Controllable preparation of tungsten/tungsten carbide nanowires or nanodots in nanostructured carbon with hollow macroporous core/mesoporous shell

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

Institute of Nuclear Energy and New Energy System Materials, School of Materials Sciences and Engineering, University of Science and Technology Beijing, Beijing 100083, *China*

(Received 4 November 2016; revised manuscript received 22 December 2016; published online 13 February 2017)

Large scale tungsten nanowires and tungsten nanodots are prepared in a controllable way. The preparation is based on mechanisms of chemical vapor transportation and phase transformation during the reduction of ammonium metatungstate (AMT) in H_2. The AMT is first encapsulated into the hollow core of nanostructured carbon with hollow macroporous core/mesoporous shell (NC-HMC/MS) and forms nanorods, which are the precursors of both tungsten nanowires and tungsten nanodots. Just by controlling H_2 flow rate and heating rate in the reduction process, the AMT nanorods could turn into nanowires (under low rate condition) or nanodots (under high rate condition). Besides, via heat treatment at 1200 °C, the as-obtained nano-sized tungsten could convert into W_2C nanorods or WC nanodots respectively. Furthermore, the diameter of the as-obtained tungsten or tungsten carbide is confined within 50 nm by the NC-HMC/MS, and no agglomeration appears in the obtained nanomaterials.

Keywords: tungsten nanowires, tungsten nanodots, mesoporous carbon, self-assembly

PACS: 81.07.–b, 81.07.Gf, 81.10.St, 81.16.Dn **DOI:** 10.1088/1674-1056/26/3/038103

1. Introduction

Tungsten nanowire is supposed to be an ideal reinforcing material in high-performance tungsten contained materials.[1] Tungsten nanowires have been used as strengthen phase for plastic composites, bullet, shot, radiation shields,[2] or used as substitute for uranium[3] along with iron and steel matrix. In addition, tungsten nanowires have been used as metal gate,[4] Li-ion battery catalyst,[5] pH sensitive electrodes,[6] hydrogen sensor,[7] electron emission sources,[8] template for nanodots,[9] etc. For this important nanomaterial, there are a few kinds of methods to prepare it, such as chemical vapor deposition,[2] conventional photolithography,[9] directional solidification of eutectic alloy[10] or vacuum pyrolysis/carbothermal treatment,[11] etc. However, problems always appeared, such as the nanowire feature of as-prepared tungsten was uncontrollable,[10–12] the catalyst/template was hardly to remove,[13,14] or it was difficult to realize large-scale.[8,9] On the other hand, tungsten nanodot is an important part of floating gate of nonvolatile memory,[15,16] and could be an ideal precursor of WC nanodot.

Tungsten carbide has been considered as a green catalyst for diverse electron-transfer reactions[17] since it possesses platinum-like behavior in surface catalysis.[18] Therefore, tungsten carbide has been widely studied as catalyst for isomerization reactions, fuel cells, hydrogenolysis, hydrogen evolution and catalytic oxidation,[17,19,20] or used in biology[21] as artificial enzymes.[22] However, large-scale, nano-sized and shaped controlled preparation of tungsten carbide has been rarely reported as far as we know.

On the other hand, due to the high chemical and thermal stability, low density, large surface area, uniform particle size and narrow pore size distribution,[23,24] nanostructured carbon with hollow macroporous core/mesoporous shell (NC-HMC/MS) was considered as the ideal template for nanomaterials[25] and important support for catalysts.[26,27] Most importantly, the unique hollow core and mesoporous shell structure of NC-HMC/MS allows it to encapsulate materials in the hollow core via the mesoporous in the shell. Therefore, it shows a great potential to be used as template or support in fields like supercapacitor,[28] drug delivery,[29] low-threshold field emitter,[30] battery,[31] electromagnetic wave and microwave absorption materials,[32] or metal/nonmetal nanoparticles encapsulation.[33–35]

Here in this paper, we propose a simple method to prepare, in a controllable way, large scale, nano-sized tungsten nanowires or nanodots, which has adopted tubular NC-HMC/MS (TNC-HMC/MS) as template. The obtained nano-sized tungsten could convert into WC nanodots or W_2C nanorods via reacting with the carbon shell while being heat treated.

