A Low-temperature in situ Template Reduction-Carbonization Route to TiC Submicrometer Hollow Spheres and Nanorods

Kaibin Tang,* Guozhen Shen, Di Chen, Changhua An, Chunrui Wang, and Yitai Qian*
Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China

(Received July 29, 2002; CL-020629)

TiC submicrometer hollow spheres and nanorods were successfully synthesized at relatively low temperature. The products were characterized by XRD, TEM, and ED procedures. A low-temperature in situ template reduction-carbonization mechanism was proposed.

In recent years there has been growing interest in materials with specific nanomorphologies because of the expectation of novel properties. Among them, the mesoscale hollow spheres are useful in many areas. For example, they can serve as extremely small containers for encapsulation, delivery of drugs, development of artificial cells, and protection of biologically active agents or as fillers and coatings.[1,2] Currently, one-dimensional (1D) nanostructured materials have also been the focus of recent scientific research due to their unusual properties and potential uses in both mesoscopic research and the development of nanodevices.[3] So now, the synthesis methods are not only to prepare the starting particles but also to coax them into the desired nanostructures.

Titanium carbide (TiC) is one of the most important metal carbides used in advanced ceramics.[4] It has yet to be applied widely from mechanical industries to chemistry and microelectronics. In previous years, different chemical and physical methods have been used to prepare TiC powders.[5–9] Recently, Dai et al. succeeded in synthesizing TiC nanorods by carbon nanotube template-mediated growth method.[10] Some catalyst-activated methods also were used to synthesize TiC nanorods (nanowires).[11] We also succeeded in synthesizing TiC nanocrystallites by a co-reduction route and a reduction carbonization route.[12]

In this work, we report a low-temperature chemical route to synthesize TiC submicrometer hollow spheres and nanorods based on the following reaction:

$$6TiCl_4 + C_6Cl_6 + 30Na \rightarrow 6TiC + 30NaCl \qquad (1)$$

To our knowledge, there have been no reports on the TiC hollow spheres or similar carbide nanostructures.

All manipulations were carried out in a dry glove box with Ar flowing. In a typical procedure, $TiCl_4$ (0.02 mol), C_6Cl_6 (0.002 mol), and Na (0.15 mol) were put into a stainless steel autoclave of 30 ml capacity (route 1); In another procedure, 0.05 g Co/Ni catalyst precursor (prepared as the method in the reference 14) was also added to the autoclave (route 2). After being sealed, the autoclave was maintained at 650 °C for 10–20 h and then allowed to cool to room temperature in furnace. The unreacted Na was removed by alcohol and the product was collected and washed several times with dilute acid and distilled water to remove NaCl and other impurities. Dried in vacuum at 70 °C for 4 h, dark gray products were obtained.

The XRD patterns were recorded on a Japan Rigaku D/max γ_A X-ray diffractometer with Cu Kα radiation. Figure 1a displays the XRD pattern of the product from route 1. One can see that all of the peaks can be indexed as the cubic, rock-salt structure of TiC with lattice parameter $a = 4.322$ Å which is consistent with the reported data ($a = 4.3274$ Å, JCPDS card, No. 32–1383). The XRD pattern of the sample from route 2 (Figure 1b) also exhibits the cubic TiC with lattice parameter $a = 4.324$ Å.

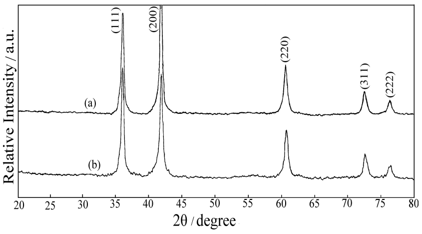

Figure 1. XRD patterns of as prepared samples, (a) without catalyst (route 1). (b) with catalyst (route 2).

The morphologies of the samples were observed with a Hitachi H-800 transmission electron microscope (TEM). Figure 2a shows the TEM image of the sample from route 1. It can be seen that the sample mainly consists of hollow sphere of 90–160 nm in diameter and the shell thickness of approximately 10–20 nm. The strong contrast between the dark edge and light center exhibits its hollow nature.[13] Selected area electron diffraction (ED) pattern (Figure 2b) shows three clear diffraction rings corresponding to the (111), (200), (220) crystal planes of cubic TiC, no obvious rings due to amorphous products e.g. amorphous carbon are detected. These results suggest that the hollow spheres are constructed by TiC polycrystallines. TEM image of the sample from route 2 shows the appearance of large amounts of nanorods with nanoparticles (Figure 2c). Typical size of the rods is found to be several hundreds nanometers in length and about 20 nm in diameter.

