Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 2877–2881

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Tungsten carbide (WC) nanopowders synthesized via novel core–shell structured precursors

Hua Lin[a,b,*], Bowan Tao[a], Jie Xiong[a], Qing Li[b], Yanrong Li[a,**]

[a]State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[b]School of Materials Science and Engineering, Southwest University, Chongqing 400715, PR China

Received 8 August 2012; received in revised form 20 September 2012; accepted 20 September 2012
Available online 28 September 2012

Abstract

WC powders with a size in the range of 20–60 nm were prepared through carbothermal reduction of a novel core–shell structured precursor in vacuum. The samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The thermolysis process of the precursor has been investigated by themogravimetric analysis and differential thermal analysis (TG–DSC). The results revealed that the single phase WC nanopowders were synthesized at 980 °C for 1 h. Spectra of XPS indicate that the surface of the specimen mainly consists of W, C and O three species elements only. The effects of experimental parameters and reaction mechanism have been explored. Mainly due to the homogeneous chemical composition of the precursor, the synthesizing temperature was greatly lower than the conventional method.

Keywords: Nanopowders; WC; Hydrothermal method; X-ray diffraction

1. Introduction

Tungsten carbide was widely used in many industrial applications because of its particular properties, such as high melting point, hardness, toughness, excellent wear and corrosion resistance [1,2]. Most of the applications of WC is being used as cement carbide in the tool industry for the production of cutting tools, mining tools, drilling tools and wear resistant applications [3–5]. It is also used as a potential catalyst substitute for noble metals like Pt, Pb and Ir in catalysis industries [6,7]. Many reports indicate that the decrease of the particle size is in favor of increasing the tool life and improving the catalytic activity [2,8,9]. So the preparation of nano-sized WC powders has become a research hotspot.

A number of methods have been used to synthesize WC nanopowders, such as mechanical alloying, solid state metathesis, hydrogen or CO by CVD method, thermal decomposition of metal complexes, and the ion arc method [10–14]. However, these common methods in preparing WC nanopowders face enormous challenges like high costs, low yields, impurities and wide particle size distributions. Presently, Kodambaka reported a carbothermal reduction method which uses carbon coated WO_3 precursor to prepare WC nanopowders [15]. This is ideal for the preparation of WC nanopowders by direct reduction tungsten oxide with carbon. It is in favor of improving the contact area between the WO_3 and carbon, increasing the reaction rate and decreasing the reaction temperature and time. In their work, the nano-sized tungsten trioxide and carbon black or high purity gases were needed as reactants. It is not commercially viable.

The hydrothermal method is an effective route for preparing a carbon coated core–shell structure, which has been attracting more and more interest [16]. In this process, metal salts and organic polymers were used as

---

*Corresponding author at: State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China. Tel./fax: +86 28 83201232.

E-mail addresses: lh2004@swu.edu.cn (H. Lin), yrli@uestc.edu.cn (Y. Li).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.09.061

source materials, and it does not need expensive reductive gas or complex equipment. Presently, a series of works have been done on the synthesis of metal @ C, oxides @ C or compound @ C [17–19]. Based on the same principle, this method can be used to synthesize carbon coated tungsten oxide structures, which would directly prepare WC nanopowders through in-situ reduction and carburization without expensive reductive gas or complex equipment. However, until now, this method has not been developed as the post synthesis method, while relative reports are rare.

In this work, we will show a facile method by using cheap materials as reactants to prepare WC nanopowders. Here, the hydrothermal method was used to prepare the carbon coated core–shell precursor which the elements W and C are tightly contacted. Then, the WC nanopowders were obtained by carbothermal reduction of the precursor at a lower temperature and a shorter reaction time in vacuum.

2. Experimental

All of the reagents used were purchased from Chendu Kelong Chemical plant. 5 g ammonium metatungstate (AMT ($(NH_4)_6(H_2W_{12}O_{40})\cdot 4H_2O$, analytical grade) was dissolved into hot deionized water), 4.6 g corn starch ($(C_6H_{10}O_5)n$, molecular weight 342.29, industrial grade) was added into the above solution and mixed them uniformly. It was then added into a Teflon-lined autoclave. The autoclave was sealed into a stainless steel tank and maintained at 200 °C for 8 h without shaking or stirring. When the autoclave had been naturally cooled to room temperature, the products were taken out and diluted. The precursors were obtained by spray-drying the products with hot air at 250 °C. Finally, the target products were obtained by heating the precursors in a vacuum furnace at 980 °C for 1 h, with the temperature rate increase of 10 K min^{-1}.

