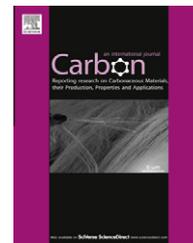


Available at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Hollow structures with bilayer graphene walls

Peter J.F. Harris *

Centre for Advanced Microscopy, J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 6AF, UK

ARTICLE INFO

Article history:

Received 30 August 2011

Accepted 28 October 2011

Available online 4 November 2011

ABSTRACT

The formation of three-dimensional shell-like structures with bilayer graphene walls is described. The structures are produced by the passage of an electric current through graphite in an arc-discharge apparatus. High resolution transmission electron microscopy is used to characterize the carbon, and provides evidence that the structures are three-dimensional rather than flat. A striking feature of the material is that it contains bilayer nanotubes seamlessly joined to larger shell-like regions. The possible growth mechanism of the carbon is discussed, and potential applications considered.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Experiments with a graphite arc have proved to be extremely fruitful for carbon research. In 1960, Bacon used a DC arc to produce graphite whiskers, scroll-like graphite fibers with outstanding mechanical properties [1,2]. This proved to be a key event in the development of carbon fibers. Thirty years later, Krätschmer et al. achieved the first bulk synthesis of C_{60} using an arc-evaporator [3], a development that gave a huge boost to fullerene research. Shortly afterward Iijima [4] produced highly perfect multiwalled carbon nanotubes using arc-evaporation, and in 1993 Iijima and Ichihashi [5] and Bethune et al. [6] showed that single-walled nanotubes could also be made in this way. Recently, yet another kind of carbon has been discovered in graphite samples which have been subjected to arc-discharge [7,8]. This new carbon apparently consists of hollow graphitic shells bounded by curved and faceted planes, typically made up of two graphene layers. The curvature and faceting appears to be due to the presence of a small number of pentagons and other non-hexagonal rings distributed in a hexagonal graphene network. The hollow structures, which can be several 100s of nm in size, are frequently decorated with nano-scale carbon particles, or short nanotubes; in some cases, nanotubes are found to be seamlessly joined to the thin shells.

In this paper, the synthesis of these novel carbon structures, and their characterization by high resolution transmission electron microscopy, is described. Evidence that the structures are three-dimensional rather than flat is presented, and the possible formation mechanism of the structures is considered, although many aspects of this remain poorly understood. In particular is not clear why the great majority of the hollow particles have bilayer, rather than monolayer or multi-layer walls. It is suggested that this may be related to the edge structure of the original graphite. The relationship between the new structures described in this paper and rather similar ones reported in 2009 by Jia et al. [9] and by Huang et al. [10] is discussed. In these latter papers, a structural transformation of graphite similar to that reported here was produced by the *in situ* heating of graphite “nanoribbons” inside a TEM. This was explained in terms of sublimation and edge reconstruction of flat graphene, but may actually have involved a transformation from flat graphite to hollow structures, as described in the present work.

The new carbon materials may have useful applications in a number of areas. With their extremely large surface-to-volume ratios they could be useful as hydrogen storage materials or in catalysis. They could also be of value in electrical devices such as supercapacitors or lithium ion batteries, where their structural stability might give them advantages

* Fax: +44 118 3784606.

E-mail address: p.j.f.harris@rdg.ac.uk

0008-6223/\$ - see front matter © 2011 Elsevier Ltd. All rights reserved.

doi:10.1016/j.carbon.2011.10.050

over materials assembled from graphene flakes by solution or other methods.

2. Experimental methods

The graphene material described in this paper was prepared in a commercial arc-evaporator, a Quorum Q150T ES, which is normally used for carbon-coating specimens for electron microscopy. In this unit the electrodes are 3 mm graphite rods, one of which is thinned to a diameter of approximately 1.4 mm and held in contact with the other electrode with a spring mechanism. The chamber is pumped by a turbomolecular pump to a pressure of approximately 3×10^{-4} mbar. Before carrying out the “evaporation”, the rods are out-gassed by passing a current of about 30 A for 1 min. For evaporation, a current of 75 A is passed for 3 s.

