

# Ultrasonic spray pyrolysis method for graphene films synthesis<sup>1</sup>

ZHE LI<sup>2</sup>

**Abstract.** Graphene films were synthesized by ultrasonic spray pyrolysis. The well-graphitized Graphene films with different layers from 2 to 8 have been obtained on nickel foam substrate by using ethanol precursor. Scanning electron microscope images show continual large area graphene films covered whole nickel foam surface, while Raman spectra confirm that as-grown multi-layer to few-layer graphene films with high quality were obtained at different zones. Transmission electron microscope results further show high degree of crystallinity of transferred graphene sheets. The procedure described can be scaled up for large-scale production at low cost.

**Key words.** Ultrasonic spray pyrolysis, graphene films, liquid precursor.

## 1. Introduction

Graphene films possess unique geometrical structure and properties for the fabrication of wide range of potential applications, including transparent electrode, Lithium battery, nanoelectronics and organic photovoltaic [1–4] etc. Micro mechanical cleavage [5], epitaxial [6], chemical and thermal reduction of graphene oxide (GO) [7], chemical vapor deposition (CVD) [8], are well-established methods to synthesis graphene sheets. Graphene flakes produced by exfoliating graphite are limited by its size and scalability [5]. Epitaxial growth of multilayer graphene on SiC single crystal at atmospheric pressure requires high temperatures above 1600 °C [9]. Films derived from liquid suspensions of graphene flakes obtained by GO reduction have not achieved the intrinsic properties of graphene [10]. Among various graphene synthesis techniques, CVD growth is particularly advantageous for the preparation of large area and high quality graphene films.

Compared with conventional gas precursor, liquid precursors are cheap, easy to use, and less flammable and thus were chose as alternative of gas precursor. Alcohol

---

<sup>1</sup>This work was financially supported by the National Science Foundation of China (No. 51272073) and the Scientific Research Fund of Hunan Provincial Education Department (No. 15C0008).

<sup>2</sup>Aeronautical Machinery Manufacturing College, Changsha Aeronautical Vocational and Technical College, Hunan Changsha, 410124, China

[11, 12], hexane [13], benzene [14], etc. were already reported as liquid precursors to synthesis graphene films successfully. Ultrasonic spray pyrolysis (USP) is an altered method of CVD, which reveals promising results for many materials synthesis [15, 16], especially for novel morphology carbon such as carbon nanotubes (CNTs), carbon nanowalls (CNWs) and carbon nanofibers (CNFs) [17–19]. In this method, ultrasonic spray is generated by an ultrasonic atomizer, when a high frequency ultrasonic is directed to a gas-liquid interface, mist forms at the surface and then swept by a carrier gas into furnace. Ultrasonic spray consist of enormous numbers of liquid drop in  $\mu\text{m}$  size spread uniformly over space, which is beneficial to the uniformity of large area films. Therefore, USP method is expected to synthesise-large area graphene films at low cost. However, to the best of our knowledge, there are no reports about this graphene growth method up to now.

In this work, a simple and inexpensive method that enables the production of graphene films with relatively high graphitization degree and controlled layers grown on nickel foam by USP using ethanol precursor was developed. This opens a new way to prepare graphene films with high quality at low cost.

## 2. Experiment

The graphene films were prepared by the ultrasonic spray pyrolysis of ethanol on nickel foam substrate. A 1 7 MHz nebulizer was used to produce the “mist” which was carried into a furnace set to  $1000\text{ }^{\circ}\text{C}$  using a mixture of argon and hydrogen (500 sccm and 200 sccm, respectively) as carrier gas. The reactants were passed through a quartz tube (100 cm in length and 45 mm in diameter) placed horizontally in an electric furnace. All experiments were conducted at atmospheric pressure.