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

© 2017 Chinese Physical Society and IOP Publishing Ltd

2. Experiments and characterization

2.1. Experiments

Hydrophilic group modified TNC-HMC/MS was dispersed into ammonium metatungstate (AMT) aqueous solution, the solid–liquid mixture was stirred for about 24 h. After filtrating and drying, the as-obtained black powder was reduced in H_2 at 650 °C for 1 h. According to the chemical vapor transport mechanism, the H_2 flow rate and heating rate are critical to the control of the final shape of nano-sized tungsten. Therefore, the reduction conditions were changed according to two rates. Namely, reducing under lower rate condition (0.1 sccm for H_2 flow rate and 5 °C/min for heating rate) to prepare tungsten nanowires and under higher rate conditions (0.3 sccm for H_2 flow rate and 5 °C/min for heating rate, 0.1 sccm for H_2 flow rate, and 70 °C/min for heating rate) to prepare tungsten nanodots. In addition, by heat treating at 1200 °C, the obtained nano-sized tungsten has reacted with the carbon shell and converted into W_2C nanorods or WC nanodots.

2.2. Characterization

X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) were used to characterize the obtained nano-sized tungsten or tungsten carbide.

3. Results and discussion

As shown in Fig. 1, the TNC-HMC/MS features mesoporous shell which is marked by arrow and lines in Fig. 1(b). The size of each mesopore is about 4 nm (Fig. 1(c)). These mesopores in the shell are very important for TNC-HMC/MS to encapsulate AMT into its hollow core, as AMT could be encapsulated through the pore without destroying the shell.

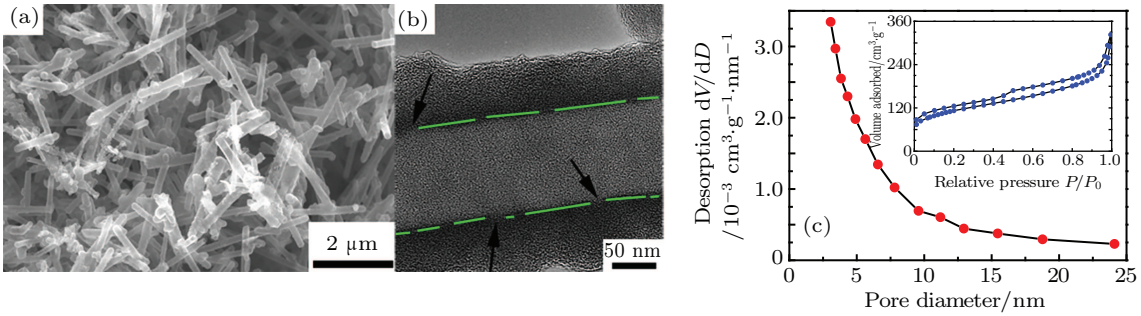


Fig. 1. (color online) FESEM image (a), TEM image (b), and BET/BJH result (c) of the modified TNC-HMC/MS.

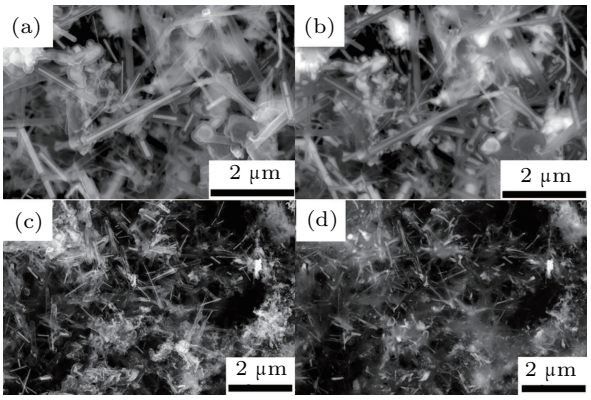


Fig. 2. FESEM images of the encapsulated AMT. Panels (a) and (c) show the secondary electron images, panels (b) and (d) present the corresponding backscatter electron images in panels (a) and (c) respectively.

