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Full filling of mesoporous carbon nanotubes by aqueous solution at room temperature

Xiao-Na Ren(任晓娜)[†], Min Xia(夏敏)[‡], Qing-Zhi Yan(燕青芝), and Chang-Chun Ge(葛昌纯)[§]

School of Materials Science and Technology, University of Science and Technology Beijing, Beijing 100083, *China*

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Carbon nanotubes (CNTs) have the ideal structure to be used as templates for nanomaterials, especially for nanowires, and the tungsten nanowire is an important nanomaterial that is used as a strengthening phase. Therefore, we have proposed to apply mesoporous CNT (mCNT) as a template to prepare tungsten nanowires. However, the tungsten precursor should fill the hollow tube of mCNT firstly, and very few related studies have been reported. In this paper, we have systematically studied the filling process of ammonium metatungstate (AMT) aqueous solution. The results reveal that owing to the mesopores in the mCNT sidewall, the AMT can be encapsulated into the tube at room temperature (RT) and we can fully fill it without destroying the structure. In addition, vibration and solute concentration are also important factors. Besides, the mesoporous sidewall and hollow tubular core structure of mCNT are prerequisites to realize full filling. Furthermore, tungsten nanowires have been obtained after reduction of AMT in mCNTs.

Keywords: mesoporous carbon nanotube (mCNT), capillarity, aqueous solution, tungsten nanowire

PACS: 68.03.Cd, 62.10.+s, 61.48.De, 81.20.–n **DOI:** 10.1088/1674-1056/28/3/036801

1. Introduction

As one of the most intensively studied materials, the carbon nanotube (CNT) has been applied as a supporter for catalysts,[1–5] wave-absorbing materials,[6,7] drugs,[8] and supercapacitor materials.[9–11] Besides, CNT has a high-stability sidewall and tubular structure; this unique structure makes it an ideal template or supporter for nanomaterials, especially for nanowires.[12] Therefore, it is always necessary to encapsulate materials into the hollow tube of the CNT. Pederson and Broughton[13] have studied the HF molecule in a finite-length tubule using a local-density-functional calculation, and their research proved for the first time that materials can be encapsulated into CNTs via capillarity. Soon afterwards, Ajayan and Lijima[14] verified this result by experiments, and for the first time filled the open-tipped CNTs with molten Pb by capillarity. According to these reports, $ErCl_3$,[15] Ag,[16] and Te[17] have been encapsulated into CNTs. In addition, theoretical calculations and experiments[18] have revealed that liquid with a surface tension of ≤ 200 mN/m can fill the CNT via capillarity, which suggests that water and organic solvents could be encapsulated into CNTs. According to this, Ag/Au/$AuCl_3$[19] and Ni/U/Co/Fe[20] have been encapsulated into CNTs via capillarity. However, these encapsulation processes require the opening of the CNT tip. Besides, the encapsulation always has a low filling rate if the solution is an aqueous solution. More importantly, if the solution is molten metal, it should be under a high temperature and only certain metals can fill the hollow tube.

The tungsten nanowire is considered to be the best strengthening phase for tungsten or tungsten-based materials because it not only has excellent mechanical properties, but also has the same element with matrix. Besides, the tungsten nanowire has been used as a strengthening phase for plastic composites, bullets, shells, radiation shields, etc.[21] At present, various methods for preparing tungsten nanowires have been reported, e.g., Fe, Ni, and Co have been used as catalysts to prepare tungsten nanowires while the catalysts remain in the product.[22–24] Direct preparation of tungsten nanowires on the Si matrix according to the vapor–solid mechanism is another way to prepare tungsten nanowires, and can avoid the unremovable catalyst.[25,26] However, the product is very sensitive to the heating location of the matrix, namely, the product often contains tungsten nanowires, nanoflakes, and nanodots.

Therefore, we have proposed to apply the mesoporous CNT (mCNT) as a W-nanowire template, which has plentiful mesopores in the sidewall and a straight hollow tubular core structure. However, fully filling the hollow core of the mCNT is critical for preparing tungsten nanowires, and has rarely been reported. Therefore, in this work, we have studied how to fully fill the mCNT tubular core by tungsten precursor via capillarity.

