Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 1671–1677
www.elsevier.com/locate/jeurceramsoc

Synthesis of transition metal carbide nanoparticles through melamine and metal oxides

M. Lei [a,b], H.Z. Zhao [b], H. Yang [b], B. Song [b], W.H. Tang [a,*]

[a] *Department of Physics, Center for Optoelectronics Materials and Devices, Zhejiang Sci-Tech University, Xiasha College Park, Hangzhou 310018, PR China*
[b] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China*

Received 23 July 2007; received in revised form 20 November 2007; accepted 30 November 2007
Available online 7 February 2008

Abstract

By a facile reaction route, we synthesized five technologically important transition metal carbide nanoparticles including cubic NbC, TaC, VC, hexagonal WC and MoC at relatively low temperatures. Here, in this rapid reaction process, we choose an organic reagent melamine and transition metal oxides as reaction precursors. The experimental results indicate that melamine is a highly efficient carburization reagent, and the metal oxides are completely converted into the corresponding carbides at relatively low temperatures. It is found that NbC, TaC, VC and WC are composed of fine nanoparticles having average size of 7, 13, 5 and 18 nm with a fairly narrow size distribution, respectively. The potential reaction mechanism between melamine and transition metal oxides and some new characteristics involved in this route are presented and discussed.

Keywords: Transition metal carbides; Nanoparticles; Electron microscopy; X-ray methods; Carbides

1. Introduction

In the past decade, much effort has been devoted to the synthesis of carbides due to their fundamental and technological importance. Transition metal carbides are especially of interest because they have many superior properties such as high melting points, good thermal and catalytic behaviors, and excellent electronic characteristics.[1–3] NbC and TaC, for example, are excellent additives in the manufacturing of hard materials, and display excellent superconductivity.[4,5] VC is also an important dopant. It can markedly change the electrical conductivity of SiC single crystal.[6,7] WC is extremely refractory and possesses excellent catalytic properties similar to those of noble metal platinum.[8,9] Traditionally, transition metal carbides have been made by powder metallurgical techniques at elevated temperatures for extended time periods.[10] For example, industrial production of NbC and TaC is usually carried out by mixing oxide and carbon at temperatures over 1500 °C, and WC is commercially manufactured by reaction of elemental starting material at 2800 °C. These methods are high-energy processes, energy intensive and result in products with large micrometer size. The metal carbides with micrometer size are brittle and difficult to convert into fully dense solids with excellent fracture resistance for high stress and temperature applications.[4,11] As catalysts, these carbides also have lower performance due to their large particle size and low surface area. Therefore, it is desired to search for some new routes to prepare fine metal carbide nanoparticles to meet the demand of industrial applications.

Recently, a series of methods have been reported to obtain transition metal carbide nanoparticles. Gas–solid reactions,[12,13] gas-phase reactions,[14] electrochemical and sonochemical methods,[15,16] rapid metathesis reactions[17–21] and polymer derived ceramics approach[22–24] have been intensively investigated. However, the route to metal carbide nanoparticles through organic compounds and oxides has been rarely investigated. In this paper, we design a highly efficient and facile reaction route assisted by carbothermal reduction to prepare transition metal carbide nanoparticles. Here, we choose an organic reagent melamine ($C_3N_3(NH_2)_3$) as a precursor with another one being

* Corresponding author. Tel.: +86 571 86843468; fax: +86 571 86843222.
E-mail address: whtang@zstu.edu.cn (W.H. Tang).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.11.013

corresponding transition metal oxides. Melamine is an important starting material for several industrial applications, for example, the syntheses of melamine–formaldehyde resins and of fireproof materials.[25] Melamine is also widely used for architecture of supramolecular structures.[26] In our previous work,[27] we use melamine as nitridation reagent to prepare eight metal nitrides successfully. However, it is interesting to note that, at higher temperatures, melamine also is an efficient carburization reagent and some transition metal oxides are completely converted into the corresponding carbides. In particular, fine NbC, TaC, VC and WC nanoparticles with a narrow size distribution can be easily obtained by this facile reaction route.