Phase identification was performed by an X-ray diffractometer (XD-3, Purkinje, Beijing) using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) at a scanning rate of 0.02°/s in the 2θ range of 30 to 88°. The transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were operated at a FEI Tecnai-G2F20 using an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with a XSAM 800 photoelectron spectrometer (Kratos, England), using nonmonochromatized Mg $K\alpha$ ($\lambda = 0.9889$ nm) X-ray as the excitation source. Thermogravimetry–differential scanning calorimetry (TG–DSC) analysis was carried out with the NETZSCH STA-409 simultaneous thermal analyzer.

3. Results and discussion

According to the previous work [20], the ammonium metatungstate would transform into WO_3, H_2O and NH_3. The corn starch would be carbonized under high temperature and pressure conditions, and then form core–shell structures. The research indicated that the optimal conditions of the process of hydrothermal are 200 °C for 8 h. Although not all of the metal ions and carbon would precipitate to form core–shell structure after the hydrothermal process, residual metal ions and carbon did not affect the preparation of the composite powders. During the spray-drying, the residual metal ions and carbon would be evenly deposited on the surface of the core–shell particles to obtain the uniform precursors. Fig. 1 is a HRTEM micrograph of the precursors prepared by hydrothermal method at 200 °C for 8 h. From the picture, one can see that the particles are typical spherical core–shell structures with the diameter of about 20–60 nm and evenly dispersed.

Fig. 2 shows the XRD patterns of the precursor and the samples obtained under different reaction conditions. Fig. 2a shows the diffraction peaks of the precursor obtained by spry-drying; here, there are no apparent peaks. It indicates that the core–shell mixtures are of an amorphous structure. Fig. 2b shows the XRD patterns obtained at 800 °C for 1 h. One can see that the carburization reaction is incomplete, which shows the phases of W and W_2C along with the major phase of WC. When the temperature was increased to 900 °C, the W phase disappeared, while the peaks corresponding to WC and W_2C increased (Fig. 2c). It indicated that the carburization intensity increased with the increase of temperature. When the temperature is increased to 980 °C, the XRD patterns consist of WC peaks without any traces of W_2C phase and tungsten metal. As is shown in Fig. 2d, all the peaks correspond to that of pure WC, which is in agreement with the reported value (JCPDS 89-2727). Fig. 2e is the diffraction patterns of powders obtained at

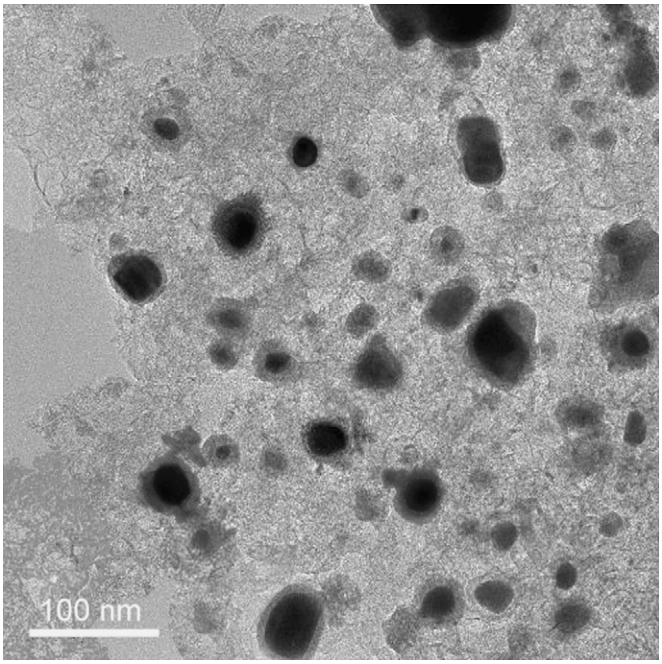

Fig. 1. HRTEM micrograph of the precursor.