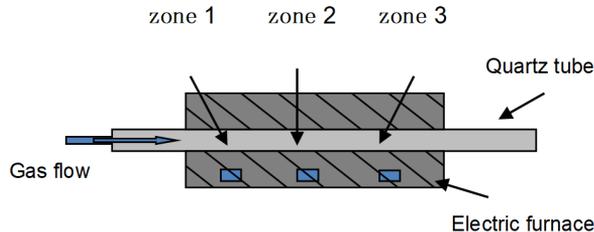


Fig. 1. Scheme of substrate zones in the quartz tube

Three pieces of nickel foam substrate (size:  $15\text{ mm}\times 15\text{ mm}\times 1.5\text{ mm}$ ) cleaned by acetone were placed in three different zones (zone 1, 2, and 3) inside the quartz tube, as shown in Fig.1. When electric furnace reached to set temperature, ultrasonic nebulizer was switched on during a certain time period, then the furnace was rapidly cooled to room temperature under Ar and  $\text{H}_2$ . The obtained products from zone 1, 2, and 3 were identified respectively as GNs-1, GNs-2, GNs-3. As-grown samples were characterized by scanning electron microscopy (SEM; Hitachi S-4800), transmission electron microscopy (TEM; Hitachi JEM-2100F), and Raman spectroscopy (LabRam HR800 with a laser wavelength of 488 nm).

Fig. 2(a)–(c) show SEM images of As-grown samples from zone 1 to 3. Typical morphology as reported [20] of the graphene films with many wrinkles grown on nickel foam was obtained for all of the samples. The formation of such wrinkles was suggested as a mechanism of strain relaxation caused by the coefficient of thermal expansion mismatch between nickel and graphene during the cool-down process [21]. It is worth noting that the surface is very clean and no amorphous carbon was observed, which might be very important in applications for transparent electronic devices. Compared Fig. 2(a) with Fig. 2(c), it is obvious to find that graphene sheet in Fig. 2(c) is more transparent than that in Fig. 2(a). Furthermore, in Fig. 2(c), nickel grain boundaries under graphene sheet are clearly visible and covered by graphene sheet with mild ripples. In the contrary, more graphene wrinkles are observed with less transparency in Fig. 2(a). This may be an intuitive evidence to estimate the layer number of graphene sheet from different zones. This demonstrated indirectly that the GNs-3 has fewer graphene layers than GNs-1. Another different SEM image from the GNs-2 (Fig. 2b) shows a continual graphene film crossing nickel grain boundaries spread over the whole substrate surface, indicating that the lateral growth rate is much quicker than the graphene nucleation rate at this zone.

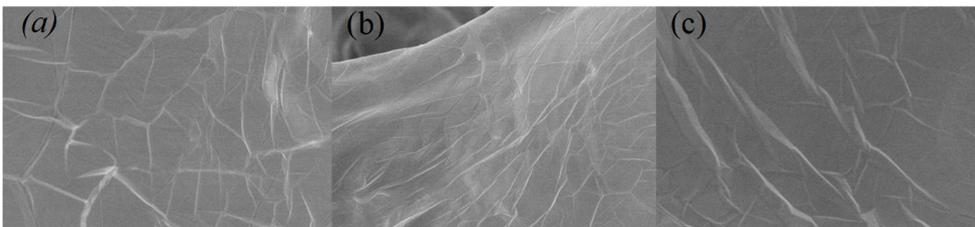


Fig. 2. SEM images of the As-grown graphene films on nickel foam from zones 1 to 3 with 1 minute growth time, (a)–(c)

Raman spectroscopy provides a quick and facile structural and quality characterization of the graphene sheets. The Raman spectra of exfoliated graphene have three major bands named D ( $\sim 1350\text{ cm}^{-1}$ ), G ( $\sim 1580\text{ cm}^{-1}$ ) and G' ( $\sim 2700\text{ cm}^{-1}$ ). The G-band is representative of the degree of graphitization associated with the graphene growth. The D-band represents the number of defects (open ends, disorder, amorphous deposit, etc.). The G' band at  $\sim 2700\text{ cm}^{-1}$  in particular is a second-order process related to a phonon near the K point in graphene, activated by double resonance (DR) processes [22, 23].

Generally, the ratio of peak intensities (ID/IG) in the Raman spectra indicates the degree of carbon ordering (graphitization), which is an important parameter for evaluating the quality of GNs. The integrated intensity ratio (IG'/IG) and full width at half maximum (FWHM) are also important factors, from which the number of layers can be estimated.