2. Experiments

It is well known that due to the surface tension of a liquid, capillarity occurs in the capillary, which follows the formula:

$$h = 2\delta\cos\theta/r\rho g, \tag{1}$$

where h is the liquid height in the capillary tube, δ is the surface tension of the liquid, θ is the contact angle between the liquid and the tube sidewall, r is the radius of the capillary

[†]Corresponding author. E-mail: renxn@ustb.edu.cn
[‡]Corresponding author. E-mail: xmdsg@ustb.edu.cn
[§]Corresponding author. E-mail: ccge@mater.ustb.edu.cn

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tube, ρ is the density of the liquid, and g is the acceleration of gravity.

In this paper, the DSA100 contact angle meter from German manufacturer KRUSS has been used to detect the surface tension of the ammonium metatungstate (AMT) solution via a vertical plate method under room temperature (RT). In addition, according to Eq. (1), we designed a series of AMT aqueous solutions with different concentrations (Table 1). Circa 0.05 g modified mCNTs were dispersed into each AMT solution, ten samples were vibrated in a constant temperature shaker at RT, and samples 11 and 12 were vibrated in constant temperature shakers at 50 °C and 80 °C, respectively. After 24 h, all of the vibrated samples were filtrated and dried.

Table 1. Details of the AMT aqueous solution.

No.	Mass of AMT/g
1	5
2	10
3	15
4	25
5	50
6	75
7	100
8	125
9	150
10	saturation
11	sample 10 heated to 50 °C
12	sample 10 heated to 80 °C

In addition, field emission scanning electron microscopy (FESEM) using a ZEISSULTRA 55 is applied to analyze the encapsulation result of different AMT solutions.

3. Results and discussion

The mCNTs used in this paper were prepared in the lab via catalytic pyrolysis. The D-band at 1345 cm^{-1} and G-band at 1592 cm^{-1} (Raman spectrum) are important to evaluate the degree of graphitization for carbon material since they represent graphitized and disordered carbon, respectively.[27,28] Figure 1(a) shows that I_D/I_G of the mCNTs is nearly 1.02,

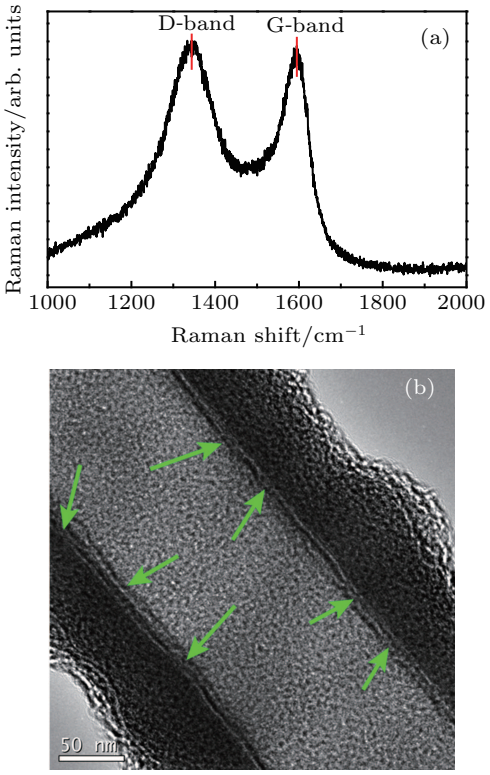


Fig. 1. (a) Raman spectrum of the mCNTs, and (b) TEM image of the mCNT.