Due to the capillarity of mesopores in the shell (Fig. 1(b)),[36,37] TNC-HMC/MS could encapsulate materials through it by the wet chemical method. Therefore, AMT can be encapsulated into the hollow core of TNC-HMC/MS via mesoporous shell when TNC-HMC/MS is dispersed into its solution. As shown in Fig. 2, most of TNC-HMC/MSs are filled with AMT, and very clearly shown by comparison between secondary electrode and back scattering images (Figs. 2(a)–2(d)). In addition, the diameter of the encapsulated AMT nanorods is about 50 nm, and the length is circa several micrometers, which are in line with the diameter and length of TNC-HMC/MS. The approximate sizes of nanorods and TNC-HMC/MS indicate that TNC-HMC/MS has been filled with AMT.

After being reduced at 650 °C, the encapsulated AMT is converted into tungsten successfully as shown in Fig. 3. However, different reduction conditions lead to different morphologies of nano-sized tungsten, which are shown in Fig. 4.

As WO_3 is the phase that destines to show up in the reduction process of AMT, the reduction process of WO_3 would generate gaseous phase of tungsten compounds ($WO_2(OH)_2$).[38–40] Therefore, according to the mechanism of chemical vapor transportation, the H_2 flow rate is a key parameter during reduction. On the other hand, tungsten oxide belongs to rhombic system and tungsten belongs to cubic system, so the phase transformation during the reduction procedure can certainly occur, and if the heating rate is as fast as possible, some phase transformation processes may be missed, thereby perhaps obtaining different products.

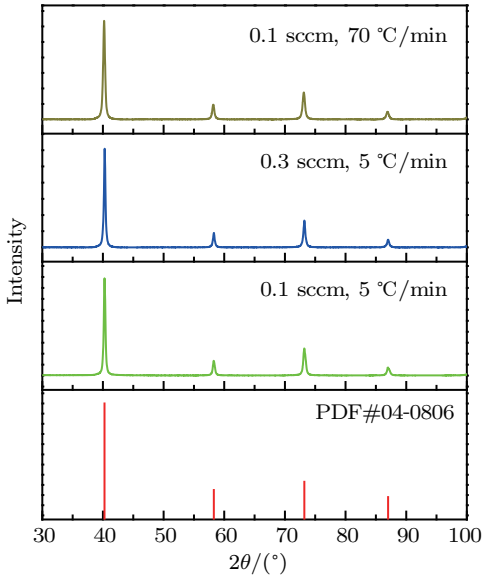


Fig. 3. (color online) XRD results of the as-obtained nano-sized tungsten prepared under different reduction conditions.

As shown in Figs. 4(a) and 4(b), tungsten nanodots in the hollow core of TNC-HMC/MS are obtained from the reduction procedure of 0.1 sccm (H_2 flow rate) and 70 °C/min (heating rate). Due to the rapid heating (70 °C/min) during reduction, sites where the composition is lost cannot be filled up by the yielded tungsten immediately, and phase transition like WO_3-to-$WO_{2.9}$ and $WO_{2.9}$-to-W may be missed, hence direct phase transformation from rhombic WO_3 to cubic W has left nanodot product.