2. Experimental procedure

All starting materials are of analytical pure grade and are purchased from commercial sources. In the typical synthesis, firstly, 8 mmol melamine ($C_3N_3(NH_2)_3$) and 2 mmol Nb_2O_5 were mixed together and then pressed to a pellet (here we use the excess of $C_3N_3(NH_2)_3$ to ensure the complete conversion of Nb_2O_5 to NbC). The pellet was put into a silica ampoule (out diameter, 15 mm; inner diameter, 12 mm). Secondly, the ampoule with the pellet was evacuated to 1×10^{-6} Pa and sealed at length of 10 cm. In succession, the ampoule was heated to 1100 °C at the rate of 5 °C min^{-1}. Then the whole system was kept at 1100 °C for half an hour. At last, the ampoule was cooled naturally to room temperature and black powder was found after cooling. The typical smell of ammonia was detected after opening the ampoule up. This phenomenon can be found in the syntheses of the following carbides. By similar methods, TaC, VC, WC and MoC can be also synthesized by the reaction of melamine and transition metal oxide Ta_2O_5, V_2O_5, WO_3 and MoO_3, respectively, at the moderate temperatures. The experimental conditions and the corresponding products are listed in Table. 1.

X-ray powder diffraction (XRD) analysis was conducted on a PaNalytical X'Pert Pro MPD X-ray diffractometer with 2θ ranging from 10° to 90°, using graphic monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology and chemical composition of the products were characterized using a Hitach (Tokyo, Japan) S-4200 field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive

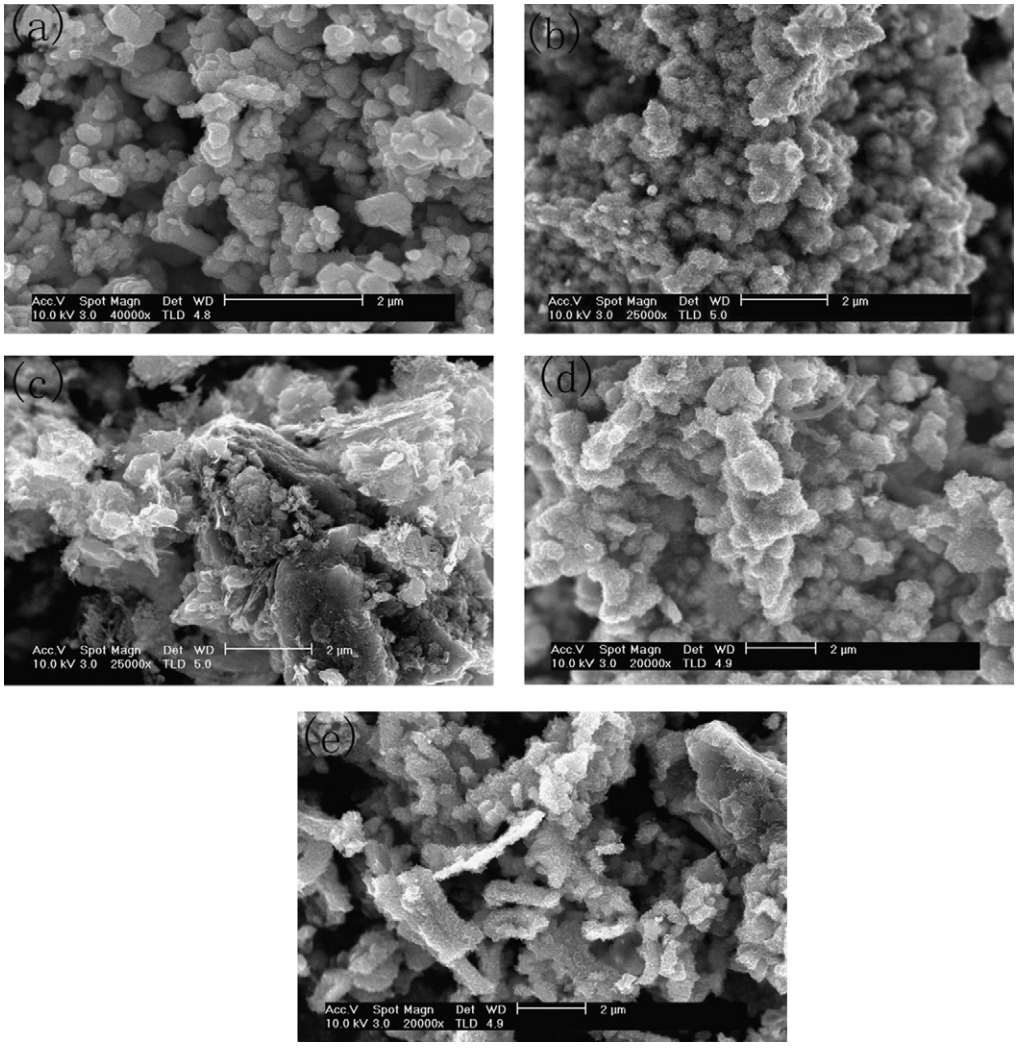

Fig. 1. SEM micrographs of the obtained transition metal carbides: (a) NbC; (b) TaC; (c) VC; (d) WC; (e) MoC.

