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To cite this version:

Pierre Trinsoutrot, Hugues Vergnes, Brigitte Caussat. Three Dimensional Graphene Synthesis on Nickel Foam by Chemical Vapor Deposition from Ethylene. Materials Science and Engineering: B, 2014, 179, pp.12-16. 10.1016/j.mseb.2013.09.018 . hal-03466842

HAL Id: hal-03466842

https://hal.science/hal-03466842v1

Submitted on 6 Dec 2021

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To link to this article : DOI:10.1016/j.mseb.2013.09.018
URL : http://dx.doi.org/10.1016/j.mseb.2013.09.018

To cite this version : Trinsoutrot, Pierre and Vergnes, Hugues and Caussat, Brigitte *Three Dimensional Graphene Synthesis on Nickel Foam by Chemical Vapor Deposition from Ethylene.* (2014) Materials science and engineering B, vol. 179 . pp. 12-16. ISSN 0921-5107

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Three dimensional graphene synthesis on nickel foam by chemical vapor deposition from ethylene

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Keywords:
Catalytic CVD
Graphene
Nickel foam
Ethylene

A B S T R A C T

3D multi-layers graphene networks were synthesized on nickel foam from ethylene between 700 and 1000 °C by chemical vapor deposition. Large nickel foam substrates were used allowing the accurate measurement of graphene masses. The weight of graphene increased with run duration and when decreasing temperature. Graphene was also present inside the hollow branches of the foam. We demonstrated that the weights of graphene formed largely exceed the masses corresponding to carbon solubility into nickel. Indeed weight percentages of graphene as high as 15% were obtained, corresponding to graphene layers of 500 nm to 1 μm thick. This means that graphene formation could not be due only to carbon dissolution into nickel and then precipitation during the cooling step. Another mechanism probably coexists, involving continuous graphene formation in presence of ethylene either by segregation from the dissolved carbon into nickel or by surface CVD growth.

1. Introduction

Graphene is a two-dimensional mono-layer of sp^2-hybridized carbon atoms. These last years, it has attracted huge attention because of its unique physical properties [1,2], in particular large surface area, exceptional electron mobility, high thermal conductivity, extraordinary mechanical robustness, ... To exploit these properties for industrial applications, both large-scale synthesis and integration of individual graphene sheets into multifunctional structures are required. One promising application concerns lithium ion batteries, whose electrochemical performances could be enhanced by developing new electrode materials of higher electronic conductivity than the existing ones [3,4]. Several approaches have been developed for the large-scale synthesis of graphene for this application, such as chemical exfoliation or reduction of graphite oxide [5,6]. But these processes lead to poorly conductive graphene due to the presence of important structural defects and of oxygen containing groups. Chemical vapor deposition (CVD) is an alternative technology able to synthesize large-area high-quality graphene on planar metal substrates [7].

Recently, some research groups have succeeded in forming three dimensional (3D) foam-like graphene macro-structures by template-directed CVD [1,3,4,8,9]. They have used nickel foams as scaffold and a reactive gaseous mixture composed of methane, hydrogen and argon at 1000 °C. They have obtained 3D networks of few-layers and high-quality graphene exhibiting high conductivity (600 S/cm), high reversible capacity and good rate performance in lithium ion batteries [3].

The mechanism of graphene formation on nickel involves first methane decomposition on the catalytic surface, then carbon dissolution into nickel and finally carbon precipitation during the cooling step due to the decrease of carbon solubility [10]. Few studies are available concerning the use of acetylene, ethylene or ethanol to form graphene on nickel substrates. Jiang et al. [11] have synthesized graphene based carbon nano-fibers on nickel fibers from ethanol at 700 °C. Xiao et al. [12] have used acetylene on nickel foam at 1000 °C to form 3D 10 nm-thick graphene with large amounts of defects. Chae et al. [13] have shown that a decrease of temperature from 1000 to 700 °C using acetylene on planar polynickel substrates at 10^{-3} Torr led to an increase of the number of graphene layers and of the amount of defects. Addou et al. [14] have formed monolayer graphene from ethylene in ultrahigh vacuum conditions (10^{-6} Torr) on Ni (1 1 1) planar substrates between 500 and 600 °C. The higher reactivity of ethylene in comparison with methane allows to decrease the deposition temperature [15]. To the best of our knowledge, ethylene has never been used to form graphene on nickel foams.