In our synthetic route, if C_6Cl_6 is substituted by CCl_4, crystalline TiC can be obtained at 450 °C,[12] however, neither TiC hollow spheres nor nanorods could be observed even though at the temperature as high as 650 °C, instead that TiC nanoparticles were obtained. A same result occurred in the presence of Co/Ni catalyst. These mean that C_6Cl_6 plays a key role in the formation of TiC hollow spheres and nanorods. Previously, we also found that reduced by alkali metals, C_6Cl_6 would be assembled into carbon nanotubes in the presence of Co/Ni catalyst,[14] while without catalyst would be sphere about 120 nm in diameter (Figure 2d). Under our present conditions, the product prepared at

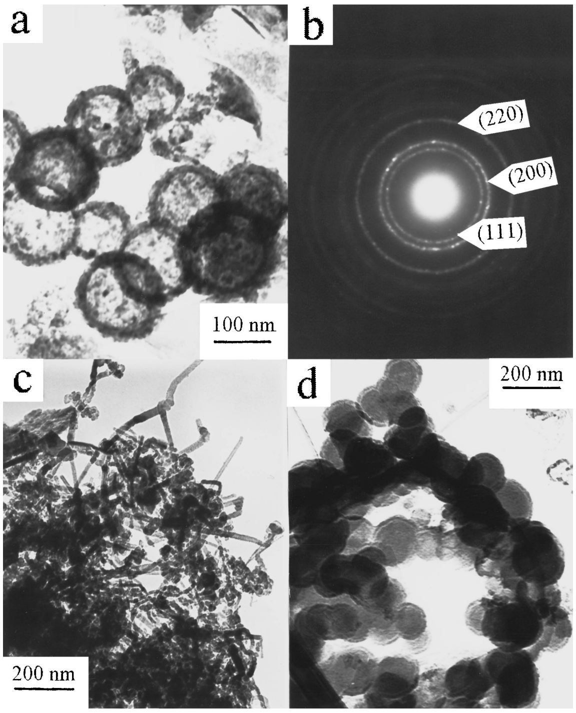

Figure 2. (a) TEM images of TiC hollow spheres, (b) ED pattern of TiC hollow sphere, (c) TEM image of TiC nanorods. (d) TEM image of C hollow spheres.

550 °C observed by XRD and TEM are α-Ti and TiC hollow spheres constructed by amorphous carbon. The product prepared at 650 °C for 1–2 h has some similarity. All these results strongly suggest that the carbon intermediates reduced from C_6Cl_6 simultaneously act as in situ templates and reaction sources to the formation of TiC nanostructures. So such a procedure can be called as an in situ templates reduction-carbonization route.

On the basis of the above analyses, the formation mechanism of TiC nanostructures could be proposed although the exact formation mechanism is not completely understood. In our reaction system, $TiCl_4$ (bp: 136 °C) and C_6Cl_6 (bp: 325 °C) exist as gas and Na (mp: 98 °C) as liquid at the processing temperature of 650 °C. From the formation enthalpies of $TiCl_4$ ($H_f = -763$ kJ/mol) and C_6Cl_6 ($H_f = -127.6$ kJ/mol), it is expected that C_6Cl_6 is firstly reduced with the increase of the processing temperature. Hexagonal plane carbon clusters would be created and then extended to form metastable hollow sphere aggregates. Subsequently, activated Ti particles reduced from $TiCl_4$ were also formed and dispersed in the molten Na. At the desire reaction temperature, the newly formed Ti particles and C spheres would react to form TiC hollow spheres. The schematic formation process of TiC hollow spheres could be illustrated as follows:

$$nC_6Cl_6 + 6n\text{Na} \rightarrow 6n\text{C (sphere aggregate)} + 6n\text{NaCl} \quad (2)$$

$$\text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl} \quad (3)$$

$$\text{Ti} + \text{C (sphere aggregate)} \rightarrow \text{TiC (hollow sphere)} \quad (4)$$

Here, excess $TiCl_4$ would provide a Ti-rich circumstance around the carbon intermediates, which is advantageous to the transfer of carbon intermediates and the formation TiC hollow spheres. Excess Na also serves as the medium for the crystallization of the formed TiC, absorbs the reaction enthalpy and maintains a relatively low overall reaction temperature.