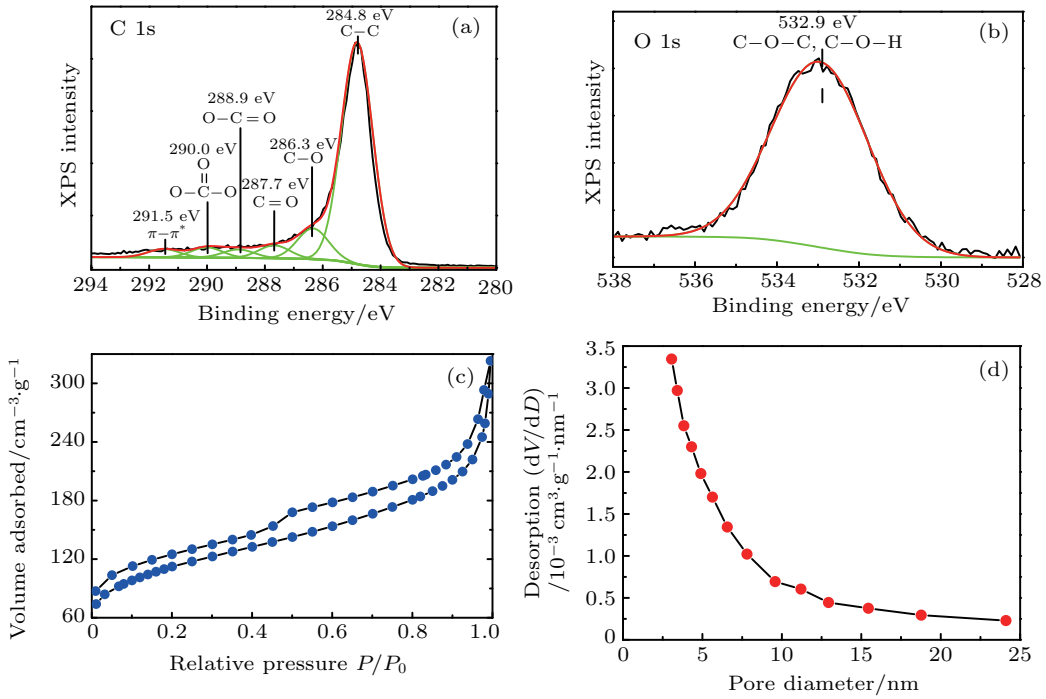


Fig. 2. (a) and (b) X-ray photoelectron (XPS) result of the modified mCNTs; (c) and (d) the adsorption–desorption curve and pore size distribution of the modified mCNTs.

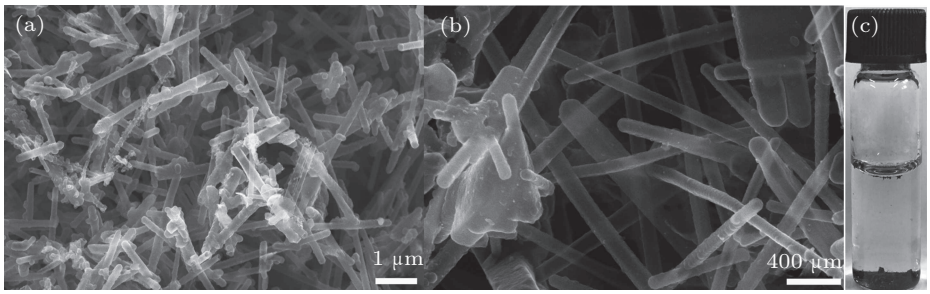


Fig. 3. (a) and (b) FESEM images of the modified mCNTs; (c) photo of mCNTs dispersed in H_2O.

indicating that the mCNT used here is nearly half graphitized and half amorphous. Combining with transmission electron microscopy (TEM) (Fig. 1(b)), it is obvious that the amorphous carbon is derived from the mesopores in the mCNT sidewall.

As shown in Fig. 2, in addition to the carbon atom from the mCNT framework (284.8 eV), the C 1s spectrum shows that it is mainly from the C–O bond (286.3 eV) (Fig. 2(a)). Besides, the O 1s spectrum of the mCNTs shows that the oxygen atom is only from the hydroxy group (532.9 eV) (Fig. 2(b)). Therefore, the mCNTs have been modified with hydroxy successfully.[29] In addition, the size of the mesopores in the mCNT sidewall is circa 4 nm (Figs. 1(b) and 2(d)), and the structural integrity of most mCNTs have been retained (Figs. 3(a) and 3(b)) after the modification process.

