm}^{-1}$ is attributed to the combination of the D and G peaks [17]. Also, from figure 2 it is clear that the coverage of multi-layer graphene on the SS substrate is fairly large. Our piezo-driven scan stage limits the confocal Raman imaging to a maximum area of $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, though the graphene features were present throughout the substrate.

Optical image and Raman maps corresponding to various regions of the Raman spectrum are shown in figure 3. Closer examination of the spectrum reveals additional features not attributed to graphene, at ~ 559 and $\sim 686\text{ cm}^{-1}$, marked

collectively as in figure 3(b). The feature at $\sim 559\text{ cm}^{-1}$ is reported for Cr_2O_3 , formed by the high temperature treatment of SS304, while the feature at $\sim 686\text{ cm}^{-1}$ is reported for MnCr_2O_4 spinel [19–21]. Raman images filtered from the spectral regions marked c, d (D band), e (G band) and f (2D band) on the Raman spectrum in figure 3(b) are shown in figures 3(c)–(f), respectively. It can be seen that the intensity of the spot marked 1 in figure 3(c) is low (dark) and that of spot 2 is high, while the intensity of 1 is high and that of 2 is low in figures 3(d)–(f). Hence, it can be said that the peaks in regions c of figure 3(b) are mutually exclusive to those of the other three images, namely (d)–(f), as established beyond doubt from the Raman maps. This suggests that whenever the features at regions c are prominent, graphene features (at regions d, e and f) are quenched, and vice versa. Thus, depending on the compositional variation of SS304, we obtain Raman features of either metal oxides (such as Cr_2O_3 , MnCr_2O_4) or graphene predominantly.

In figure 4(a) a Raman image for a $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ area is shown, on which different regions have been labeled 1, 2, 3, 4 and 5. Spectra (with 150 grooves mm^{-1} grating) from these labeled regions of figure 4(a), along with that of graphite, are gathered in figure 4(b). The number of graphene layers is estimated from the intensities, shapes and positions of the G peak and 2D band. The Raman spectrum from the region 5 corresponds to the Cr_2O_3 and MnCr_2O_4 spinel. For further illustration, a high resolution Raman spectrum from the regions 1–4 and graphite with the 1800 grooves mm^{-1} grating is presented in figure 5. The I_G/I_{2D} ratios of the Raman spectrum from regions 1–4 and graphite are ~ 0.73 , ~ 0.91 , ~ 0.95 , ~ 1.21 and ~ 2.36 respectively, while the corresponding positions of the 2D band are ~ 2686 (full width at half maximum (FWHM) of ~ 32), ~ 2689 (~ 38), ~ 2693 (~ 42), ~ 2703 (~ 64) and ~ 2710 (~ 72) cm^{-1} . The Raman spectrum from region 1 shows the typical features of single-layer graphene such as an I_G/I_{2D} ratio ~ 0.7 and a symmetric 2D band centered around 2686 cm^{-1} , as shown in figure 5(b), with a full width at half maximum (FWHM) of $\sim 32\text{ cm}^{-1}$. This very low FWHM for the 2D band is comparable to the lowest reported [17]. Similarly, regions 2–4 correspond