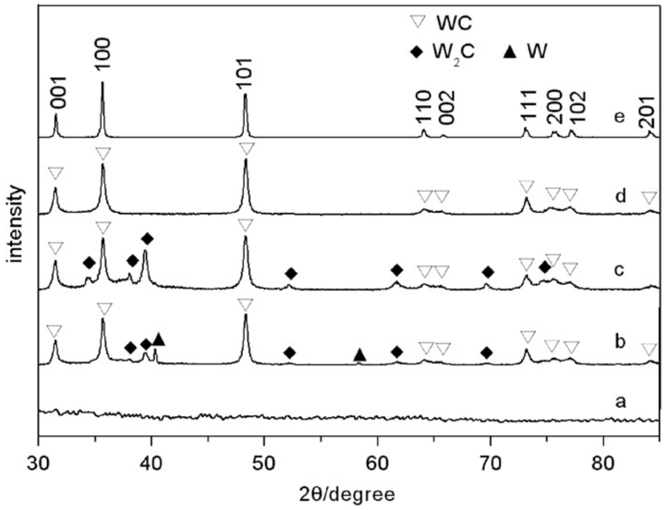

Fig. 2. XRD patterns of precursor (a) and the samples prepared at 800 °C, 1 h(b); 900 °C, 1 h (c); 980 °C, 1 h (d); 1100 °C, 1 h (e).

1100 °C for 1 h. Compared with Fig. 2d, the line of Fig. 2e has no remarkable changes, indicating that the reaction is over at 980 °C.

In this work, the optimal synthesis condition of WC is at 980 °C for 1 h. The reaction temperature is lower (200 °C–500 °C) than the previous reports [15,21]. The reaction time is lower (3–70 h) than those conventional methods [22]. The TEM micrograph of synthesized samples was shown in Fig. 3. Point out that the powders are spherical with a diameter in the range from 20 to 60 nm.

Fig. 4 presents the W 4f (a), O 1s (b) and C1s (c) binding energy spectra of the WC nanopowders obtained at 980 °C for 1 h. As shown in Fig. 4a, the W 4f region displays three peaks centered at 37.5, 34.23 and 32.06 eV. The peaks at 32.06 and 34.23 eV are corresponding to WC, and the additional peak at 37.5 eV is assigned to tungsten oxides (W^{6+}) because the sample would be oxidized in the presence of air at room temperature. Here, the W and W_2C cannot be observed which is consistent with the XRD result in Fig. 2d and hints the complete transformation from W to WC. Spectra of O 1s XPS energy region contains two peaks 532.65 eV (Oh) and 530.42 eV (Od), as shown in Fig. 4b. The peak of Oh is considered to hydroxyl oxygen (OH^-) which mainly originated from air and can be removed by drying the sample at certain temperature. The peak of Od is ascribed to tungsten trioxide (W^{6+}) due to the oxidation of WC exposure to the air. The C 1s signal (Fig. 4c) is comprised of two peaks 284.5 eV (Cf) and 283.45 eV (Cc). The Cc peak is due to the photoelectrons ejected from the carbon in tungsten carbide lattice. The Cf peak corresponds to free carbon contaminated on the surface of carbides and the free carbon in the sample due to the provision of excess carbon in the reaction system. These results agree with the previous reports [23–25].

In order to understand the physical phenomena occurring during the thermal processing, simultaneous TG–DSC measurements were carried out for the precursor. The results are given in Fig. 5. As shown in Fig. 5, a long broad endothermic peak occurs from room temperature to 800 °C, which exhibits the mass slowly declining. This is a complex process which may own to a loss of adsorbed and included water of the precursor, while a part of tungsten trioxide was reduced. According to precious research, the reduction of tungsten trioxide may have one or more products: $WO_{2.9}$, $WO_{2.72}$, WO_2, and W. The involved reaction can be expressed as Eq. (1). The sharp endothermic peak at 873 °C with large mass loss is due to the reduction from WO_{3-x} to WC (Eq. (2)). A small exothermic peak at 972 °C in DSC curve may attribute to the crystallization of WC. When increasing the temperature to 950 °C, the TG is a straight line without any mass change as the temperature increases, which indicates that the reaction is over and pure WC is formed. This result is in accord with the XRD result. In the actual process, we found an important issue that the reaction temperature is lower than 900 °C. The main products are W_2C instead of WC. In addition, the heating rate also seriously affected the experimental results. Research results indicate that the improvement of the heating rate is in favor of the production of WC. When the heating rate is lower than 5 °C min^{-1}, the main products are W_2C instead of WC as well. Once W_2C is generated, it is very hard to get rid of in the subsequent process, even by elevating temperature or