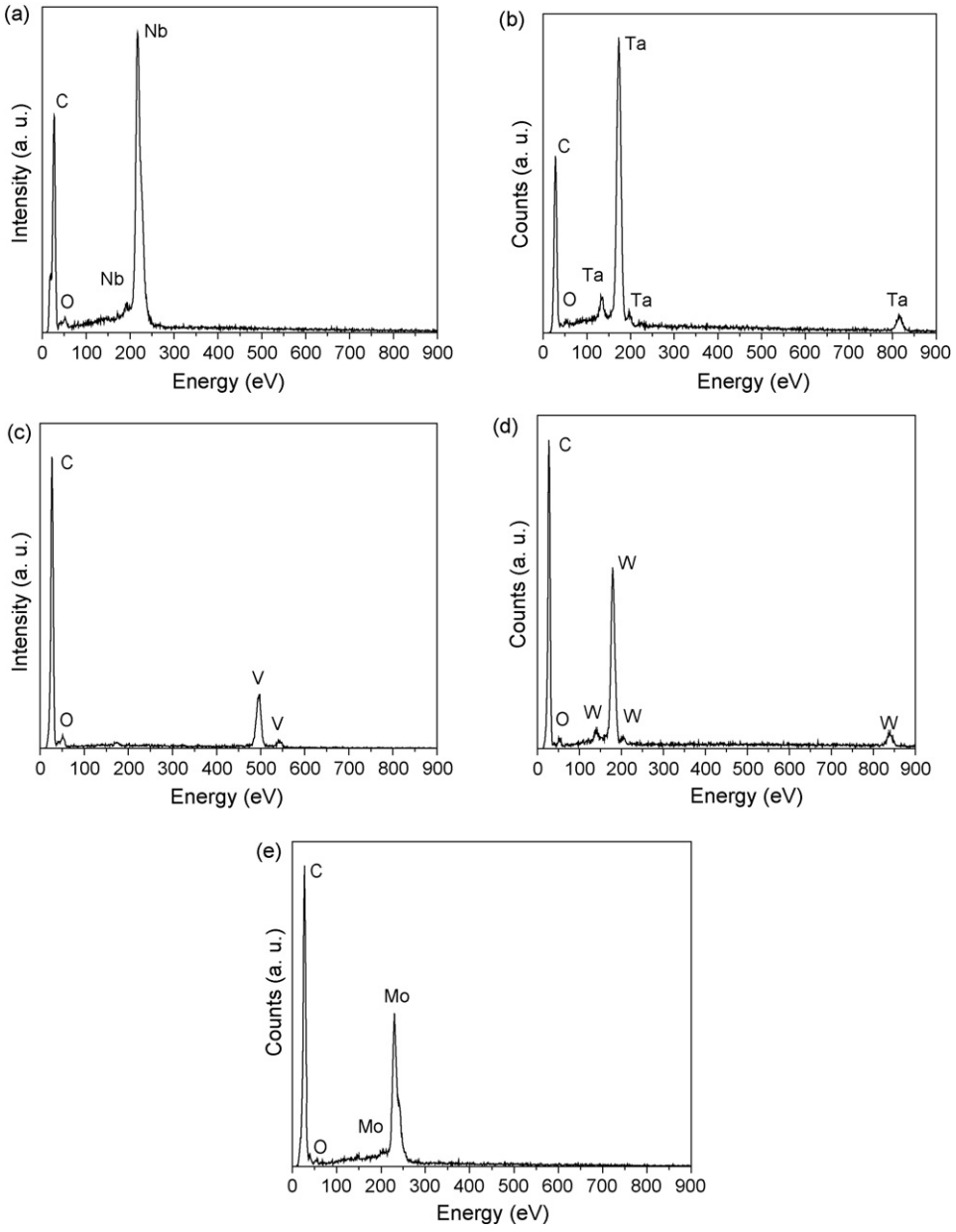

Fig. 2. EDX measurement of the obtained transition metal carbides: (a) NbC; (b) TaC; (c) VC; (d) WC; (e) MoC.