Following evaporation, the thinner carbon rod was found to have slightly shortened, and a small deposit was formed in the area where the two rods made contact, as shown in Fig. 1. This was collected and prepared for TEM by grinding in an agate mortar under isopropanol, mixing in an ultrasonic bath and depositing onto lacey carbon TEM grids. The microscope used was a JEOL 2010, with a point resolution of 0.19 nm, operated at an accelerating voltage of 200 kV. Images

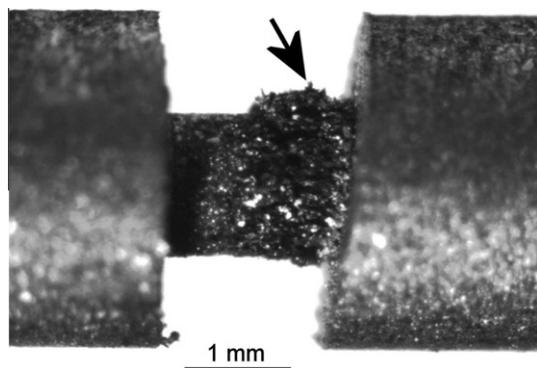


Fig. 1 – Photograph of graphite rods following passage of current in arc-evaporator. Arrow indicates deposit containing unusual graphene material.

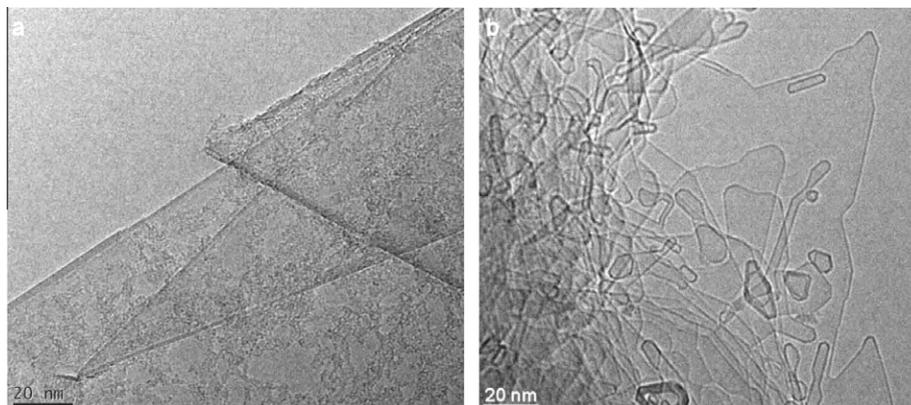


Fig. 2 – (a) Transmission electron micrograph of carbon from fresh graphite rod. (b) Micrograph at same magnification showing transformation in structure following arc-discharge.

were recorded digitally using a Gatan Orius 200 camera. Samples from the fresh graphite rods were also imaged, for comparison with the carbon collected after arcing.

3. Results

A typical image of material from the fresh graphite rod is shown in Fig. 2(a). As expected, this consists mainly of flat crystallites, ranging from a few 100 nm to about 5 μm in size, containing up to 100 layers. The crystallites were often folded and buckled, and were covered with small amounts of finely-divided material. However, nanotubes or other fullerene-related structures were not seen in the fresh graphite.

The carbon collected from the graphite rods following arcing contained some “normal” graphite, but this was accompanied by many regions which had a very different appearance. One of these areas is shown in Fig. 2(b). Here, the outline of the structure is much more irregular than in the fresh graphite, with many curved and unusually-shaped features, including re-entrant structures. The material is decorated with numerous short nanotubes or nanoparticles. The proportion of carbon in the arc-treated samples which had this altered structure is difficult to estimate with any accuracy, but typically it appeared that about 50% had been transformed in this way.

Micrographs recorded at higher magnifications indicated that the thin structures consisted largely of bilayer graphene. An example is shown in Fig. 3. The bilayer spacing, determined from this and other images, was generally somewhat larger than the interplanar spacing for graphite, being typically around 0.4 nm. The possible cause of the preferential formation of bilayer graphene is discussed below. Single-layer graphene was only rarely seen; regions with three or more layers were more common. The nanotubes and nanoparticles which were supported on the larger structures were also generally bilayer, although nanoparticles with many layers were sometimes seen.