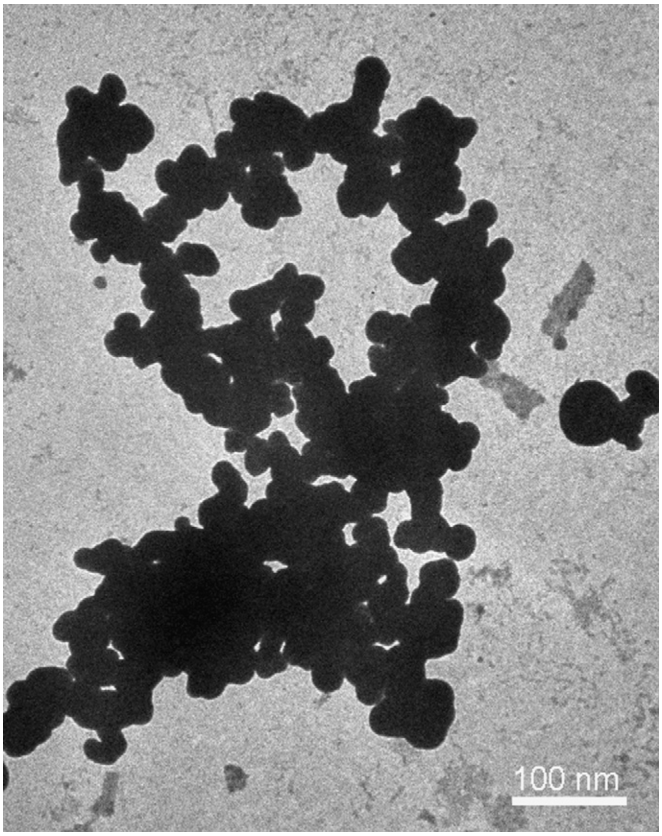

Fig. 3. TEM micrograph of WC prepared at 980 °C for 1 h.