In this paper, we report the synthesis of 3D graphene networks on nickel foam from ethylene between 700 and 1000 °C at ambient pressure. Large catalytic substrates were used allowing the accurate measurement of graphene masses.

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Table 1
Experimental conditions tested and results obtained.

Run	Temperature (°C)	Annealing duration (min)	Deposition duration (min)	Weight of the nickel foam (g)	Weight of graphene (g)	Wt% of deposited graphene
Ni26	1000	5	5	1.7026	0.0100	0.59
Ni28	1000	5	20	1.4559	0.0128	0.88
Ni27	1000	40	20	1.6891	0.0127	0.75
Ni22	850	5	20	1.3002	0.0084	0.65
Ni25	850	40	20	1.6898	0.0149	0.88
Ni29	800	40	20	1.7002	0.0313	1.8
Ni30	750	40	20	1.6988	0.1308	7.7
Ni33	750	40	40	1.5232	0.2361	15.5
Ni31	700	40	20	1.6022	0.1522	9.5

2. Experimental

The CVD synthesis of graphene was carried out in a 100 mm quartz tube of 1400 mm in length. A three zones furnace of 760 mm length surrounds the reactor. The 1.8 mm-thick nickel foam samples (99.9% Alantum, 40 mm × 60 mm) were placed in the central isothermal zone of the reactor, using a substrate holder which maintains them vertically during the process. They were heated between 700 and 1000 °C in a H_2 and Ar flow and annealed for 5 to 40 min. Then 15 sccm of ethylene were introduced into the reactor during 5–40 min with the same Ar and H_2 flow rates. The samples were then cooled to room temperature under the same Ar/H_2 flow rates without carbon precursor. All experiments were performed at 700 Torr.

The samples were systematically weighed before and after graphene synthesis on a Mettler Toledo (AX105 Delta Range) balance (accuracy of ±0.0003 g). Raman spectroscopy (confocal Raman microscope Labram–Horiba Yvon Jobin) with a laser excitation wavelength of 532 nm and optical microscopy were used to evaluate the thickness, crystalline quality and uniformity of the graphene at room temperature. Each spectrum was obtained by 5 acquisitions of 30 s accumulation time. Nine measurements were systematically performed for each sample on pre-definite positions covering the whole foam surface. The morphology of graphene films was analyzed in cross-section using Scanning Electron Microscopes (Jeol JSM 6700F and SEM Hitachi 5500) after having cut the foam at the center of the samples.

3. Results and discussion

Table 1 presents the operating conditions tested and the graphene weights obtained. The nickel foam scaffold used to form