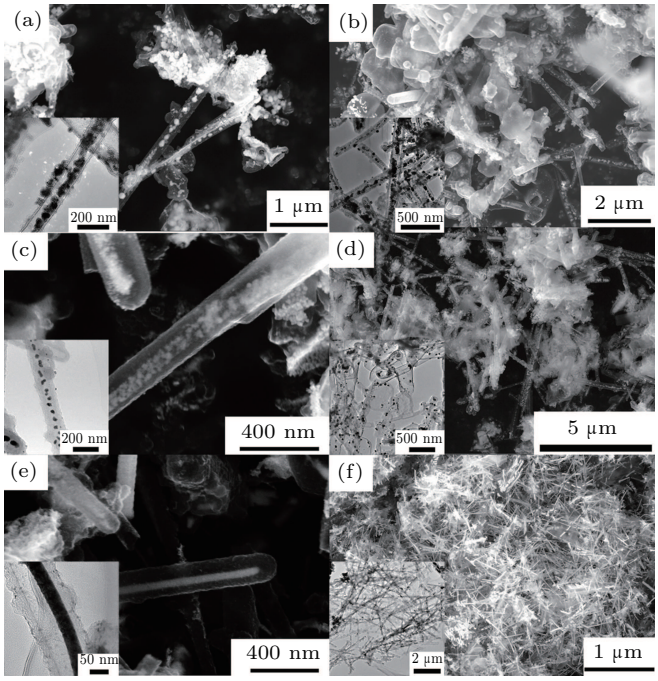


Fig. 4. FESEM images of the obtained nano-sized tungsten and their corresponding TEM images (insert). Panels (a) and (b) show the images of tungsten reduced through 0.1 sccm and 70 °C/min procedure; panels (c) and (d) indicate the images of tungsten obtained from 0.3 sccm and 5 °C/min reduction process; panels (e) and (f) present the images of tungsten obtained under 0.1 sccm and 5 °C/min conditions.

Besides, the nanodots each have a diameter of about 50 nm, which is approximately the diameter of the hollow core of TNC-HMC/MS, and this indicates that the TNC-HMC/MS confines the growth of tungsten nanodots. Furthermore, as agglomeration is an annoying problem of nanomaterials, the obtained tungsten nanodots do not have such a problem. The well dispersed tungsten nanodots in the hollow core of TNC-HMC/MS indicate that TNC-HMC/MS can not only confine the growth of tungsten but also buffer their aggregation.

Interestingly, distinct result is obtained when the heating rate is slowed down (0.1 sccm, 5 °C/min) as shown in Figs. 4(e) and 4(f). Nanowires with a diameter of about 50 nm and length of about several micrometers are obtained. Like what was mentioned before, the TNC-HMC/MS also confines the growth of nanowires and buffers their aggregation. Unlike what has been obtained from the rapid heating procedure, slower heating rate results in nanowires rather than nanodots. The reason to cause this interesting result is supposed to be fact that slower heating reduction procedure allows the reduced tungsten to fill up the vacancy derived from phase transition and gaseous reduction product like NH_3 or H_2O, and no or less $WO_2(OH)_2(g)$ has been transferred by H_2.

As mentioned before, along with gaseous NH_3 and H_2O, gaseous tungsten compound is yielded through the following reaction:[40]

$$WO_3(s) + H_2O(g) \rightarrow WO_2(OH)_2(g). \quad (1)$$

The unreduced WO_3 would react with generated $H_2O(g)$ according to chemical equation (1) and release gaseous $WO_2(OH_2)$. Therefore, the higher H_2 flow rate (0.3 sccm) can carry away more unreduced $WO_2(OH)_2(g)$ and left more or larger vacancies. The vacancy cannot be filled up by the yielded tungsten as soon as it is generated, since the rapid H_2 flow generates another vacancy and the yielded tungsten is too busy to fill up vacancy. On the other hand, the rapid H_2 flow reduces the carried $WO_2(OH)_2$ at the same time, but takes the reduction product to another side or even outside of TNC-HMC/MS. As shown in Figs. 4(c) and 4(d), like the rapid heat reduction, fast H_2 flow rate can also be used to prepare large-scale tungsten nanodots but this is mainly based on the mechanism of chemical vapor transportation. Moreover, the nanodots each have a diameter of about 50 nm, and TNC-HMC/MS play the same role, as mentioned above. In addition, the most important point is that the obtained nanowires or nanodots are formed without catalysts, which are all self-assembled.