Figure 3 show typical Raman spectra of samples from three zones. All the spectra indicate the presence of G-band (at  $\sim 1590\text{ cm}^{-1}$ ). For the defect-related D bands, the intensity of D band almost disappears, indicating a higher quality of the as-

obtained graphene. The  $IG'/IG$  and FWHM of the sample from zone 1 are 1.1 and  $64\text{ cm}^{-1}$ , suggesting that the sample is predominantly composed of multilayer flakes. Furthermore, the Raman spectrum of the sample from zone 2 reveals a symmetric  $G'$  peak with FWHM of about  $38\text{ cm}^{-1}$  and  $IG'/IG$  of 2.0, confirming the presence of 5–8 layers dominant. Whereas, for the sample from zone 3,  $IG'/IG$  is about 3.0 and the FWHM of the  $G'$  peak is about  $34\text{ cm}^{-1}$ , which indicates the as-obtained graphene flakes are less than 5 layers.

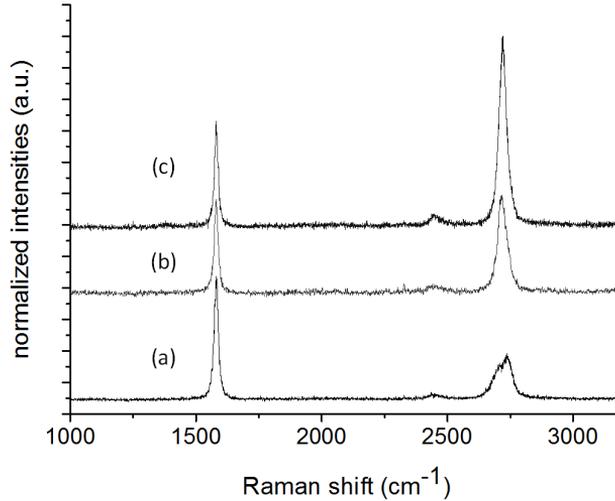


Fig. 3. Typical Raman spectra of As-grown graphene films on nickel foam

It is well known that graphene formation on Ni substrate is a carbon segregation or precipitation process. When ethanol is nebulized and carried to high temperature zone, some C-H-O radicals are decomposed on the surface of Ni. A limited quantity of carbon atoms is incorporated into the Ni substrate to precipitate in the form of graphene layers [23]. During this process, the density of ethanol mist arrived at the Ni substrate declined from zone 1 to 3 because of the grade distribution along flow direction for ethanol mist. Consequently, the numbers of carbon atom dissolved into the Ni substrates gradually decreased as USP growth proceeded from zone 1 to 3, resulting in difference of the graphene layers grown at different zones. This result means that the number of graphene layers is sensitive to the carbon concentration at reactant zone.

To test and verify the above result, parallel experiment was carried out with 5 minutes growth time. Fig. 4 presents surface morphology of prepared samples from zone 1 to 3 with 5 minutes growth time. From Fig. 4, parts (a) and (b), much fringe of graphene sheets was observed with obvious fold and terraces, which suggests that the graphene layers is too much to maintain an integral continual membrane. In comparison, Fig. 4(c) presents a smooth surface corresponding to the continual film.

Figure 5 compares typical Raman curves of samples from zone 1 (curve (a)), 2 (curve (b)) and 3 (curve (b)) with 5 minutes growth time. Curves (a) and (b) exhibit similar shape with FWHM of  $G'$  band about  $79\text{ cm}^{-1}$ , which associate with

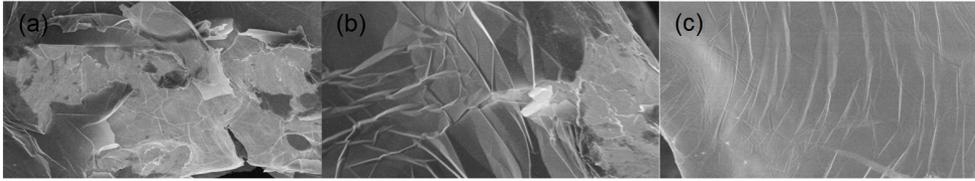


Fig. 4. SEM images of the As-grown graphene films on nickel foam from zone 1 to 3 with 5 minutes growth time. (a)–(c)