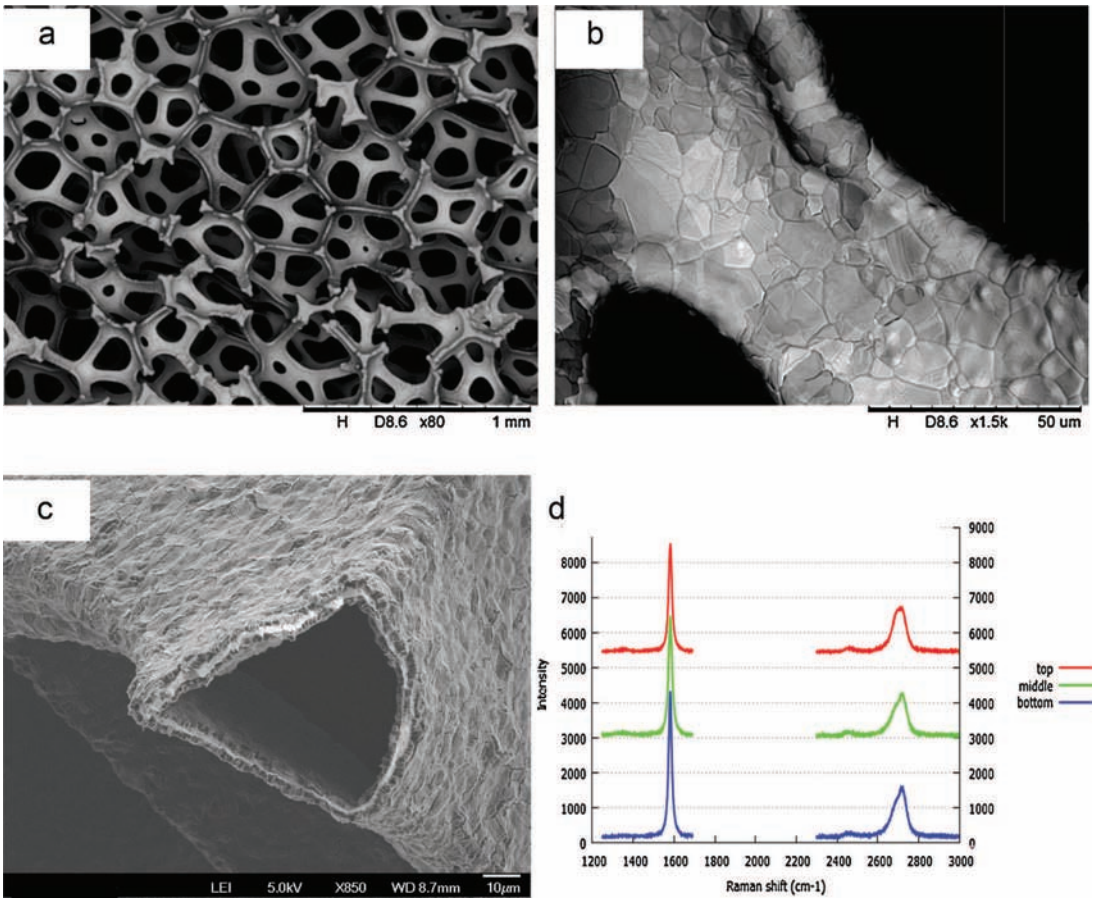

Fig. 1. (a) SEM view of the nickel foam. (b) SEM view of the nickel surface after annealing at 1000 °C. (c) FEG SEM view of a cut branch after run Ni31. (d) Raman spectra of graphene at various points of the foam after run Ni22.

graphene network is a 3D porous structure with hollow branches and quite circular pores of 50–200 μm in diameter, as shown in Fig. 1a. After graphene synthesis, thanks to the thermal treatment applied, the foam is constituted of polycrystalline nickel grains in the range of 2–20 μm (Fig. 1b). Numerous Raman spectra and SEM analyses have been performed after graphene formation. They indicate that the foam is fully and uniformly covered by graphene even at its bulk and even after 5 min of deposition, as found by other studies [8,9]. Graphene is also present inside the branches of the foam, with a thickness equivalent to that outside the foam, as revealed by SEM views (Fig. 1c).

On the Raman spectra, the average number of graphene layers is estimated from the 2D (~2670 cm^{-1})/G (~1582 cm^{-1}) peaks ratios. The graphene crystalline quality can be deduced from the ratio between the disorder-induced D-peak (~1350 cm^{-1}) and the G peak. It is worth noting that when using methane, the 2D/G peak ratios often vary from 0.5 to 3, corresponding to few layers to multi-layers (>3) graphene on a sample, according to the position on the foam [8,9]. This is true also on nickel planar substrates [10,16] and has been attributed to the fact that carbon preferentially precipitates out at the grain boundaries of polycrystalline nickel substrates. When using ethylene, the 2D/G peaks ratios are always comprised between 0.32 and 0.38, indicating that graphene is everywhere multi-layers (Fig. 1d). This could be due to the higher reactivity of ethylene in comparison with methane [15]. So, it could be less sensitive to the catalytic surface state.