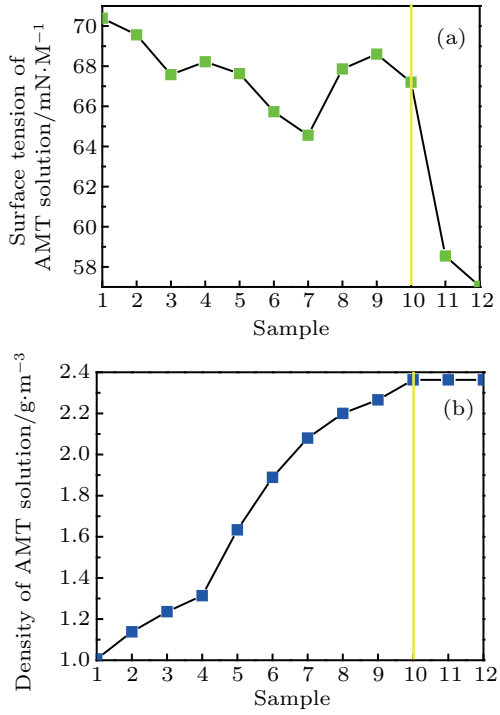


Fig. 4. (a) Surface tension and (b) density of the as-prepared AMT solution. The yellow line is the boundary between RT and heated samples.

As shown in Fig. 3(c), the hydrophilic mCNTs can be dispersed into water, which means that the water can spread out on the sidewall of mCNTs. Therefore, the contact angle of water and the mCNT sidewall is 0°, and $\cos\theta$ is 1. Moreover, the size of mesopores in the mCNT sidewall is about 4 nm, and thus r can be assumed a constant. As a result, the encapsulation ratio of AMT is proportional to δ/ρ according to Eq. (1).

As shown in Fig. 4, the surface tension of the AMT solution concentration is between 57 mN/m to 71 mN/m even after being heated to 80 °C, which conforms to the calculation result of Dujardin.[18] However, δ/ρ of the AMT solution (Fig. 5) becomes lower when the density gets higher. This indicates that the AMT filling height in the mesopores of the mCNT will be lower as the density becomes higher.

Interestingly, the experimental results are not consistent with the aforementioned analysis results. As shown in Figs. S1–S10 in the Supplementary Material (all of the red arrows in the figures indicate the positions that have not been filled, and the green ones indicate the positions that have been filled), all of the ten AMT solutions can be encapsulated into mCNT at RT, and even fully fill it. However, according to Eq. (1), when the concentration of the AMT solution increases, the encapsulation ratio of the AMT aqueous solution should decrease; meanwhile, the encapsulation ratio increases at the beginning and then decreases. Samples 1–3 (Figs. 6 and S1–S3) have lower concentrations, and AMT has filled less mCNTs and each at a lower ratio, which reveals that the AMT solution with a lower concentration means a relatively lower encapsulation ratio. When the concentration becomes higher (samples 4 and 5, Figs. 7, S4, and S5), nearly all of the mCNTs have encapsulated AMT and almost every mCNT has been fully filled.

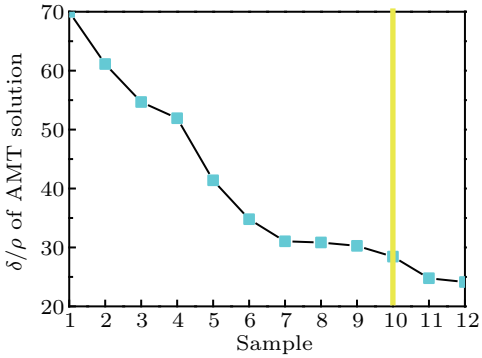


Fig. 5. δ/ρ of the as-prepared AMT solution. The yellow line is the boundary between RT and heated samples.