multi-layer graphene structure. However, obvious D band presented only in curve (a) confirmed that more fringes and defects for the sample from zone 1, as shown in Fig. 4(a). For the sample from zone 3, FWHM of G' band is about  $50 \text{ cm}^{-1}$  with  $\text{IG}'/\text{IG}$  of 1.4, corresponding to graphene layers of 5 to 8. Therefore, these results indicate that longer growth time give rise to the increase of carbon species decomposed at the reaction zone. With evaporation and reaction effect, concentration of carbon species declines from the inlet end to the outlet end obviously, which caused different morphologies and layer number of obtained graphene films.

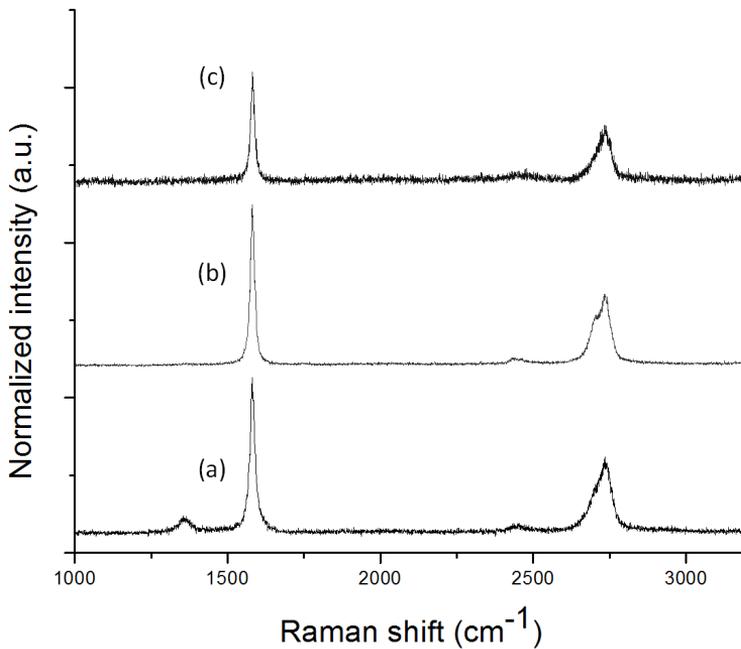


Fig. 5. Typical Raman spectra of As-grown graphene films from zone 1 (curve (a)), 2 (curve (b)) and 3 (curve (c)) with 5 minutes growth time

To further characterize the graphene films obtained from zone 2 and 3, direct wet chemical transfer of graphene from nickel foam to TEM grid was implemented. Figure 6(a) shows TEM image of the graphene sheets (zone 2, 1 minute growth) with the wrinkles and folded zones. Figure 6(b) displays flat few-layer graphene

zone with high transparency at the edge site, in which the electron diffraction (ED) pattern (upper right inset) shows a hexagonal spot pattern, confirming the threefold symmetry of the arrangement of carbon atoms. This is the symbol of single crystal graphene material. All of these results suggest that the USP method is favored for the growth of graphene films in a suitable environment, and a large area continual graphene film with high quality can be obtained from zones 2 and 3.

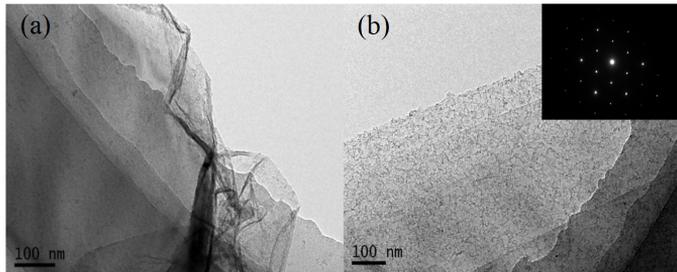


Fig. 6. TEM images of the fabricated graphene sheets transferred to copper grid, (a) wrinkles and folded fringe; (b) flat fringe, the upper right inset is the ED pattern

### 3. Conclusion

USP method was used to synthesis graphene films under ambient pressure. It is proved that the graphene films synthesized by this method have similar quality as that of conventional CVD method. By its simplicity, rapidness and compatibility with other carbon nanomaterial, it is an appropriate way using liquid precursor to grow large area graphene films with layers control at low cost.