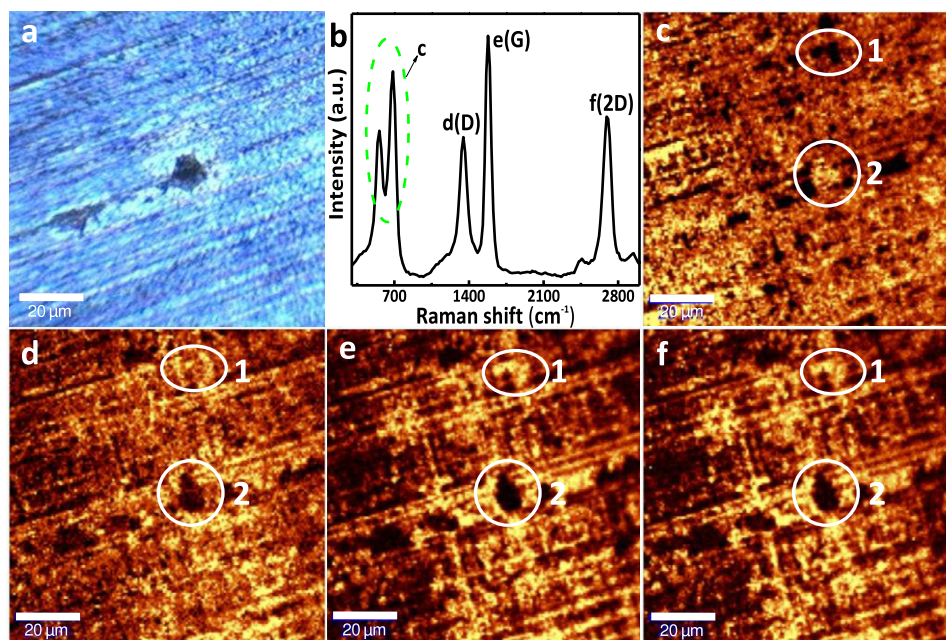


Figure 3. (a) Optical image; (b) single-spot Raman spectrum; and Raman images filtered from the regions (c) 540–695 cm^{-1} , (d) D band (1300–1400 cm^{-1}), (e) G band (1550–1650 cm^{-1}) and (f) 2D band (2650–2730 cm^{-1}) for a $100 \mu\text{m} \times 100 \mu\text{m}$ area.

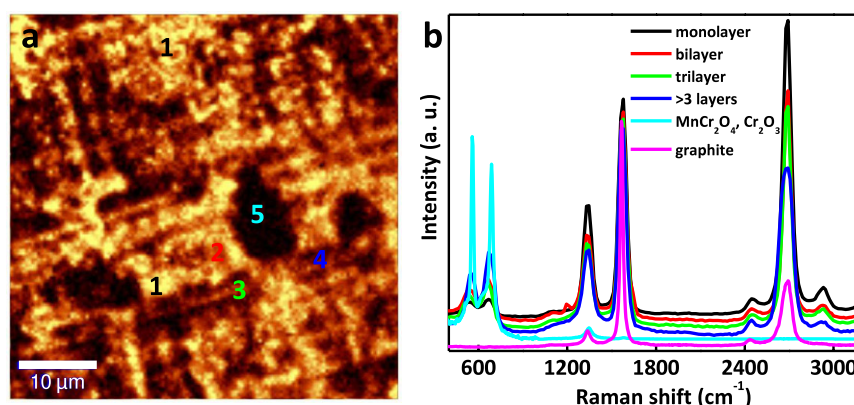


Figure 4. (a) Raman image (filtered for 2650–2730 cm^{-1}) showing areas of (1) single-, (2) bi-, (3) tri- and (4) multi-layers of graphene; the region marked 5 contains Cr_2O_3 and MnCr_2O_4 spinel. (b) The corresponding spectra with a 150 grooves mm^{-1} grating, after normalizing with respect to the G peak, for a $50 \mu\text{m} \times 50 \mu\text{m}$ area.

to bi-, tri- and multi-layers of graphene. This is evident from the broadening of the FWHM from ~ 32 to $\sim 64 \text{ cm}^{-1}$, accompanied by the red shift in the position of the 2D band from ~ 2686 for single-layer to $\sim 2703 \text{ cm}^{-1}$ for multi-layer graphene, as shown in figure 5(b). As the number of layers increases, the iTO phonon mode becomes branched, resulting in the broadening of the 2D band. For more than five layers, the Raman spectrum of graphene becomes hardly distinguishable from that of graphite [18]. The positions of the D and G bands remain the same for different numbers of layers, as evident from figure 5(a). The ratio of the intensities of the G band to the 2D band is more than the expected ratio of 0.25 for graphene transferred onto SiO_2 substrate. Such enhancement in the ratio suggests that the grown graphene is doped with electrons from the substrate [22]. This is evident from the high intensity of

the D band and the position of the 2D band, which for undoped graphene is $\sim 2680 \text{ cm}^{-1}$.