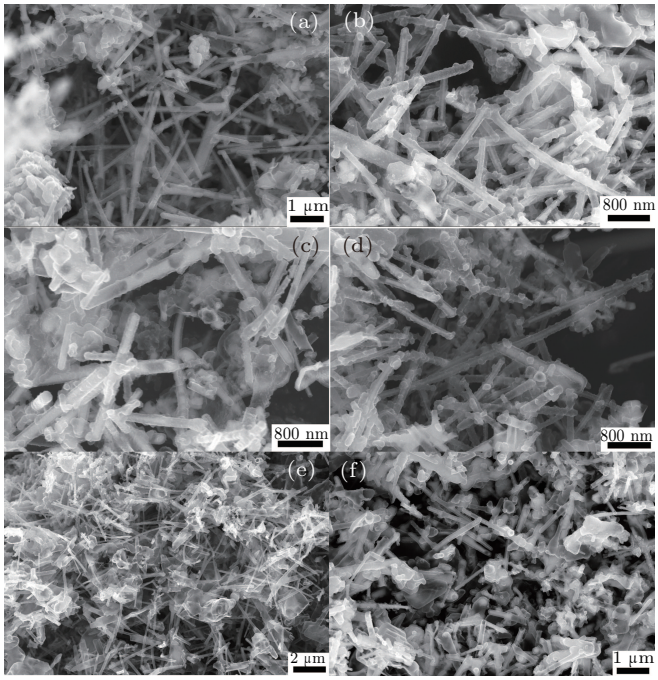


Fig. 6. FESEM images: (a) and (b) sample 1, (c) and (d) sample 2, and (e) and (f) sample 3.

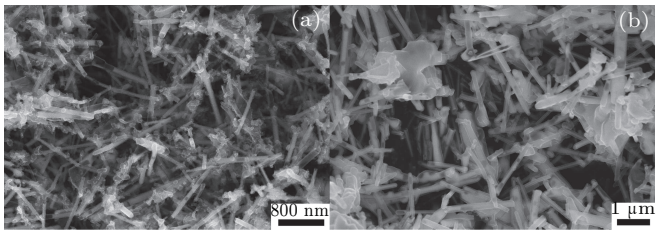


Fig. 7. FESEM images of (a) sample 4 and (b) sample 5.

The ratio of AMT encapsulation becomes lower when the concentration becomes higher (samples 6 and 7, Figs. 8, S6, and S7), but the filling rate is still higher than 95% (estimated), and each filled mCNT is fully filled. When the concentration becomes closer to saturation (samples 8 and 9, Figs. 9, S8, and S9), most mCNTs remain filled; meanwhile, the solidified AMT outside the tube embeds mCNTs. More importantly, only some open-tipped mCNTs are fully filled, and the solidified AMT buries most of the mCNTs. Moreover, some exposed mCNTs have not been filled. However, the heated saturation AMT solution at 50 °C and 80 °C (Fig. 10) has a much lower surface tension, and the filling rate is higher than that at RT.

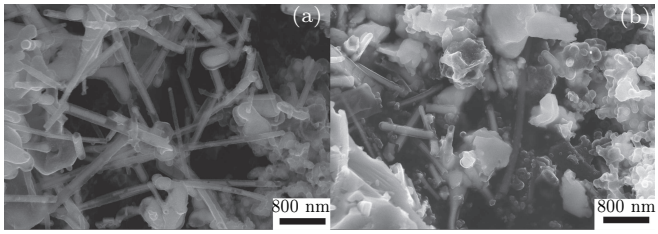


Fig. 8. FESEM images of (a) sample 6 and (b) sample 7.

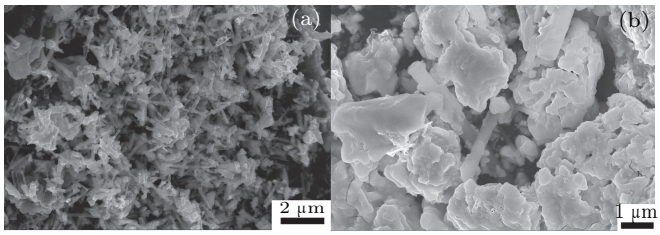


Fig. 9. FESEM images of (a) sample 8 and (b) sample 9.