It is believed that the unusual structures observed in the arc-treated carbon are three-dimensional rather than flat, for reasons discussed below. The three-dimensional structure appears to result from the presence of pentagons and other non-hexagonal rings in the bilayer graphene network. In this

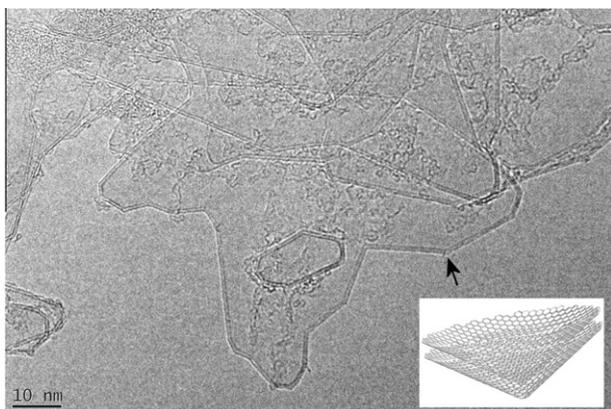


Fig. 3 – Typical structure of carbon following arc-discharge. Almost all of the material in this image is bilayer. Inset shows suggested structure of feature indicated by arrow.

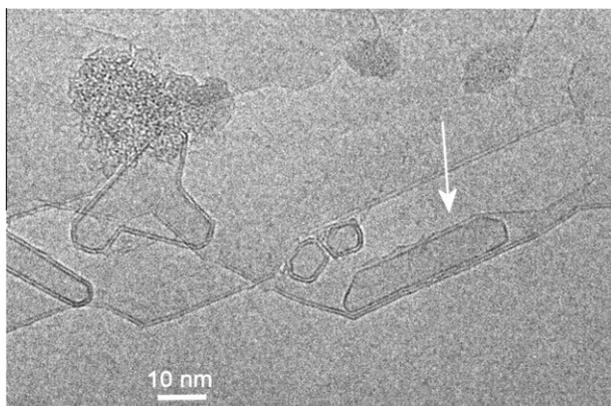


Fig. 4 – Hollow graphene structure with single-walled nanotube apparently encapsulated inside (arrowed).

interpretation, a pentagon at the point indicated by the arrow in Fig. 3 would give this part of the material a conical shape, as illustrated in the inset. The cone angle created by a single pentagon is 113° . In practice, quite a wide range of angles are observed at these faceted edges. This is not surprising, since the observed structures would only have the exact 113° angle if they were oriented with the pentagonal ring exactly parallel to the electron beam, and were not subject to any distorting strains.

The structures in the arc-treated carbon display a number of features which suggest they are three-dimensional and hollow. One notable observation is that small nanoparticles or nanotubes are sometimes seen apparently inside larger structures. Fig. 4 shows an example, where a small, single-walled nanotube appears to be encapsulated in a bilayer structure. Another striking feature of the graphitic material was that nanotubes were often observed to be joined to the larger regions. Several examples of this are shown in at low magnification in Fig. 5(a). The tubes were generally 3–6 nm in diameter. Higher resolution images, such as that in Fig. 5(b), showed that the nanotubes were almost invariably bilayer, and were seamlessly joined to the larger structures. This provides further evidence that the large bilayer structures are three-dimensional rather than flat, since it is difficult to envisage a way in which nanotubes, with their circular cross-section, could be connected to flat, few layer, graphene without being seriously distorted, at least in the vicinity of the junction.

The exact nature of the junctions between the tubes and the larger shell-like regions is not known at present. A number of authors have analyzed the possible ways in which a nanotube could be joined to a graphene sheet (e.g. [11–13]), but these have all involved tubes bonded to flat graphene planes. In the present case, the nanotubes seem to be joined to cone-shaped regions. It is possible that the junctions may be similar to those observed in certain nanotube tips where