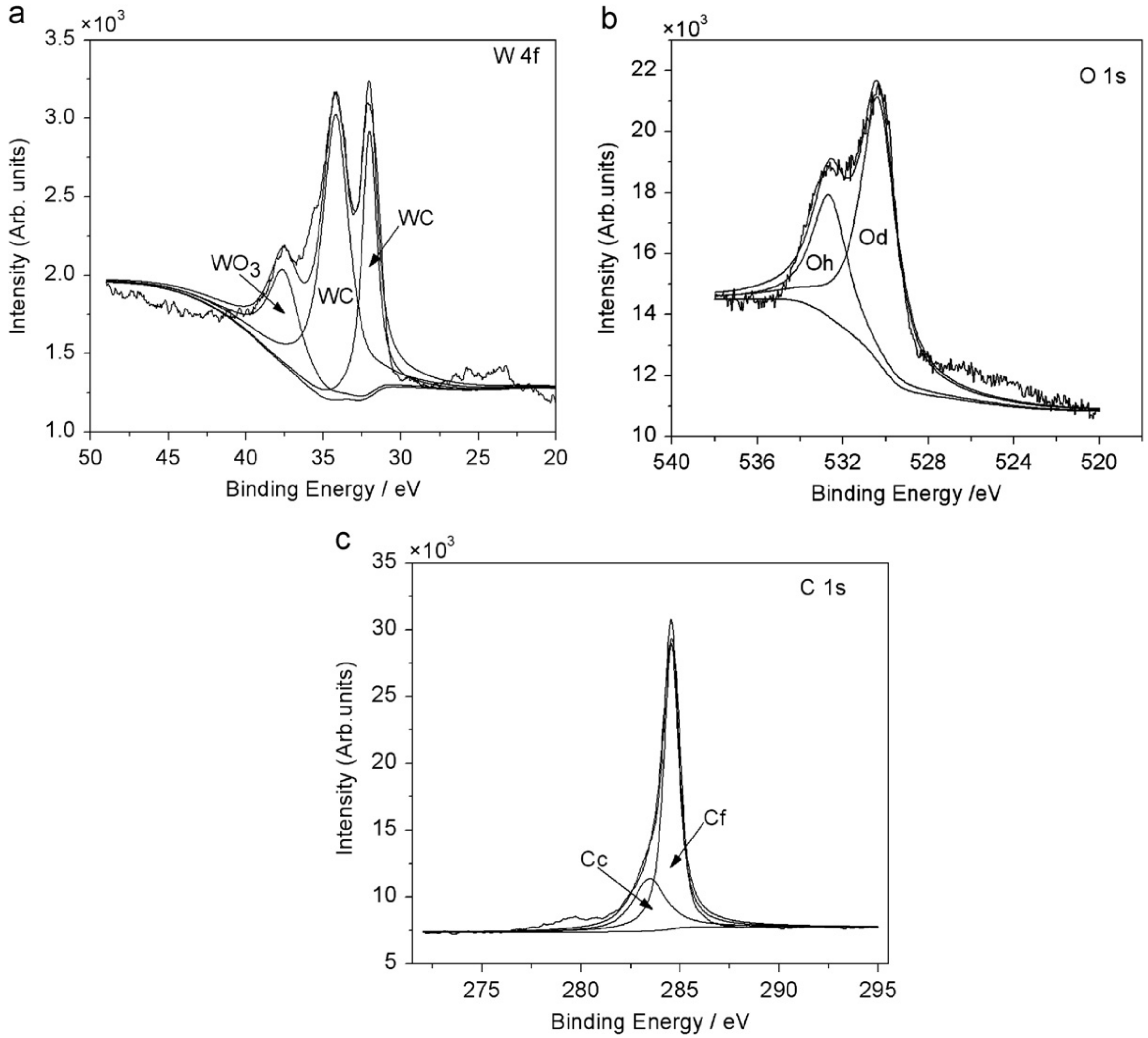

Fig. 4. XPS spectrum of W 4f (a), O 1s (b) and C 1s (c) energy peaks for WC nanopowders obtained at 980 °C for 1 h.

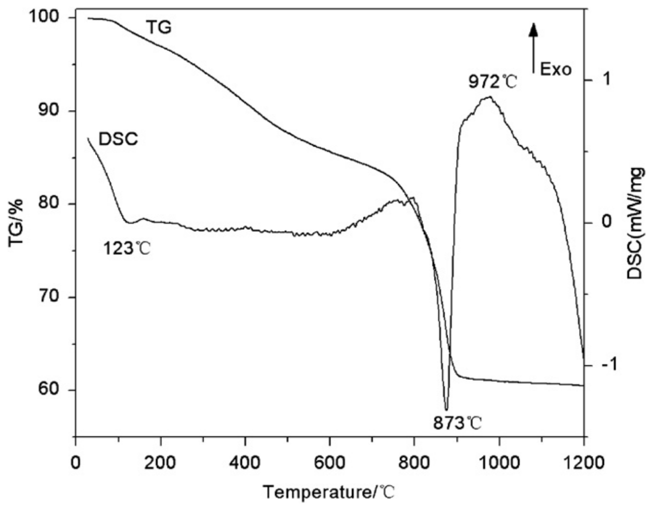

Fig. 5. TG–DSC curves of thermoanalysis of the precursor running at 10 °C/min in Ar flow.

prolonging holding time. However, this theory still needs further research.

$$WO_3+C=WO_{3-x}+CO \quad (1)$$

$$WO_{3-x}+C=WC+CO \quad (2)$$

4. Conclusion

In summary, the single phase WC nanopowders with a diameter from 20 to 60 nm were successfully synthesized at 980 °C for 1 h by an easy and convenient carbothermal route. Here, the corn starch was used as the carbon source, while the hydrothermal method was used to prepare core–shell precursors. This approach is cheaper and more controllable, and can obtain better quality powders at a lower temperature and a shorter time than the conventional methods. This process is ideal for cost-effective industrial production.

Acknowledgments

This work is supported by Fundamental Research Funds for the Central Universities (No. XDJK2010C009) and Chongqing Key Natural Science Foundation (cstc2012jjB50011).

References

[1] T. Fukatsua, K. Koborib, M. Uekia, Micro-grained cemented carbide with high strength, International Journal of Refractory Metals and Hard Materials 10 (1991) 57–60.

[2] S. Wahlberg, I. Grenthe, M. Muhammed, Nanostructured hard material composites by molecular engineering 1. Synthesis from soluble tungstate salts, Nanostructured Materials 9 (1997) 105–108.

[3] P. Ettmayer, Hardmetals and cermets, Annual Review of Materials Science 19 (1989) 145–164.

[4] S.I. Cha, S.H. Hong, G.H. Ha, B.K. Kim, Mechanical properties of WC-10Co cemented carbides sintered from nanocrystalline spray conversion processed powders, International Journal of Refractory Metals and Hard Materials 19 (2001) 397–403.