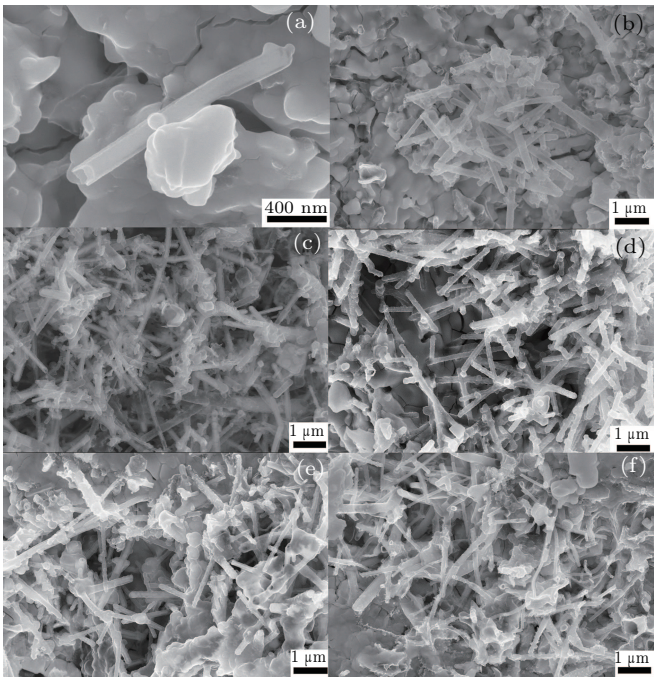


Fig. 10. FESEM images: (a) and (b) sample 10, (c) and (d) sample 11, and (e) and (f) sample 12.

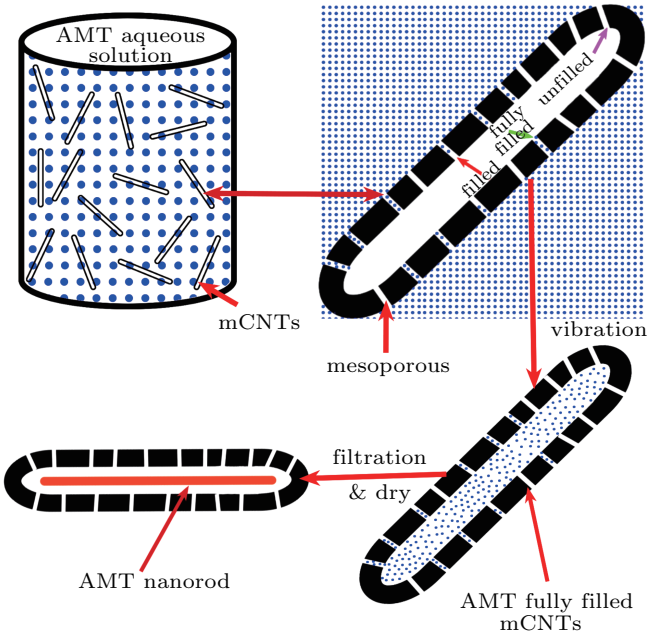


Fig. 11. Schematic diagram of the encapsulation process.

After analysis, based on capillarity and the unique mCNT structure, the AMT filling process is assumed as follows (Fig. 11). The AMT solution primitively wets the sidewall

of the mCNT, and then permeates into the wall via capillarity and fills the mesopores; the vibration helps AMT in the mesopores subsequently enter the hollow core of the mCNT. This process takes place in cycles, and finally AMT fully fills the whole cavity of the mCNT.

It is noteworthy that the experimental and calculated results are different. The reason for this interesting phenomenon is assumed as follows. The AMT has a very high solubility in water. When the concentration becomes higher, there will be much more AMT per unit volume; as a result of the combined effect of capillarity and AMT concentration, more and more AMT fills the hollow tube of mCNTs when its concentration becomes higher. Therefore, the key point of how to fully fill mCNTs at RT should include the unique structure, capillarity, vibration, and mass concentration of the solute.

In addition, based on the aforementioned study, we have obtained different nano-shaped AMT in mCNTs,[29] and prepared tungsten nanowires.[12]

4. Conclusions

The AMT encapsulation ratio in mCNT has been systematically studied according to the capillarity between the mCNT and the solution. The results reveal that without opening the mCNT tip, AMT can fill the hollow core of the mCNT with a wide range of concentrations. Besides, when the concentration is circa 15%–30% of saturation, AMT can fully fill the mCNT. After analysis, the AMT filling process is assumed as follows. The AMT solution is absorbed into the mesopores in the sidewall of mCNTs via capillarity, and then the absorbed solution gradually permeates into the hollow core of mCNTs with the help of vibration; finally, AMT fully fills the nanotube. Therefore, the unique structure of the mCNT (the mesoporous sidewall with a hollow tubular core) is a prerequisite to fully fill the mCNT at RT without destroying its structure. More importantly, vibration or other external forces and the mass concentration of the solution are also keys to fully filling mCNTs. Besides, the reduction of the AMT of fully filled mCNTs has produced fine-structured tungsten nanowires.

