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Short communication

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

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ABSTRACT

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 co-exists, 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 poly-nickel 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

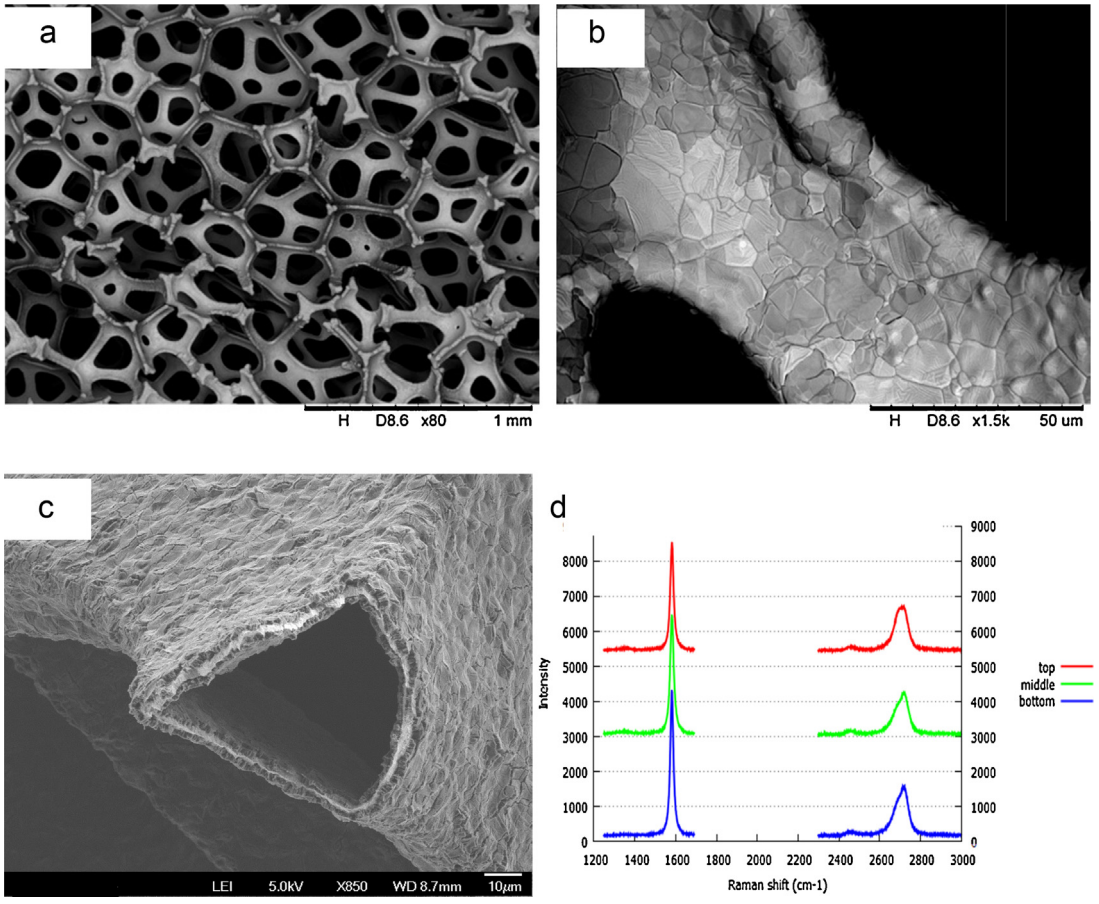

Fig. 1. (a) SEM view of the nickel foam. (b) SEM view of the nickel surface after annealing at 1000 °C. (c) FEG SEM view of a cut branch after run Ni31. (d) Raman spectra of graphene at various points of the foam after run Ni22.