X-ray spectroscopy (EDX). The magnified morphology, particle size and high-resolution lattice fringe images of samples were obtained on a Philips CM12 transmission electron microscope (TEM) operation at 100 and 200 keV, respectively. The samples for TEM were dispersed in ethanol by sonication and deposited on carbon-coated copper grids.

3. Results and discussion

In the typical synthesis, the sample obtained by the reaction between melamine and Nb_2O_5 was collected and characterized. It can be observed that the product was irregular aggregates consisting of many crystallites (Fig. 1a). The corresponding energy-dispersive X-ray spectroscopy (EDX) data indicate that only Nb, C and trace amount of O element can be detected

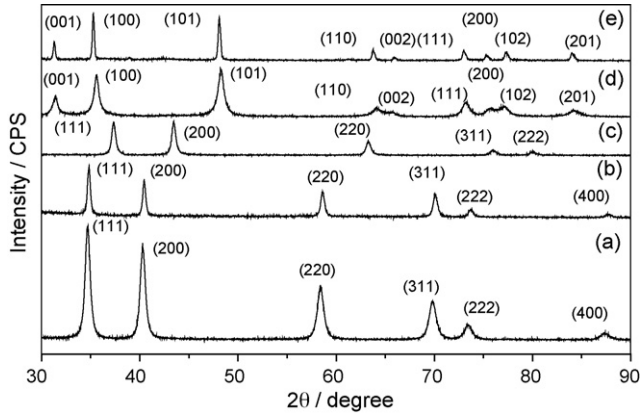

Fig. 3. XRD pattern of the obtained transition metal carbides: (a) NbC; (b) TaC; (c) VC; (d) WC; (e) MoC.

(Fig. 2a). Trace amount of O element probably comes from the O_2 and H_2O absorbed on the surface of the sample. To further determine chemical composition of the sample, chemical element analysis is employed. The analysis result indicates that the atomic ratio of Nb and C element is 1:1.3, and no N element is detected. The excessive C element in the sample can be identified as byproduct amorphous carbon decomposed by excessive melamine at high temperatures. The powder X-ray diffraction pattern (Fig. 3a) can be indexed as cubic NbC with cell constant of $a = 0.447$ nm, agreeing well with the calculated diffraction pattern (ICDD-PDF No. 3-1364). The widening of the observed peaks is due to the size effect of the sample grains, which can be confirmed by the TEM observation. The transmission electron microscope (TEM) image indicates that the sample consists