The graphene growth is found to be highly sensitive to various parameters, the most important being the growth temperature and the cooling rate. To explore the effect of both on the graphene growth, we have repeated the experiment at various growth temperatures and cooling rates (supplementary information, figures S3 and S4 available at stacks.iop.org/Nano/22/165701/mmedia). The optimum growth temperature to obtain maximum graphene coverage was found to be 850°C . At this temperature, the cooling rate was varied from ~ 40 to $200^\circ\text{C min}^{-1}$. At very high cooling rates ($\geq 140^\circ\text{C min}^{-1}$) no signatures of graphene were observed. At low cooling rates, Raman analysis of the samples showed features similar to those of graphite. Our analysis suggests that sedimentation

Table 1. Various chemical species present on the surfaces of PS and GS.

Element	Prominent feature	Sample type	Deconvoluted XPS components (eV)	Possible chemical species
C	C 1s	PS	282.8, 284.5, 285.7, 288.6	Metal carbide, adsorbed carbon, organic impurities and carboxyl group
		GS	285.2, 288.6	sp ² hybrid carbon and carboxyl
Cr	Cr 2p _{3/2}	PS	574.2, 575.9, 577.3	Metallic chromium, chromium carbide and CrO
		GS	575.9, 577, 577.9	Chromium carbide, MnCr ₂ O ₄ spinel and Cr ₂ O ₃
Mn	Mn 2p _{3/2}	PS	640.5	MnO
		GS	640.1, 641.3, 642.3, 643.5	Mn ₃ C, Mn ₂ O ₃ , MnO ₂ and MnCr ₂ O ₄
Fe	Fe 2p _{3/2}	PS	706.7, 707.9, 709	Metallic Fe, Fe ₃ C and FeO
		GS	710, 711.1, 712.4	FeO, Fe ₃ O ₄ and Fe ₂ O ₃
Ni	Ni 2p _{3/2}	PS	852.9	Metallic Ni
		GS	—	

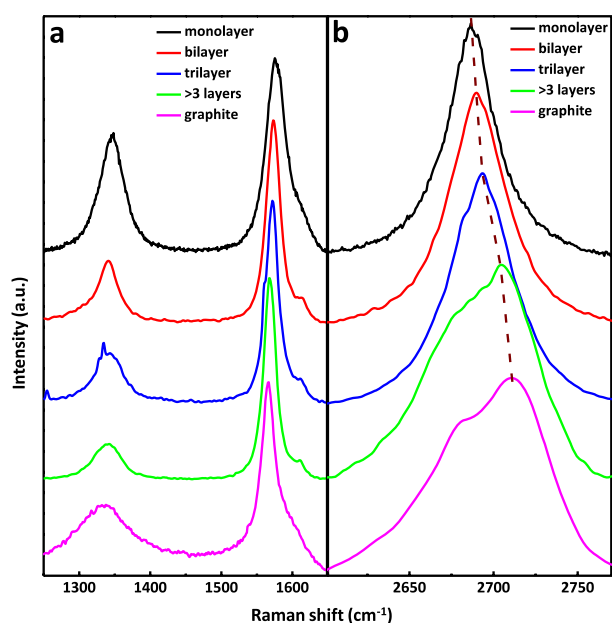


Figure 5. Evolution of the Raman spectra with increasing number of layers, measured using 1800 grooves mm⁻¹ grating. In (a) the D band is positioned at 1347 cm⁻¹ and the G band is positioned at 1578 cm⁻¹, without any considerable change with increase in the number of layers. In (b) the 2D band position undergoes a blue shift from 2686 cm⁻¹ for graphene to 2703 cm⁻¹ for multi-layer graphene along with an increase in FWHM from 32 to 64 cm⁻¹. The features corresponding to graphite are also included for comparison.

of carbon to form graphene was optimum at a cooling rate of ~100 °C min⁻¹. We have also conducted experiments with the SS304 itself, without any carbon source, as the carbon in SS304 itself can act as the source of carbon. However this yielded graphene with a very low coverage (supplementary information, figure S5 available at stacks.iop.org/Nano/22/165701/mmedia). The CVD method is economical and we suggest that the total time taken for the experiment can be reduced if the time required for flushing is reduced by employing a vacuum pump.