### References

- [1] SUKANG BAE, HYEONGKEUN KIM, YOUNGBIN LEE, XIANGFAN XU, JAE-SUNG PARK, YI ZHENG, JAYAKUMAR BALAKRISHNAN, TIAN LEI, HYE RI KIM, YOUNG IL SONG, YOUNG-JIN KIM, KWANG S. KIM, BARBAROS ÖZYILMAZ, JONG-HYUN AHN, BYUNG HEE HONG, SUMIO IJIMA: *Roll-to-roll production of 30-inch graphene films for transparent electrodes*. *Nature Nanotechnology* 5 (2010), 574–578.
- [2] ARAVA LEELA MOHANA REDDY, ANCHAL SRIVASTAVA, SANKETH R. GOWDA, HEMTEJ GULLAPALLI, MADAN DUBEY, PULICKEL M. AJAYAN: *Synthesis of nitrogen-doped graphene films for lithium battery application*. *ACS Nano* 11 (2010), No. 4, 6337–6342.
- [3] A. H. CASTRO NETO, F GUINEA, N. M. R. PERES, K. S. NOVOSELOV, A. K. GEIM: *The electronic properties of graphene*. *Reviews of Modern Physics* 81 (2009), No. 1, 109–162.
- [4] L. GOMEZ, YI ZHANG, C. W. SCHLENKER, KOUNGMIN RYU, M. THOMPSON, CHONGWU ZHOU: *Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics*. *ACS Nano* 4 (2010), No. 5, 2865–2873.
- [5] K. S. NOVOSELOV, A. K. GEIM, S. V. MOROZOV, D. JIANG, Y. ZHANG,