The influence of temperature has then been studied for an annealing duration of 40 min and a deposition duration of 20 min, as detailed in Table 1. The main result obtained is that for all runs, the mass of graphene is higher than the mass of carbon corresponding to the C solubility into nickel at the operating temperature (for instance 0.26 wt% at 1000 °C). We verified that this was also true for the works of Bi et al. [8] and Chen et al. [9] on nickel foam from methane. This means that the mechanism of graphene formation on nickel can not be due only to carbon dissolution into nickel and then precipitation during cooling, contrarily to what is generally recognized in the literature [10,17]. Graphene could also be formed by a continuous mechanism existing as long as ethylene is present, either of isothermal carbon segregation from the carbon dissolved into nickel or of CVD surface growth. Some authors [18,19] have already mentioned the possible contribution of CVD surface growth for graphene formation on planar nickel from methane. So, it is likely that such continuous mechanism also exists on any form of nickel substrates from any carbon gaseous precursor. The great advantage of nickel foams compared to nickel planar substrates is that they allow forming measurable weights of graphene.

Another result is that the wt% of graphene increases when decreasing temperature, from 0.75% to a max. value of 9.5% at 700 °C (Fig. 2a). However, the quality of graphene is strongly dependant of the temperature. Characteristic Raman spectra obtained for each temperature (Fig. 2b) indicate that at 700 °C, the 2D and G bands are well-defined, which is characteristic of carbon sp^2 hybridation, then of graphene [20]. The shouldering visible on the G band can be attributed to the crystalline defects revealed by the high D/G peak ratio. According to the 2D/G ratio, graphene is multi-layers. At 750 °C, graphene is also multi-layers but with a less marked D band. At 800 and 850 °C, multi-layers graphene without D band is obtained. At 1000 °C, the 2D band does not appear anymore and the G band is broad and poorly defined, which could be linked to the presence of a great variety of C— bonds, with a lot of defects as revealed by the D peak. So for these conditions, a temperature of 1000 °C does not allow the formation of graphene but probably of amorphous carbon, as indicated by the absence of the 2D band [20]. The fact that contrarily to methane, ethylene allows to form more selectively carbon nanomaterial around 750–850 °C rather than at