The inside tungsten could react with the carbon shell at 1200 °C as shown in Fig. 5. Due to the confining of TNC-HMC/MS, the shape of the nano-size tungsten is inherited. Therefore, the prepared nano-sized tungsten should be ideal precursor for nano tungsten carbide. However, the following interesting results are obtained: the tungsten nanowires result

in W_2C and the tungsten nanodots lead to WC. In addition to the shape retention, W nanowires provide greater W content and W_2C can be generated. In the same way, W nanodots are converted into WC. Again, the well dispersed W_2C nanorods and WC nanodots prove the important space confinement effect of TNC-HMC/MS as mentioned before.

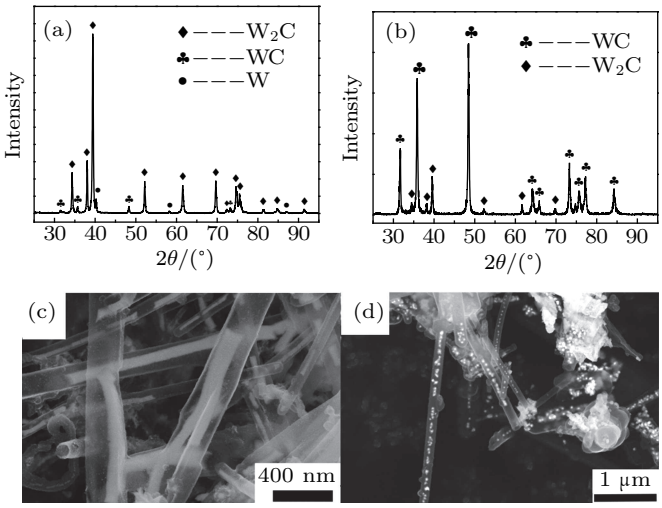


Fig. 5. XRD results and the FESEM images of the obtained tungsten carbide, showing ((a), (c)) W_2C nanorods, and ((b), (d)) WC nanodots.

4. Conclusion and perspectives

AMT is encapsulated into the hollow core of TNC-HMC/MS via mesopores in its shell just by stirring. Based on the phase transformation and chemical vapor transportation mechanism, the variation of reduction parameters of AMT, nanorods generates different-morphology nano-sized tungsten. That is, under the lower H_2 flow rate (0.1 sccm) and lower heating rate (5 °C/min) condition tungsten nanowires are obtained. While under the higher H_2 flow rate (0.3 sccm) or rapid heating (70 °C/min) reduction conditions, tungsten nanodots are gained. The obtained nanowires/nanodots are self-assembled in TNC-HMC/MS without catalyst. Besides, the tungsten nanowires/nanodots could convert into tungsten carbide nanorods/nanodots respectively, which is a sort of important catalyst. All of the nano-sized tungsten or tungsten carbide have a diameter of about 50 nm, which indicates that TNC-HMC/MS plays the roles of template and confining material growth. Furthermore, the well dispersed nano-sized materials obtained in this work indicate another important role of TNC-HMC/MS-space confinement effect.