[5] S.H. Jhi, S.G. Louie, M.L. Cohen, J. Ihm, Vacancy hardening and softening in transition metal carbides and nitrides, Journal of Physical Review Letters 86 (2001) 3348–3351.

[6] M. Nie, P.K. Shen, M. Wu, Z.D. Wei, H. Meng, A study of oxygen reduction on improved Pt-WC/C electrocatalysts, Journal of Power Sources 162 (2006) 173–176.

[7] L. Leclercq, M. Provost, H. Pastor, J. Grimblot, A.M. Hardy, L. Gengembre, G. Leclercq, Catalytic properties of transition metal carbides, Journal of Catalysis 117 (1989) 371–383.

[8] M.F. Zawrah, Synthesis and characterization of WC–Co nanocomposites by novel chemical method, Ceramics International 33 (2007) 155–161.

[9] K. Jia, T.E. Fischer, Sliding wear of conventional and nanostructured cemented carbides, Wear 203–204 (1997) 310–318.

[10] M.S. El-Eskandarany, A.A. Mahday, H.A. Ahmed, A.H. Amer, Synthesis and characterizations of ball-milled nanocrystalline WC and nanocomposite WC–Co powders and subsequent consolidations, Journal of Alloys and Compounds 312 (2000) 315–325.

[11] L.E. Toth, Transition metal carbides and nitrides, Academic Press, New York, 1971.

[12] L. Leclercq, K. Imura, S. Yoshida, T. Barbee, M. Boudart. Synthesis of new catalytic materials: metal carbides of the group VI B elements, Preparation of catalysts II, Proceedings of the Second International Symposium Louvain-la-Neuve. 1978, pp. 627–639.

[13] S. Wanner, L. Hilaire, P. Wehrer, J.P. Hindermann, G. Maire, Obtaining tungsten carbides from tungsten bipyridine complexes via low temperature thermal treatment, Applied Catalysis A 203 (2000) 55–70.

[14] Z.Q. Li, H.F. Zhang, X.B. Zhang, Y.Q. Wang, X.J. Wu, Nanocrystalline tungsten carbide encapsulated in carbon shells, Nanostructured Materials 10 (1998) 179–184.

[15] R. Koc, S.K. Kodambaka, Tungsten carbide (WC) synthesis from novel precursors, Journal of the European Ceramic Society 20 (2000) 1859–1869.

[16] W. Schartl, Crosslinked spherical nanoparticles with core–shell topology, Advanced Materials 12 (2000) 1899–1908.

[17] K.T. Lee, Y.S. Jung, S.M. Oh, Synthesis of tin-encapsulated spherical hollow carbon for anode material in lithium secondary batteries, Journal of the European Ceramic Society 125 (2003) 5652–5653.

[18] S. Han, Y. Yun, K.W. Park, Y.E. Sung, T. Hyeon, Simple solid-phase synthesis of hollow graphitic nanoparticles and their application to direct methanol fuel cell electrodes, Advanced Materials 15 (2003) 1922–1925.

[19] X.L. Dong, Z.D. Zhang, S.R. Jin, B.K. Kim, Carbon-coated Fe–Co(C) nanocapsules prepared by arc discharge in methane, Journal of Applied Physics 86 (1999) 6701–6706.

[20] H. Lin, Q. Li, F. Mu, J. Zou, Preparation of WC–Co Nanocomposite Powders Through In Situ Reduction and Carbonization, China Patent no. 201110303977.7, 2011.

[21] G.A. Swift, R. Koc, Formation of WC powders using carbon coated precursors, Journal of Materials Science 35 (2000) 2109–2113.

[22] P. Huang, Principles of Powder Metallurgy, Metallurgy Industry, Beijing, 2004.

[23] H.X. Ji, C.C. Amato-Wierda, Chemical vapor deposition of Ti–W–C thin films, Surface and Coatings Technology 148 (2001) 262–267.

[24] K.A. Beadle, R. Gupta, A. Mathew, J.G. Chen, B.G. Willis, Chemical vapor deposition of phase-rich WC thin films on silicon and carbon substrates, Thin Solid Films. 516 (2008) 3847–3854.

[25] Y. Jin, D. Liu, X. Li, R. Yang, International Journal of Refractory Metals and Hard Materials 29 (2011) 372–375.