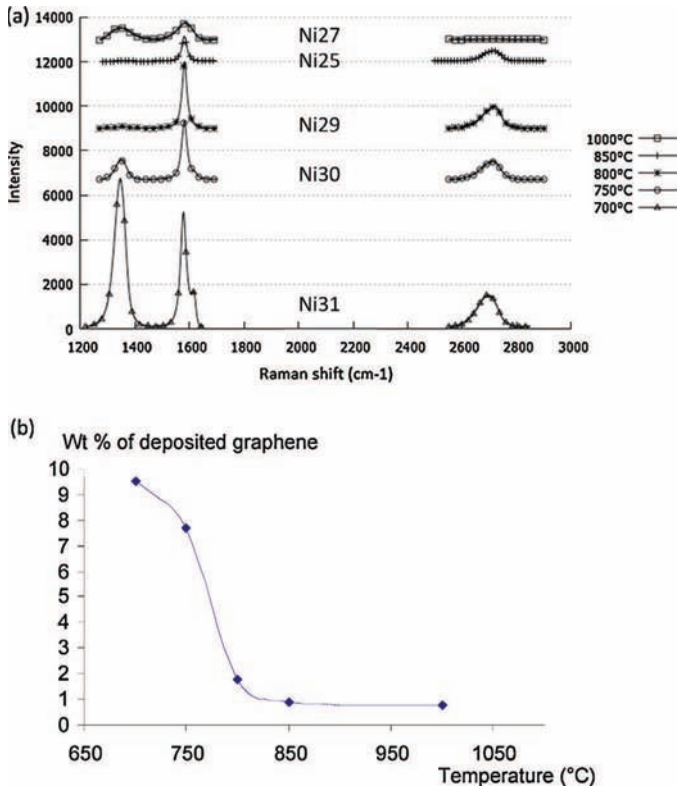

Fig. 2. (a) Characteristic Raman spectra of graphene after runs Ni25, Ni27, Ni29, Ni30, Ni31, (b) Influence of deposition temperature on graphene wt%.

higher temperature is well-known for carbon nanotubes, due to its higher reactivity [21].

The thickness of graphene formed at 750 °C estimated from cross-section SEM analyses ranges between 500 and 900 nm (Fig. 3a). Similar or even higher values were measured at 700 °C (Fig. 3b, see dotted lines). These thicknesses and the weights of graphene formed are clearly much higher than those reported in the literature from methane or acetylene. Indeed, Chen et al. [1] formed mono to few layers graphene for 5 min of deposition. Bi et al. [8] obtained 4 wt% max. of graphene presenting 3–10 layers for 30 min of deposition. Chen et al. [9] formed 1.7 wt% max. of graphene for run durations of 10 min. These much higher values could be due to the higher reactivity of ethylene in comparison with methane, to the presence of graphene inside the foam branches and to the higher precursor flow rate and run duration used in our case. At 850 °C and 1000 °C, the thickness has been estimated close to several tens of nm. Such thick carbon layers could appear as closer to graphite than to graphene. But the 2D band of the Raman spectra obtained for temperatures between 700 and 850 °C (Fig. 2b) is clearly typical of graphene, knowing that for graphite, the 2D peak is formed of two bands [20].

For the thickest layers between 700 and 800 °C, the cross-section morphology appears to be of cream-slice type and graphene presents a high surface roughness due to the formation of numerous cracks. These cracks are certainly due to differences of thermal expansion coefficients between nickel and graphene [13] and their formation is probably favoured when the graphene thickness increases. When the thickness is lower (samples obtained at 850 and 1000 °C, Fig. 3c and d), a smoother morphology close to that reported in the literature from methane [9] is observed. It is worth noting that for these samples, two distinct layers of graphene appear in the cross-section SEM views. They could be related to the co-existence of the two mechanisms of graphene formation previously detailed. This behaviour was not observed for the thicker