To understand the origin of the observed Raman features (mainly peaks at 559 and 686 cm⁻¹) and chemical nature of the surface, XPS and SEM-EDAX investigations were carried out. Figure 6 shows the XPS spectra of graphene grown SS304 (GS) and the parent SS304 (PS) substrates. The survey spectra,

figure 6(a), of both samples show characteristic elements such as C, Cr, Fe, Mn, Ni and Si along with O. The C 1s intensity of GS was higher than that of PS; the same is the case with Cr 2p and Mn 2p. However, the intensities of Fe 2p and Ni 2p were found to be very weak for GS, while they were prominent for PS. The GS surface showed characteristic features of oxides of Cr and the other constituent metals. For a detailed analysis, similar regions in the resolved and normalized spectra of both the PS and GS substrates were compared. The presence of elements in various chemical forms has been summarized in table 1 and briefly discussed below.

The deconvoluted C 1s spectrum of PS, figure 6(b), shows three distinct Gaussian features, indicating the presence of transition metal carbide(s), adsorbed carbon and organic impurities on the surface [23], while the C 1s spectrum of GS shows two features with the prominent feature corresponding to covalent sp² hybridized carbon [22, 24], confirming the presence of graphene, i.e., carbon in zero-valent state, whereas the other component shows the presence of carboxyl functional groups on the formed graphene. The Cr 2p spectrum of GS shows three features, indicating the presence of chromium carbide, MnCr₂O₄ spinel and Cr₂O₃ [22]. These are the two species (MnCr₂O₄ spinel and Cr₂O₃) which give rise to the distinct Raman features at 559 and 686 cm⁻¹ respectively.

The Mn 2p spectrum, figure 6(d), of PS shows the presence of MnO, while the same for GS shows a 2p_{3/2} feature with three components indicating the presence of Mn₃C, Mn₂O₃ and MnO₂, in accordance with the MnCr₂O₄ phase [22]. The assignment of the surface species corresponds to the most probable cases considering the available data. The data suggest that during the process of heating, Mn is migrating to the SS surface in the form of MnCr₂O₄ and other Mn oxides and hence increasing the Mn concentration at the surface [25]. This is also evident from the Mn 2p_{3/2} intensity of GS which appears to be negligible in the case of PS. The Fe 2p_{3/2} spectra, figure 6(e), of both the PS and GS substrates show a three component feature similar to those of the other transition metals. The spectral features suggest that GS is composed of oxides of iron: Fe₃O₄, Fe₂O₃ and FeO. FeO present on the PS acts as the source of oxygen for the oxidation of dissolved carbon to form CO, which is then disproportionate to graphite and CO₂ upon direct heating of the SS. In the case of alcohol as an additional carbon source, the CO required for the disproportionation can also be due to the pyrolysis of