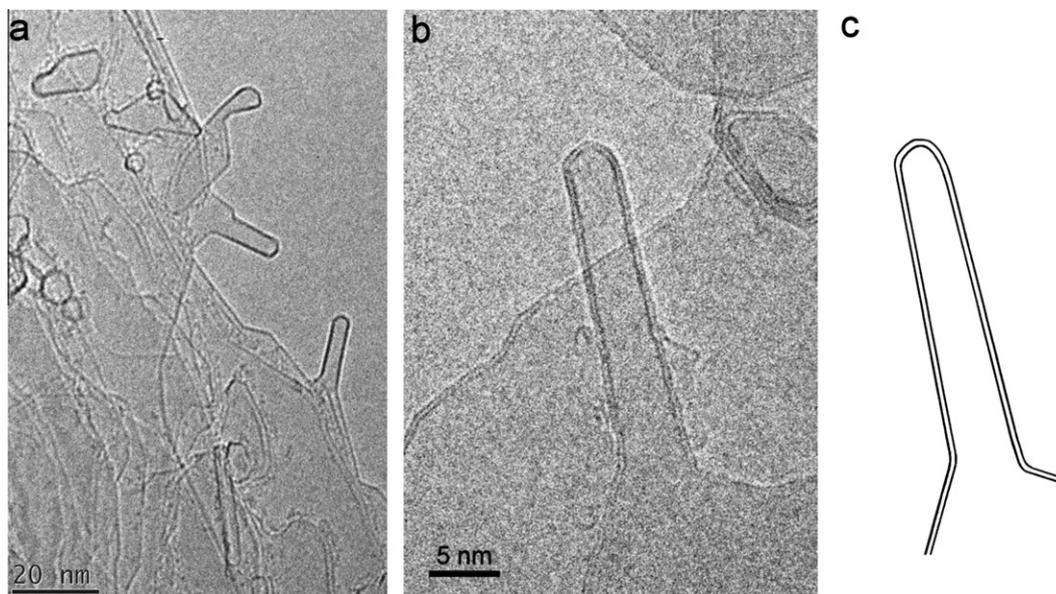


Fig. 5 – Nanotubes joined to larger hollow regions. (a) Intermediate magnification micrograph; (b) higher magnification image of different region; (c) sketch of the structure shown in (b).

a short cylindrical region joins a conical structure [14]. Such structures involve a -60° disclination, believed to be due to the presence of a heptagonal ring, but more work is needed to establish the precise structure of these connections.

4. Discussion

A striking transformation in the structure of graphite as a result of the passage of an electric current in an arc-discharge apparatus has been described. This apparently involves the formation of three-dimensional shell-like structures bounded by very thin walls, which in most cases consist of bilayer graphene. As mentioned in the previous section, there are several reasons for believing that these new structures are three-dimensional and hollow rather than flat. These include the observation that small nanoparticles or nanotubes are sometimes seen encapsulated inside larger structures, and that nanotubes are often found to be seamlessly joined to the thin shells. In order to obtain direct evidence that the structures are three-dimensional, it will be necessary to carry out tomographic TEM imaging, and such experiments are planned.

The mechanism of the transformation is not known at present, but it is possible that the key to understanding the process may lie in the edge structure of graphite. It is well established that graphite planes often have “closed” edges, so that the layers resemble folded sheets [15–19], as illustrated in Fig. 6(a). The transformations reported in this paper may simply involve an “opening” of the layers, as shown schematically in Fig. 6(b). Such a process might be initiated by the nucleation of pentagonal rings at the closed edges: it is clear from the presence of nanotube-like structures in the carbon that pentagons are present. It also seems clear that the electric current passing through the carbon, rather than simply the high temperature, is responsible for the transformation. However, further work is needed to gain a more detailed understanding of the process.

Transformations rather similar to those described here were reported in two studies published in 2009 by Jia et al. [9] and Huang et al. [10]. These studies involved *in situ* Joule heating of graphite nanoribbons inside a TEM, which resulted in the formation of complex edge structures. In both papers the authors drew a different conclusion about the nature of the transformation to that given here: the process was discussed in terms of sublimation and edge reconstruction of flat graphene. It seems more likely that they were actually seeing a transformation from flat graphite to hollow structures, as described in the present work, rather than sublimation. However, there was one important difference between the structures seen in the Jia and Huang studies and the ones reported here. The hollow structures described in the present

study were almost invariably bounded by bilayer graphene walls, while the structures in the 2009 work were virtually all single layer. This may reflect differences in the precursor graphites used for these experiments. In the present work it has been suggested that the precursor graphite had edges in which two adjacent bilayers were joined, as shown in Fig. 6(a). It may be that in the precursor graphite used by Jia and Huang, only adjacent monolayers were joined. This raises interesting questions about the edge structures of graphites, an area that has not yet been studied in detail.