References

[1] Kireeti K V M K and Jha N 2017 *J. Power Sources* **364** 392
[2] Xu D, Lu P, Dai P, Wang H and Ji S 2012 *J. Phys. Chem. C* **116** 3405
[3] Ovejero G, Sotelo J L, Romero M D, Rodríguez A, Ocaña M A, Rodríguez G and García J 2006 *Ind. Eng. Chem. Res.* **45** 2206
[4] Rehman S, Khan K, Zhao Y and Hou Y 2017 *J. Mater. Chem. A* **5** 3014
[5] Park J, Moon W G, Kim G P, Nam I, Park S, Kim Y and Yi J 2013 *Electrochim. Acta* **105** 110
[6] Li Z, Ye Z, Roberts J A and Zhao G L 2011 *J. Appl. Phys.* **110** 074107
[7] Tan K H, Ahmad R and Johan M R 2013 *Mater. Chem. Phys.* **139** 66
[8] Dineshkumar B, Krishnakumar K, Bhatt A, Paul D, Cherian J, John A and Suresh S 2015 *Indian J. Cancer* **52** 262
[9] Wang Q, Yan J, Wang Y, Ning G, Fan Z, Wei T, Cheng J, Zhang M and Jing X 2013 *Carbon* **52** 209
[10] Jiang H, Lee P S and Li C 2013 *Energy Environ. Sci.* **6** 41
[11] Jiang H, Li C, Sun T and Ma J 2012 *Nanoscale* **4** 807
[12] Ren X N , Xia M, Yan Q Z and Ge C C 2017 *Chin. Phys. B* **26** 038103
[13] Pederson M R and Broughton J Q 1992 *Phys. Rev. Lett.* **69** 2689
[14] Ajayan P M and Lijima S 1993 *Nature* **361** 333
[15] Kitaura R, Ogawa D, Kobayashi K, Saito T, Ohshima S, Nakamura T, Yoshikawa H, Awaga K and Shinohara H 2008 *Nano Res.* **1** 152
[16] Sloan J, Wright D M, Bailey S, Brown G, York A P E, Coleman K S, Green M L H, Sloan J, Wright D M, Hutchison J L and Woo H G 1999 *Chem. Commun.* **0** 699
[17] Medeiros P V C, Marks S, Wynn J M, Vasylenko A, Ramasse Q M, Quigley D, Sloan J and Morris A J 2017 *ACS Nano* **11** 6178
[18] Anon 1994 *Sci. Wash.* **265** 1850
[19] Chu A, Cook J, Heesom R J R, Hutchison J L, Green M L H and Sloan J 1996 *Chem. Mater.* **8** 2751
[20] Tsang S C, Chen Y K, Harris P J F and Green M L H 1994 *Nature* **372** 159
[21] Huang H, Wu Y Q, Wang S L, He Y H, Zou J, Huang B Y and Liu C T 2009 *Mater. Sci. Eng. A* **523** 193
[22] Ma Y, Li J, Liu W and Shi Y 2012 *Nanoscale Res. Lett.* **7** 1
[23] Wang C, He Y, Wang S, Zhang Q and Liu X 2012 *J. Cryst. Growth* **338** 214
[24] Wang S L, He Y H, Zou J, Wang Y, Huang H, Huang B Y, Liu C T and Liaw P K 2008 *Nanotechnology* **19** 345604
[25] Vaddiraju S, Chandrasekaran H and Sunkara M K 2003 *J. Am. Chem. Soc.* **125** 10792
[26] Wang S, He Y, Fang X, Zou J, Wang Y, Huang H, Costa P M F J, Song M, Huang B, Liu C T, Liaw P K, Bando Y and Golberg D 2009 *Adv. Mater.* **21** 2387
[27] Datsyuk V, Kalyva M, Papagelis K, Parthenios J, Tasis D, Siokou A, Kallitsis I and Galiotis C 2008 *Carbon* **46** 833
[28] Xu X, Tan H, Xi K, Ding S, Yu D, Cheng S, Yang G, Peng X, Fakeeh A and Kumar R V 2015 *Carbon* **84** 491
[29] Ren X, Xia M, Yan Q and Ge C 2016 *Chem. Phys. Lett.* **662** 286