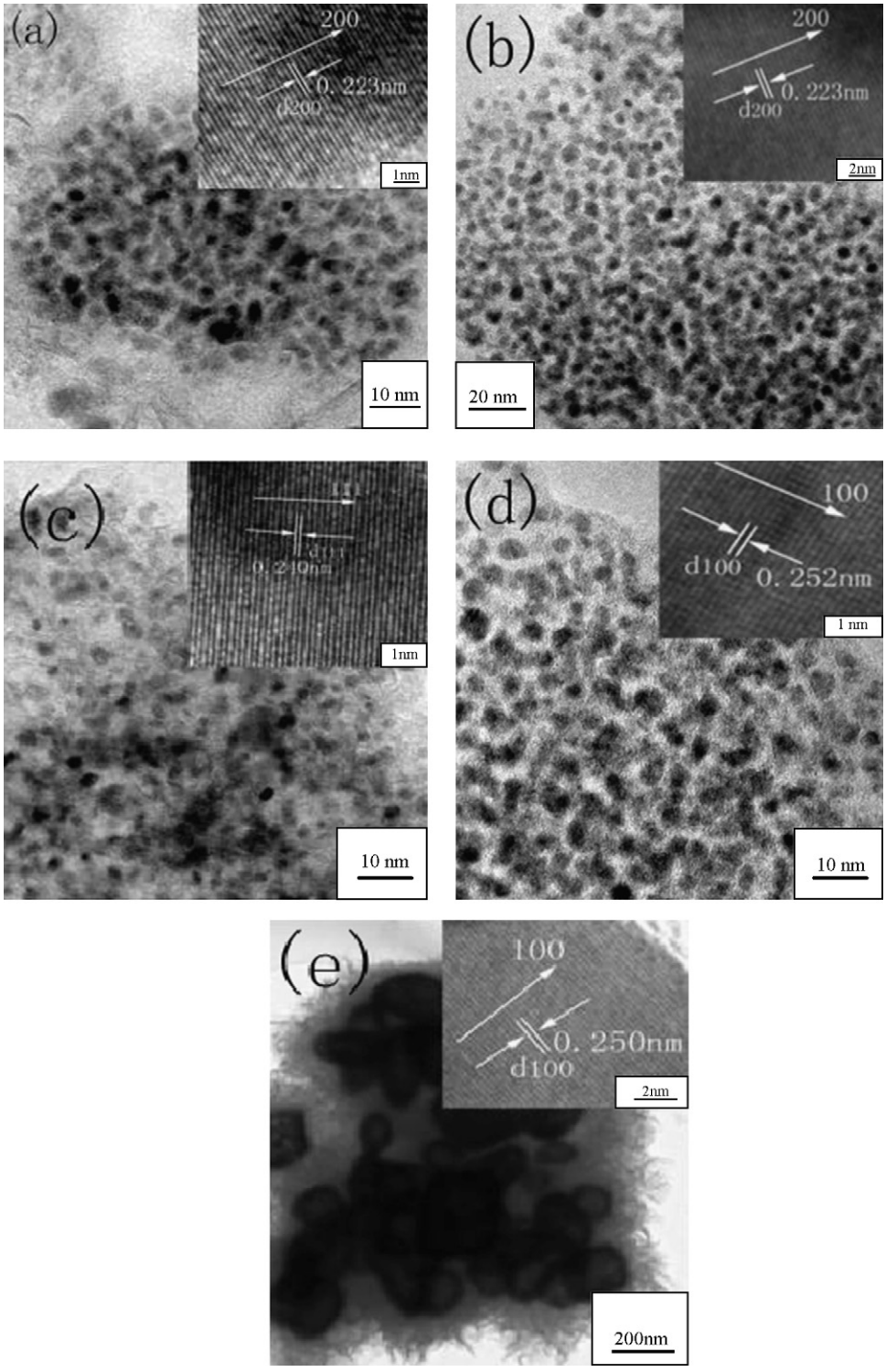

Fig. 4. TEM micrographs of the obtained carbides: (a) NbC; (b) TaC; (c) VC; (d) WC; (e) MoC. The inset of each images imply the lattice of the corresponding carbides.

Table 1
Summary of the reactions between transition metals and melamine

Starting oxide	Molar ratio	Temperature (°C)	Products	Space groups	Cell constants (nm)	Average size (nm)
Nb_2O_5	4:1	1100	NbC	$Fm-3m$	$a=0.4467$	7
Ta_2O_5	4:1	1100	TaC	$Fm-3m$	$a=0.4452$	13
V_2O_5	8:1	1200	VC	$Fm-3m$	$a=0.4163$	5
WO_3	6:1	1150	WC	$P-6m2$	$a=0.2901$, $b=0.2837$	18
MoO_3	6:1	1150	MoC	$P-6m2$	$a=0.2903$, $b=0.2787$	180

of many nanoparticles having an average size of 7 nm with a fairly narrow distribution (Fig. 4a). It is also found that these NbC nanoparticles are glued into an amorphous matter. This amorphous matter is identified as byproduct amorphous carbon. Nanoparticles aggregate with each other through the amorphous carbon, which forms the irregular aggregates exhibited by the SEM image (Fig. 1a). This phenomenon can be also found in the other metal carbides synthesized by this route. High-resolution TEM (HRTEM) image shown in the inset of Fig. 4a clearly exhibits the lattice fringe spacing for (2 0 0) plane of cubic NbC ($d_{200}=0.223$ nm), giving further evidence that the as-prepared sample is NbC.