References

[1] Hou L Z, Wang S L, Chen G L, He Y H and Xie Y 2013 *Trans. Nonferrous Met. Soc. China* **23** 2323
[2] 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
[3] Levitt A P (US Patent) 5 440 995 [1995-08-15]
[4] Lee Y H, Choi C H, Jang Y T, Kim E K, Ju B K, Min N K and Ahn J H 2002 *Appl. Phys. Lett.* **81** 745
[5] Gu Z J, Li H Q, Zhai T Y, Yang W S, Xia Y Y, Ma Y and Yao J N 2007 *J. Solid State Chem.* **180** 98
[6] Fenster C, Smith A J, Abts A, Milenkovic S and Hassel A W 2008 *Electrochem. Commun.* **10** 1125
[7] Choi J and Kim J 2009 *Sens. Actuators B Chem.* **136** 92
[8] Choi C H, Jang Y T, Ju B K, Lee Y H, Oh M H, Ahn J H and Min N K 2002 *SID Symp. Dig. Tech. Pap.* **33** 369
[9] Lee Y H, Kim D H, Shin K S, Choi C H, Jang Y T and Ju B K 2003 *Appl. Phys. Lett.* **82** 3535
[10] Milenkovic S and Hassel A W 2009 *Phys. Status Solidi A* **206** 455
[11] Li Y D, Li X L, Deng Z X, Zhou B C, Fan S S, Wang J W and Sun X M 2002 *Angew. Chem. Int. Ed.* **41** 333
[12] Liu Z Q, Mitsuishi K and Furuya K J 2004 *Appl. Phys.* **96** 619
[13] Wang C, He Y H, Wang S L, Zhang Q and Liu X L 2012 *J. Cryst. Growth* **338** 214
[14] Bien D C, Saman R M, Badaruddin S A M and Lee H W 2011 *Nanoscale Res. Lett.* **6** 1
[15] Pei Y, Nishijima M, Fukushima T, Tanaka T and Koyanagi M 2008 *Appl. Phys. Lett.* **93** 113115
[16] Choi S, Yang H, Chang M, Baek S, Hwang H, Jeon S, Kim J and Kim C 2005 *Appl. Phys. Lett.* **86** 251901
[17] Dai W L, Ding J, Zhu Q, Gao R and Yang X 2016 *Catal.* **28** 1
[18] Levy R B and Boudart M 1973 *Science* **181** 547
[19] Meng H and Shen P K 2005 *J. Phys. Chem. B* **109** 22705
[20] Moreno-Castilla C, Alvarez-Merino M A, Carrasco-Marín F and Fierro J L G 2001 *Langmuir* **17** 1752
[21] Rosenbaum M, Zhao F, Schröder U and Scholz F 2006 *Angew. Chem. Int. Ed.* **45** 6658
[22] Li N, Yan Y, Xia B Y, Wang J Y and Wang X 2014 *Biosens. Bioelectron.* **54** 521
[23] Yoon S B, Sohn K, Kim J Y, Shin C H, Yu J S and Hyeon T 2002 *Adv. Mater.* **14** 19
[24] Ni Y B, Shao M W, Tong Y H, Qian G X and Wei X W 2005 *J. Solid State Chem.* **178** 908
[25] Dai H J, Wong E W, Lu Y Z, Fan S S and Lieber C M 1995 *Nature* **375** 769
[26] Liang C D, Li Z J and Dai S 2008 *Angew. Chem. Int. Ed.* **47** 3696
[27] Mu Y Y, Liang H P, Hu J S, Jiang L and Wan L J 2005 *J. Phys. Chem. B* **109** 22212
[28] Wang Q, Yan J, Wang Y B, Ning G Q, Fan Z J, Wei T, Cheng J, Zhang M L and Jing X Y 2013 *Carbon* **52** 209
[29] Prodana M, Voiculet A, Garea S, Radu M, Iovu H, Demetrescu I and Dinischiotu A 2014 *Cent. Eur. J. Chem.* **12** 1008
[30] Jha A, Banerjee D and Chattopadhyay K K 2011 *Carbon.* **49** 1272
[31] Li Q Q, Li W Q, Feng Q, Wang P, Mao M M, Liu J B, Zhou L M, Wang H T and Yao H M 2014 *Carbon* **80** 793
[32] Tan K H, Ahmad R and Johan M R 2013 *Mater. Chem. Phys.* **139** 66
[33] Dinesh J, Eswaramoorthy M and Rao C N R 2007 *J. Phys. Chem. C* **111** 510
[34] Xiong Y J, Xie Y, Li X X and Li Z Q 2004 *Carbon* **42** 1447
[35] Yusof Y and Johan M R 2014 *Cryst. Eng. Comm.* **16** 8570
[36] Tsang S C, Chen Y K, Harris P J and Green M L 1994 *Nature* **372** 159
[37] Ajayan P M and Lijima S 1993 *Nature* **361** 333
[38] Sarin K 1975 *J. Mater. Sci.* **10** 593
[39] Venables D S and Brown M E 1996 *Thermochim. Acta.* **285** 361
[40] Xu F S, Tse S D, Al-Sharab J F and Kear B H 2006 *Appl. Phys. Lett.* **88** 243115