- S. V. DUBONOS, I. V. GRIGORIEVA, A. A. FIRSOV: *Electric field effect in atomically thin carbon films*. *Science* 306 (2004), No. 5696, 666–669.
- [6] I. FORBEAUX, J.-M. THEMLIN, J.-M. DEBEVER: *Heteroepitaxial graphite on 6H-SiC(0001): Interface formation through conduction-band electronic structure*. *Physical Review B* 4 (2009), 16396–16406.
- [7] SUNGJIN PARK, R. S. RUOFF: *Chemical methods for the production of graphenes*. *Nature Nanotechnology* 4 (2009), 217–224.
- [8] A. REINA, XIAOTING JIA, J. HO, D. NEZICH, HYUNGBIN SON, V. BULOVIC, M. S. DRESSELHAUS, JING KONG: *Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition*. *Nano Letters* 9 (2009), No. 1, 30–35.
- [9] K. V. EMTSEV, A. BOSTWICK, K. HORN, J. JOBST, G. L. KELLOGG, L. LEY, J. L. MCCHESENEY, TAISUKE OHTA, S. A. RESHANOV, J. RÖHRL, E. ROTENBERG, A. K. SCHMID, D. WALDMANN, H. B. WEBER, T. SEYLLER: *Applications of hybrid genetic algorithms in seismic tomography*. *Nature Materials* 8 (2009), 203–207.
- [10] C. MATTEVI, GOKI EDA, S. AGNOLI, S. MILLER, K. ANDRE MKHOYAN, OZGUR CELIK, D. MASTROGIOVANNI, C. CRANOZZI, E. CARFUNKEL, MANISH CHHOWALLA: *Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films*. *Advanced Functional Materials* 19 (2009), No. 16, 2577–2583.
- [11] XIAOCHEN DONG, PENG WANG, WENJING FANG, CHING-YUAN SU, YU-HSIN CHEN, LAIN-JONG LI, WEI HUANG, PENG CHEN: *Growth of large-sized graphene thin-films by liquid precursor-based chemical vapor deposition under atmospheric pressure*. *Carbon* 49 (2011), No. 11, 3672–3678.
- [12] ABDELADIM GUERMOUNE, TARUN CHARI, FILIP POPESCU, SHADI S. SABRI, J. GUILLEMETTE, HELGI S. SKULASON, T. SZKOPEK, M. SIAJAB: *Chemical vapor deposition synthesis of graphene on copper with methanol, ethanol, and propanol precursors*. *Carbon* 49 (2011), No. 13, 4204–4210.
- [13] A. SRIVASTAVA, C. GALANDE, LIJIE CI, LI SONG, CHAITRA RAI, D. JARIWALA, K. F. KELLY, P. M. AJAYAN: *Novel liquid precursor-based facile synthesis of large-area continuous, single, and few-layer graphene films*. *Chemistry of Materials* 22 (2010), No. 11, 3457–3461.
- [14] GUI-PING DAI, PETER H. COOKE, SHUGUANG DENG: *Direct growth of graphene films on TEM nickel grids using benzene as precursor*. *Chemical Physics Letters* 531 (2012), 193–196.
- [15] J. D. ATKINSON, M. E. FORTUNATO, S. A. DASTGHEIB, M. ROSTAM-ABADI, M. J. ROOD, K. S. SUSLICK: *Synthesis and characterization of iron-impregnated porous carbon spheres prepared by ultrasonic spray pyrolysis*. *Carbon* 49 (2011), No. 2, 587–598.
- [16] HANGXUN XU, JINRUI GUO, K. S. SUSLICK: *Porous carbon spheres from energetic carbon precursors using ultrasonic*. *Advanced Materials* 24 (2012), No. 45, 6028–6033.
- [17] I. KHATRI, T. SOGA, T. JIMBO, S. ADHIKARI, H. R. ARYAL, M. UMENO: *Synthesis of single walled carbon nanotubes by ultrasonic spray pyrolysis method*. *Diamond and Related Materials* 18 (2009), Nos. 2–3, 319–323.
- [18] JIANHUI ZHANG, ISHWOR KHATRI, NAOKI KISHIA, SHARIF M. MOMINUZZAMAN, TETSUO SOGA, TAKASHI JIMBO: *Low substrate temperature synthesis of carbon nanowalls by ultrasonic spray pyrolysis*. *Thin Solid Films* 44 (2009), No. 6, 700–702.
- [19] JIANFENG BAO, NAOKI KISHI, ISHWOR KHATRI, TETSUO SOGA, TAKASHI JIMBO: *Catalyst-free synthesis of carbon nanofibers by ultrasonic spray pyrolysis of ethanol*. *Materials Letters* 68 (2012), 240–242.
- [20] ZONGPING CHEN, WENCAI REN, LIBO GAO, BILU LIU, SONGFENG PEI, HUI-MING CHENG: *Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition*. *Nature Materials* 10 (2011), 424–428.
- [21] SEUNG JIN CHAE, FETHULLAH GÜNES, KI KANG KIM, SOO MIN KIM, HYEON-JIN SHIN, SEON-MI YOON, JAE-YOUNG CHOI, MIN HO PARK, CHEOL WOONG YANG, DIDIER PRIBAT, YOUNG HEE LEE: *Synthesis of large-area graphene layers on poly-nickel substrate by chemical vapor deposition: Wrinkle formation*. *Advanced Materials* 21 (2009), No. 22, 2328–2333.

- [22] Y. MIYASAKA, A. MATSUYAMA, A. NAKAMURA, J. TEMMYO: *Graphene segregation on Ni/SiO<sub>2</sub>/Si substrates by alcohol CVD method*. *Physics Status Solidi C* 8 (2011), No. 2, 577–579.
- [23] YOUPIN GONG, XUEMIN ZHANG, GUANGTONG LIU, LIQIONG WU, XIUMEI GENG, MINGSHENG LONG, XIAOHUI CAO, YUFEN GUO, WEIWEI LI, JIANBAO XU, MENGTAO SUN, LI LU, LIWEI LIU: *Layer-controlled and wafer-scale synthesis of uniform and high-quality graphene films on a polycrystalline nickel catalyst*. *Advanced Functional Materials* 22 (2012), No. 15, 3153–3159.

Received April 30, 2017