By a similar method, the other four transition metal carbides were synthesized at moderate temperatures, respectively. The corresponding SEM images and the EDX analysis are shown in Figs. 1 and 2, respectively. The results show that all these products are composed of many irregular aggregates, and mainly consist of corresponding transition metal element and C element. We also use the chemical element analysis method to further determine the chemical composition of these samples. The results show that C element is excessive and no N element is detected, indicating the samples have undergone the formation of the metal carbides. The powder X-ray diffraction patterns of these four products (shown in Fig. 3b–e) are indexed, and the cell constants are listed in Table 1. The cell constants are consistent with their known values in the ICDD-PDF reference patterns, and the XRD results indicate that metal oxides are completely converted into the metal carbides within the instrumental resolution. All the diffraction peaks can be indexed to cubic TaC (ICDD-PDF No. 35-0801), cubic VC (ICDD-PDF No. 73-0476), hexagonal WC (ICDD-PDF No. 25-1047) and hexagonal MoC ((ICDD-PDF No. 45-1015), respectively. These products are further characterized by TEM and high-resolution TEM which make it possible to observe the size of products and confirm the phase identifications by XRD patterns, respectively. It can be seen from Fig. 4b–d that the high content of monodispersed TaC, VC and WC nanoparticles with mean size of 13, 5 and 18 nm are achieved, respectively. As for the MoC, the particle size (shown in Fig. 4e) is significantly larger and the size distribution is broader than the as-prepared TaC, VC and WC. These metal carbide nanoparticles are all glued into amorphous carbon. Nanoparticles aggregate with each other through the amorphous carbon to form the irregular aggregates exhibited by the SEM images (Fig. 1b–e). This byproduct carbon can be removed by the following methods: firstly, these carbide products are dispersed in ethanol by sonication and drying at 60 °C; Subsequently, the products were put into a tube furnace under flowing ammonia gas at 750 °C for an hour. The amorphous carbon can be removed by the reaction between the amorphous carbon and NH_3 gas. High-resolution TEM clearly exhibits the different plane spacing again for these four transition metal carbides before carbon removal: $d_{200}=0.223$ nm (the inset of Fig. 4b) for cubic TaC; $d_{111}=0.240$ nm (the inset of Fig. 4c) for cubic VC; $d_{100}=0.252$ nm (the inset of Fig. 4d) for hexagonal WC, and $d_{100}=0.250$ nm (the inset of Fig. 4e) for hexagonal MoC. These values agree well with the known data in the ICDD-PDF reference patterns, further confirming the phase identifications by XRD measurements.

These results suggest that the reaction route is very effective in synthesizing a variety of transition metal carbides. A striking feature of this route is that the reaction temperature is much lower than the reported in conventional methods, and fine carbide nanoparticles with rather small size can be easily and directly obtained. In our previous work[27], we successfully synthesized a series of metal nitrides including NbN, TaN and VN, using melamine and metal oxides as precursors at relatively low temperatures (the corresponding reaction temperatures were listed in the literature[27]). However, at higher temperatures, it is interesting to find that metal oxides are completely converted into the corresponding metal carbides such as NbC, TaC and VC, and no metal nitrides are found. Therefore, the reaction processes can be divided into several stages. Schnick et al. have proven that melamine can condense into different intermediates and release ammonia at different temperatures, respectively[26]. Several important intermediates such as melam ($(C_3N_3)_2(NH_2)_4(NH)$), melem ($C_6N_7(NH_2)_3$), melon ($(C_6N_7)_3(NH_2)_3(NH)_3$) and graphitic carbon nitride materials (g-C_3N_4) can be obtained with increasing temperature. Then, g-C_3N_4 can further release some chemically reactive hydrogen-, carbon-, and nitrogen-containing atomic species such as $C_3N_3^+$, $C_2N_2^+$ and $C_3N_2^+$ over 600 °C.[28–31] These highly active carbon nitride species may play triple roles as the reduction, nitridation and carburization reagent. Firstly, these chemically active species will reduce the metal oxides into the corresponding active metal atoms. Secondly, these active metal atoms will further react with carbon nitride species to form metal nitrides. Finally, with increasing temperature, the subsequent carburization processes between the metal nitrides and carbon nitride species will occur and lead to the corresponding carbides. The overall reaction processes can be speculated to occur as follows:

$$yC_3N_4 + 3M_xO_y \rightarrow 3xM + 2yN_2 + 3yCO \quad (1)$$

$$C_3N_4 + 4M \rightarrow 4MN + 3C \quad (2)$$

$$2C_3N_4 + 6MN \rightarrow 6MC + 7N_2 \quad (3)$$

The experimental observations further provide useful clues to understand the reaction mechanism. In the first reduction process, though we did not observe the metal elements reduced from the metal oxides, we suppose that metal oxides may be converted into high active metal atoms because we have proven that some metal oxides, such as Co_2O_3, Ni_2O_3, ZnO and CuO, can be converted into the corresponding metal element using melamine as precursor. These results give further evidence that the reduction process indeed exists. In the second process, metal nitrides are obtained at the moderate temperatures reported in our previous work.[27] In the final process, with increasing reaction temperature, the as-prepared nitrides will be further converted into the more stable metal carbides. The carburization processes are very fast and no nitrides are found in the final products, indicating that the pure carbides can be easily obtained at high temperatures. We have also used the metal element and melamine as precursors to prepare metal nitrides and carbides. The results reveal that metal nitrides and carbides can be obtained at similar experimental conditions using metal oxides as precursors. These results indicate that the second and final process exist indeed. We also used the metal nitrides and melamine as starting materials to prepare metal carbides. It is found that metal carbides can be also obtained, which further prove the final process. However, we cannot prove whether metal nitrides can be directly converted into carbides. The metal nitrides may be firstly reduced into the active metal atom. Then, carburization reactions between the metal atom and the carbon nitride species will occur and finally lead to the corresponding carbides. Thus, the exact mechanism needs to be further investigated.

4. Conclusions

We demonstrate a facile and efficient route for the synthesis of five important transition metal carbides using melamine as precursor. The experimental results indicate that melamine is a highly efficient carburization reagent, and the transition metal oxides are completely converted into the corresponding carbide at relatively low temperatures. Except for MoC, these carbides are composed of fine dispersed nanoparticles with a fairly narrow size distribution, suggesting that these nanoparticles can be more useful from the viewpoint of technical application. The reaction pathway includes a three-step process for the synthesis of these transition metal carbides. An important feature of this novel route is that intermediate carbon nitride species play tripe roles as reduction, nitridation and carburization reagent.