In the presence of Co/Ni catalyst, the agglomeration of carbon clusters may be prevented. Some of the carbon clusters would assemble into nanotubal intermediate. At the processing temperature of 650 °C, they would react with gaseous $TiCl_4$ and Na to form TiC nanorods through a process similar to that reported in the reference.[10] The yield of TiC nanorods would depend on the formed carbon nanotubal intermediates.

In summary, we succeeded in synthesizing TiC submicrometer hollow spheres and nanorods through the reduction of $TiCl_4$ and C_6Cl_6 by metal sodium at 650 °C. An in situ template reduction-carbonization formation mechanism is proposed. In this work, first example of hollow sphere in carbides is provided. It is believed that such a method could be extended to fabricate similar nanostructures for other important carbides and extensive studies will be given.

This work was supported by the National Natural Science Foundation of China and the 973 Projects of China.

References

1 E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedl, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Bassett, and C. Morrell, *Nature*, **386**, 410 (1997); H. Huang and E. E. Remsen, *J. Am. Chem. Soc.*, **121**, 3805 (1999).
2 M. Ohmori and E. Matijevic, *J. Colloid Interface Sci.*, **150**, 594 (1992).
3 S. Iijima, *Nature*, **354**, 56 (1991); R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature*, **360**, 444 (1992).
4 E. K. Stroms, "The Refractory Carbides, Refractory Materials Series," Academic Press, New York (1967), Vol. 2; L. E. Toth, "Transition Metal Carbides and Nitrides," Academic Press, New York (1971); H. O. Pierson, "Handbook of Refractory Carbides and Nitrides," Noyes Publications, Westwood (1996).
5 I. N. Mihailescu, N. Chitica, V. S. Teodorescu, M. Popescu, M. L. De Giorge, A. Luches, A. Perrone, C. Boulmer-Leborgne, J. Hermann, B. Dubreuil, S. Urdea, A. Barborica, and I. Iova, *J. Appl. Phys.*, **75**, 5286 (1994).
6 Z. A. Munir and W. Lai, *Combust. Sci. Technol.*, **88**, 210 (1993).
7 P. R. Tayler, S. A. Pirzada, and T. D. MoColm, *Plasma Synth. Process. Mater., Proc. Symp.*, **1993**, 179.
8 L. L. Ye and M. X. Quan, *Nanostruct. Mater.*, **5**, 25 (1995).
9 M. S. Hsu, M. A. Meyers, and A. Berkowitz, *Scr. Metall. Mater.*, **32**, 805 (1995).
10 H. Dai, E. W. Wang, Y. Z. Lu, S. Fan, and C. M. Lieber, *Nature*, **375**, 769 (1995).
11 C. H. Liang, G. W. Meng, W. Chen, Y. W. Wang, and L. D. Zhang, *J. Cryst. Growth*, **220**, 296 (2000); S. R. Qi, X. T. Huang, Z. W. Gan, X. X. Ding, and Y. Cheng, *J. Cryst. Growth*, **219**, 485 (2000).
12 Q. Lu, J. Hu, K. Tang, B. Deng, Y. Qian, G. Zhou, and X. Liu, *Chem. Phys. Lett.*, **314**, 37 (1999); J. Hu, Q. Lu, K. Tang, B. Deng, Y. Qian, G. Zhou, X. Liu, and J. Wu, *Chem. Lett.*, **2000**, 474.
13 P. V. Braun and S. I. Stupp, *Mater. Res. Bull.*, **34**, 463 (1999).
14 Y. Jiang, Y. Wu, S. Zhang, C. Xu, W. Yu, Y. Xie, and Y. Qian, *J. Am. Chem. Soc.*, **122**, 12383 (2000).