The material reported in this paper could be described as “three-dimensional graphene”. In recent years a number of groups have described the production of three-dimensional structures constructed from graphene, or graphene oxide, but these materials differ in significant ways from the structures reported here. In most cases the methods used to assemble the graphene flakes have involved suspending them in a solvent, using chemical methods to link them together and then removing the solvent in a controlled way [20–23], although a chemical vapor deposition method has also been reported [24]. These techniques produce porous graphene structures, with pore sizes typically of the order of a few 10s of μm . In these structures the graphene fragments are held together by weak Van der Waals type forces, suggesting they would possess a relatively low rigidity, and that the pore structure would be prone to collapse. The new carbon structures described in the present paper differ from these materials in that the porosity is on a much smaller scale, and results from the presence of a small number of pentagons, plus a few other non-hexagonal rings, distributed throughout the graphene network. The “three-dimensionality” is thus a consequence of the chemical bonding configuration in the structure, producing far greater strength and resilience than in the materials produced by assembling graphene flakes.

Concerning potential applications of the three-dimensional graphene structures, these could lie in a number of areas, although it is recognized that none of these have yet been demonstrated. One possible application might be hydrogen storage, since forms of carbon rather similar to those described here have been shown to have good H_2 storage capabilities. Thus, Orimo et al. reported in 1999 that “nanostructured graphite” prepared by mechanical milling of synthetic graphite can have high H_2 uptakes [25]. Carbon nanohorns have also been shown to have potentially useful H_2 storage properties [26]. Theoreticians have suggested that “pillared graphene”, a three-dimensional network constructed from graphene and short nanotubes, could adsorb 6% of its weight in hydrogen at room temperature and pressure [27]. Although the present material is a disordered rather than an ordered network, its H_2 storage characteristics might be similar to those of “pillared graphene”.

The new structures may also have applications in electrical devices. A number of studies have demonstrated that various forms of modified graphene can be used to produce supercapacitors with high specific energy densities (e.g. [28–30]). The graphenes used in these studies are typically produced by exfoliating graphite [28] or by chemical vapor deposition [30]. Although these materials initially have the high surface areas required for supercapacitors, it is not clear that they would retain these surface areas under operating

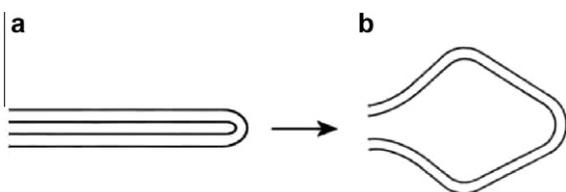


Fig. 6 – Schematic illustration of transformation of folded graphene sheets into hollow structure.

conditions: the flat graphene flakes would have a tendency to clump together. In contrast, the curved and faceted shells described in the present paper would be much more likely to retain their surface area. As well as supercapacitors, there has been great interest in using graphene in the anodes of lithium ion batteries [31]. The large internal volume, stability and high conductivity of the structures described here suggest they might also be useful in this area.

Finally it is interesting to reflect that, although the products of carbon arcs have been studied intensively since Bacon's work in 1960, and carbon arcs themselves have been used since the early 19th century, it appears that the kind of structures described in this paper were not observed before 2009. As Peter Thrower perhaps knows better than anyone, carbon is a material which continues to produce surprises.