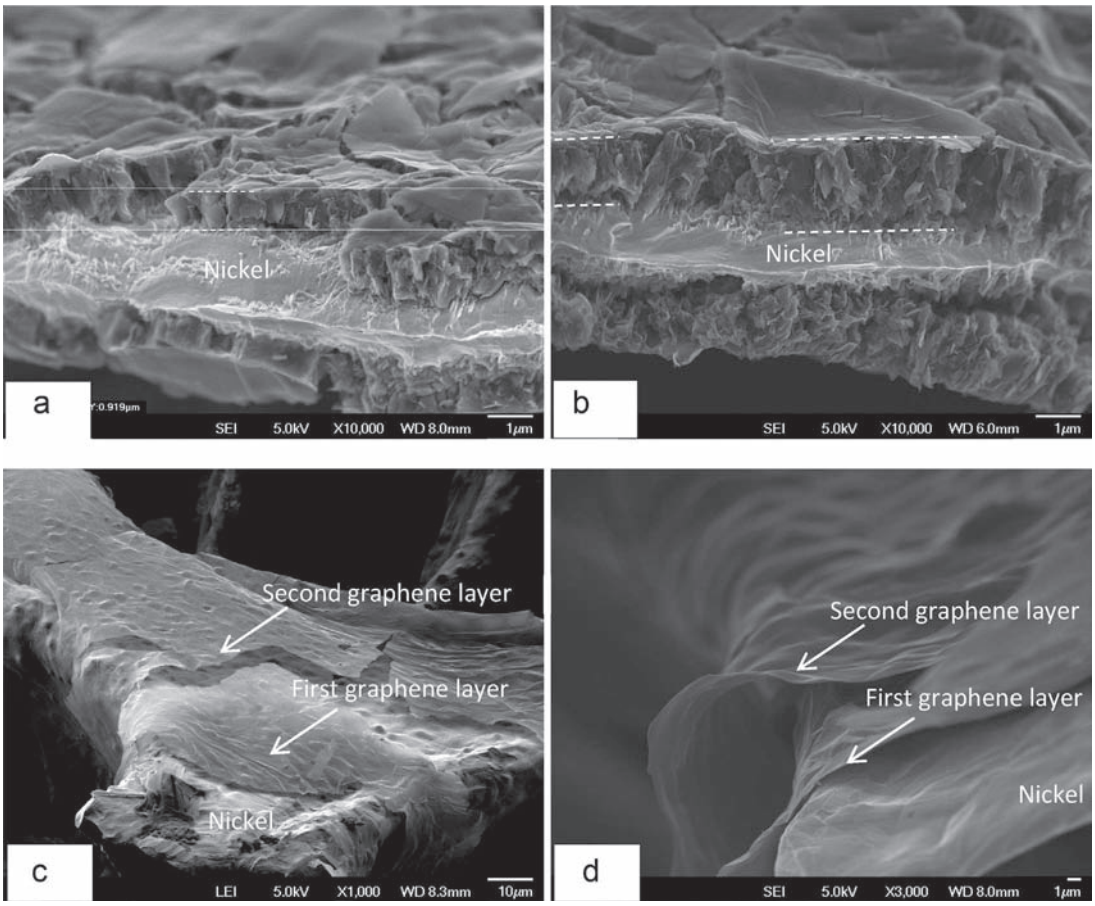

Fig. 3. FEG SEM view of graphene (a) after run Ni31, (b) after run Ni30, (c) after run Ni22, (d) after run Ni28.

graphene, but more precise analyses are necessary to verify if two kinds of graphene structure could be distinguished.

The influence of deposition duration has been studied at 750 and 1000 °C (Table 1). In both cases, the graphene weight clearly increases with run duration, reaching 15.5 wt% for 40 min of deposition at 750 °C. Such evolution was also observed by Bi et al. [8] from methane. This confirms that the mechanism does not only involve carbon precipitation during the cooling step, but also a continuous mechanism in presence of the carbon precursor. Such high masses of 3D graphene are very promising, especially for Li-ion battery applications [4].

An increase of graphene weight is also observed at 850 °C when increasing annealing duration (Table 1), but the effect is less marked than that of deposition duration, confirming the relatively low sensitivity of ethylene to the nickel crystalline state.

4. Conclusions

Weight percentages as high as 15% of 3D graphene networks can be produced by chemical vapour deposition from ethylene on nickel foam, between 750 and 850 °C. Such graphene masses largely exceed the weights corresponding to carbon solubility into nickel at these temperatures. This means that the mechanisms of graphene formation on nickel could involve carbon precipitation during the cooling step, but also continuous graphene formation from either the dissolved carbon brought by the carbon precursor supply or surface CVD growth. This assumption is reinforced by the fact that (i) the weight of graphene increases with deposition duration and (ii) two distinct layers of graphene appear for the thinnest layers, which could be related to two different mechanisms. The thickness of graphene formed at 700 and 750 °C can be as high as 1 μm, with cream slice morphology, numerous cracks and high surface roughness. Electrochemical studies are in progress to test this material as anode of Li-ion batteries.

Acknowledgements

The work was supported by the FP7-NMP GRENADA European project. The authors acknowledge M. Molinier and E. Prevot from LGC/INP de Toulouse, for technical support.

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