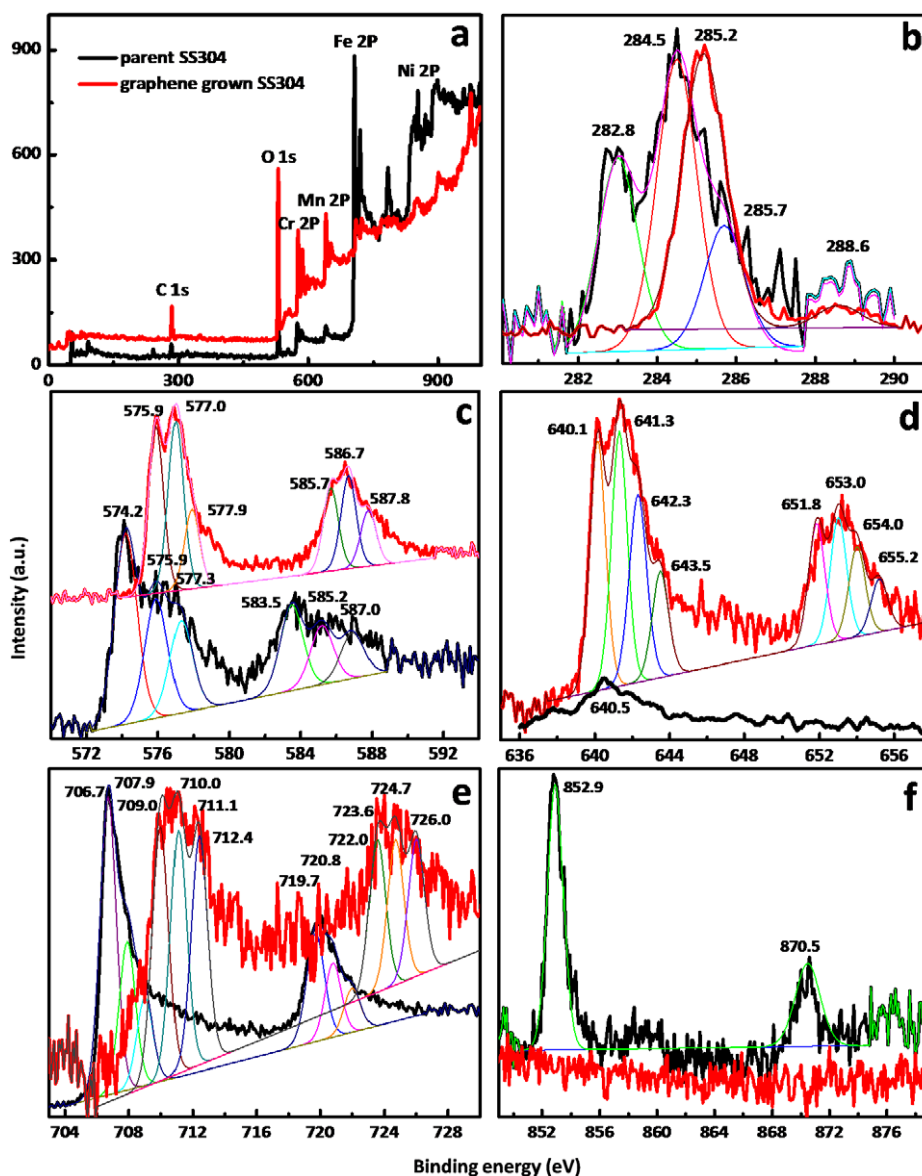


Figure 6. (a) The x-ray photoelectron survey spectra and the regions corresponding to (b) C 1s, (c) Cr 2p, (d) Mn 2p, (e) Fe 2p, and (f) Ni 2p for graphene grown and parent SS304 substrates, measured with monochromatic Al $K\alpha$ x-rays. The various components were fitted. The spectrum for GS was translated vertically upwards in (c) for better clarity.

ethanol. However, the presence of Cr or Mn species at the GS surface favors the formation of the MnCr_2O_4 phase or their respective metal carbides by reacting with the reduced carbon, thereby preventing the formation of graphene. Therefore, the cooling rate is crucial to have an optimum growth of single- or few-layered graphene. This is evident from the mutually exclusive nature of the peaks as established in figure 3. The Ni 2p region of the survey spectra, figure 6(a), of both PS and GS suggests the presence of metallic Ni in both [23], except that the surface concentration of Ni is very low to be detected by monochromated XPS, as evident from figure 6(f).

Thus it is evident that the surface of GS contains several oxides of transition metals, oxides of Cr and Mn in particular, namely Cr_2O_3 and MnCr_2O_4 spinel. These are in good agreement with the Raman data and are responsible for the two Raman peaks labeled as 'c' in figure 3(b). These species hinder

graphene growth, as evident from the mutually exclusive nature in the Raman images (figures 3(c)–(f)). The Raman and XPS analyses, along with the vibrational characterization of untreated commercial PS and GS, conclusively establish that the presence of excess Cr and Mn retards the growth of graphene, while FeO helps in forming the reduced sp^2 hybridized carbon and hence graphene. The role of a particular growth temperature and cooling rate on the formation of graphene can be justified by considering several competing events which are optimized at the given set of parameters.

4. Conclusions

The present study has shown that it is possible to grow highly organized graphene samples by a simple thermal CVD method, using a laboratory assembled setup. Our method of synthesis

using a hot wall split tube furnace and a relatively cheap substrate (SS304) and carbon source (ethanol) proves to be economical for the synthesis of graphene. The presence of single-, bi- and tri-layers of graphene over a large area is established by Raman spectroscopy and microscopy. Raman spectroscopic data in combination with XPS analysis suggest that some oxide species of Mn and Cr along with a spinel structured compound MnCr_2O_4 play a key role in the non-homogeneity of the formed graphene. The detailed knowledge of the chemical species present on the surface can be useful in preparing graphene based catalytic surfaces on SS304. The present studies may be extended to create an iron based catalyst system for single-layer graphene growth.

Acknowledgments

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