REFERENCES

- [1] Bacon R. Growth, structure and properties of graphite whiskers. *J Appl Phys* 1960;31(2):283–90.
- [2] Thrower PA. Roger Bacon 1926–2007 – obituary. *Carbon* 2007;45(6):1143–4.
- [3] Krätschmer W, Lamb LD, Fostiropoulos K, Huffman DR. Solid C_{60} : a new form of carbon. *Nature* 1990;347(6291):354–8.
- [4] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354(6348):56–8.
- [5] Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1-nm diameter. *Nature* 1993;363(6430):603–5.
- [6] Bethune DS, Kiang CH, de Vries MS, Gorman G, Savoy R, Vasquez J, et al. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature* 1993;363(6430):605–7.
- [7] Harris PJF. Ultrathin graphitic structures and carbon nanotubes in a purified synthetic graphite. *J Phys: Condens Matter* 2009;21(35):355009.
- [8] Harris PJF. Structural transformation of graphite by arc-discharge. *Philos Mag* 2011;91(18):2355–63.
- [9] Jia X, Hofmann M, Meunier V, Sumpter BG, Campos-Delgado J, Romo-Herrera JM, et al. Controlled formation of sharp zigzag and armchair edges in graphitic nanoribbons. *Science* 2009;323(5922):1701–5.
- [10] Huang JY, Ding F, Yakobson BI, Lu P, Qi L, Li J. In situ observation of graphene sublimation and multi-layer edge reconstructions. *Proc Natl Acad Sci USA* 2009;106(25):10103–8.
- [11] Baowan D, Cox BJ, Hill JM. Two least squares analyses of bond lengths and bond angles for the joining of carbon nanotubes to graphenes. *Carbon* 2007;45(15):2972–80.
- [12] Li YF, Li BR, Zhang HL. The computational design of junctions between carbon nanotubes and graphene nanoribbons. *Nanotechnology* 2009;20(22):225202.
- [13] Ivanovskaya VV, Zobelli A, Wagner P, Heggie MI, Briddon PR, Rayson MJ, et al. Low-energy termination of graphene edges via the formation of narrow nanotubes. *Phys Rev Lett* 2011;107(6):065502.
- [14] Iijima S, Ichihashi T, Ando Y. Pentagons, heptagons and negative curvature in graphitic microtubule growth. *Nature* 1992;356(6372):776–8.
- [15] Ugarte D. Morphology production structure of graphitic soot particles generated in arc-discharge C60. *Chem Phys Lett* 1992;198(6):596–602.
- [16] Buseck PR, Huang BJ, Keller LP. Electron-microscope investigation of the structures of annealed carbons. *Energy Fuels* 1987;1(1):105–10.
- [17] Murayama H, Maeda T. A novel form of filamentous graphite. *Nature* 1990;345(6278):791–3.
- [18] Gogotsi Y, Libera JA, Kalashnikov N, Yoshimura M. Graphite polyhedral crystals. *Science* 2000;290(5490):317–20.
- [19] Liu Z, Suenaga K, Harris PJF, Iijima S. Open and closed edges of graphene layers. *Phys Rev Lett* 2009;102(1):015501.
- [20] Lee SH, Kim HW, Hwang JO, Lee WJ, Kwon J, Bielawski CW, et al. Three-dimensional self-assembly of graphene oxide platelets into mechanically flexible macroporous carbon films. *Angew Chem Int Ed* 2010;49(52):10084–8.
- [21] Chen W, Yan L. In situ self-assembly of mild chemical reduction graphene for three-dimensional architectures. *Nanoscale* 2011;3(8):3132–7.
- [22] Worsley MA, Pauzauskie PJ, Olson TY, Biener J, Satcher JH, Baumann TF. Synthesis of graphene aerogel with high electrical conductivity. *J Am Chem Soc* 2010;132(40):14067–9.
- [23] Lv W, Tao Y, Wang Ni, Zhou Z, Su FY, Chen XC, et al. One-pot self-assembly of three-dimensional graphene macroassemblies with porous core and layered shell. *J Mater Chem* 2011;21(33):12352–7.
- [24] Chen ZP, Ren WC, Gao LB, Liu BL, Pei SF, Cheng HM. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nat Mater* 2011;10(6):424–8.
- [25] Orimo S, Majer G, Fukunaga T, Züttel A, Schlapbach L, Fujii H. Hydrogen in the mechanically prepared nanostructured graphite. *Appl Phys Lett* 1999;75(20):3093–5.
- [26] Tanaka H, Kanoh H, El-Merraoui M, Steele WA, Yudasaka M, Iijima S, et al. Quantum effects on hydrogen adsorption in internal nanospaces of single-wall carbon nanohorns. *J Phys Chem B* 2004;108(45):17457–65.
- [27] Dimitrakakis GK, Tylianakis E, Froudakis GE. Pillared graphene: a new 3-D network nanostructure for enhanced hydrogen storage. *Nano Lett* 2008;8(10):3166–70.
- [28] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-based ultracapacitors. *Nano Lett* 2008;8(10):3498–502.
- [29] Du QL, Zheng MB, Zhang LF, Wang YW, Chen JH, Xue LP, et al. Preparation of functionalized graphene sheets by a low-temperature thermal exfoliation approach and their electrochemical supercapacitive behaviors. *Electrochim Acta* 2010;55(12):3897–903.
- [30] Miller JR, Outlaw RA, Holloway BC. Graphene double-layer capacitor with ac line-filtering performance. *Science* 2010;329(5999):1637–9.
- [31] Liang M, Zhi L. Graphene-based electrode materials for rechargeable lithium batteries. *J Mater Chem* 2009;19(33):5871–8.