References

1. Yu, C. C., Ramanathan, S., Dhandapani, B., Chen, J. G. and Oyama, S. T., Bimetallic Nb–Mo carbide hydroprocessing catalysts: synthesis, characterization, and activity studies. *J. Phys. Chem. B*, 1995, **101**, 512–518.
2. Niu, S. Q. and Hall, M. B., Theoretical studies on reactions of transition-metal complexes. *Chem. Rev.*, 2000, **100**, 353–406.
3. Rohmer, M. M., Benard, M. and Poblet, J. M., Structure, reactivity, and growth pathways of metallocarbohedrenes M_8C_{12} and transition metal/carbon clusters and nanocrystals: a challenge to computational chemistry. *Chem. Rev.*, 2000, **100**, 495–542.
4. Gurin, V. N. and Korsukova, M. M., Crystal growth of refractory compounds from solutions in metallic melts. *Prog. Cryst. Growth Charact.*, 1983, **6**, 59–101.
5. Sadoway, D. R., The electrochemical processing of refractory-metals. *J. Miner. Met. Mater.*, 1991, **47**, 15–19.
6. Bickermann, M., Epelbaum, B. M., Hofmann, D., Straubinger, T. L., Weingartner, R. and Winnacker, A., Incorporation of boron and vanadium during PVT growth of 6H–SiC crystals. *J. Cryst. Growth*, 2001, **233**, 211–218.
7. Bickermann, M., Weingartner, R. and Winnacker, A., On the preparation of vanadium doped PVT grown SiC boules with high semi-insulating yield. *J. Cryst. Growth*, 2003, **254**, 390–399.
8. Levy, R. B. and Boudart, M., Platinum-like behavior of tungsten carbide in surface catalysis. *Science*, 1973, **181**, 547–549.
9. Hudson, M. J., Peckett, J. W. and Harris, P. J. F., Low-temperature sol–gel preparation of ordered nanoparticles of tungsten carbide/oxide. *Ind. Eng. Chem. Res.*, 2005, **44**, 5575–5578.
10. Nelson, J. A. and Wagner, M. J., High surface area Mo_2C and WC prepared by alkalide. *Chem. Mater.*, 2002, **14**, 1639–1642.
11. Gurin, V. N. and Derkachenko, L. I., Growth habit of crystals of refractory compounds prepared from high-temperature solutions. *Prog. Cryst. Growth Charact.*, 1993, **27**, 163–199.
12. Xiao, T. C., York, P. E. A., Williams, C. V., Al-Megren, H., Hanif, A., Zhou, X. *et al.*, Preparation of molybdenum carbides using butane and their catalytic performance. *Chem. Mater.*, 2000, **12**, 3896–3905.
13. Volpe, L. and Boudart, M., Compounds of molybdenum and tungsten with high specific surface area. *J. Solid State Chem.*, 1985, **59**, 332–347.
14. Lu, J., Hugosson, H., Eriksson, O., Nordstrom, L. and Jansson, U., Chemical vapour deposition of molybdenum carbides: aspects of phase stability. *Thin Solid Films*, 2000, **370**, 203–212.
15. Shapoval, V. I., Malyshev, V. V., Tishchenko, A. A. and Kushkhov, K. B., Physicochemical properties of tungsten carbide powders prepared from tonic melts. *Inorg. Mater.*, 2000, **36**, 1020–1023.
16. Hassine, N. A., Binner, J. G. P. and Cross, T. E., Synthesis of refractory-metal carbide powders via microwave carbothermal reduction. *Int. J. Refract. Met. Hard Mater.*, 1995, **13**, 353–358.
17. Gillan, E. G. and Kaner, R. B., Synthesis of refractory ceramics via rapid metathesis reactions between solid-state precursors. *Chem. Mater.*, 1996, **8**, 333–343.
18. Nartowski, A. M., Parkin, I. P., Mackenzieb, M. and Craven, A. J., Solid state metathesis: synthesis of metal carbides from metal oxides. *J. Mater. Chem.*, 2001, **11**, 3116–3119.
19. Nartowski, A. M., Parkin, I. P., Mackenzieb, M., Craven, A. J. and MacLeodb, I., Solid state metathesis routes to transition metal carbides. *J. Mater. Chem.*, 1999, **9**, 1275–1281.
20. Nartowski, A. M., Parkin, I. P., Craven, A. J. and Mackenzieb, M., Rapid, solid-state metathesis routes to metal carbides. *Adv. Mater.*, 1998, **10**, 805–808.
21. Song, B., Jian, J. K., Wang, G., Lei, M., Xu, Y. P. and Chen, X. L., Facile and general route to nitrides by a modified solid-state metathesis pathway. *Chem. Mater.*, 2007, **19**, 1497–1502.
22. Jiang, Z. P. and Rhine, W. E., Synthesis and prolysis of novel polymeric precursors to TiC/Al_2O_3 and AlN/TiN nanocomposites. *Chem. Mater.*, 1994, **6**, 1080–1086.
23. Jansen, M., Highly stable ceramics through single source precursors. *Solid State Ionics*, 1997, **101**, 1–7.
24. Dutremez, S., Gerbier, P., Guerin, C., Henner, B. and Merle, P., Metal alkoxide/ hexa-2,4-diyne-1,6-dioil hybrid polymers: synthesis and use as precursors to metal carbides and nitrides. *Adv. Mater.*, 1998, **10**, 465–470.
25. Kimizuka, N., Kawasaki, T., Hirata, K. and Kunitake, T., Tube-like nanostructures composed of networks of complementary hydrogen-bonds. *J. Am. Chem. Soc.*, 1995, **117**, 6360–6361.
26. Jurgens, B., Irran, E., Senker, J., Kroll, P., Muller, H. and Schnick, W., Melem (2,5,8-triamino-tris-trianzine), an important intermediated during condensation of melamine rings to graphitic carbon nitride: synthesis, struc-

ture determination by X-ray powder diffractometry, solid-state NMR, and theoretical studies. *J. Am. Chem. Soc.*, 2003, **125**, 10288–10300.
27. Zhao, H. Z., Lei, M., Chen, X. L. and Tang, W. H., Facile route to metal nitrides through melamine and metal oxides. *J. Mater. Chem.*, 2007, **16**, 4407–4412.
28. Khabashesku, V. N., Zimmerman, J. L. and Margrave, J. L., Powder synthesis and characterization of amorphous carbon nitride. *Chem. Mater.*, 2000, **12**, 3264–3270.
29. Gillan, E. G., Synthesis of nitrogen-rich carbon networks form an energetic molecular azide precursor. *Chem. Mater.*, 2000, **12**, 3906–3912.
30. Lotsch, B. V. and Schnick, W., Thermal conversion of guanylurea dicyanamide into graphitic carbon nitride via prototype CN*x* precursors. *Chem. Mater.*, 2005, **17**, 3976–3982.
31. Zhao, H. Z., Lei, M., Yang, X. A., Jian, J. K. and Chen, X. L., Route to GaN and VN assisted by carbothermal reduction process. *J. Am. Chem. Soc.*, 2005, **127**, 15722–15723.