

Formation of TaC Nanorods with a Low-Temperature Chemical Route

Liang Shi,^{†,††} Yunle Gu,[†] Luyang Chen,[†] Zeheng Yang,[†] Jianhua Ma,[†] and Yitai Qian^{*†}

[†]Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China

^{††}Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China

(Received June 14, 2004; CL-040684)

Tantalum carbide (TaC) nanocrystals have been successfully synthesized at 650 °C through a solid-state reaction in an autoclave. Transmission electron microscopy images show that the TaC crystallites consist of nanorods with a typical size of about 40 × 800 nm. Some uniform particles with an average size of about 40 nm also exist in the sample.

Tantalum carbide (TaC) is an important material among transition metal carbides. It has many attractive properties such as high melting point (3880 °C), outstanding hardness, high chemical stability, and excellent electronic conductivity. For these properties, TaC has been used in many special working conditions.

It is well known that the shape and size of nanocrystals have an important influence on their physical properties and applications. As a specific nanomorphology, one-dimensional nanorods can be used as building blocks for many functional materials, which have great potential applications in electronic and optoelectronic devices. As for TaC, its nanorods can serve as the building blocks for nanometer microelectron devices used in special working conditions.

TaC has been synthesized by a lot of methods such as sol-gel, self-propagating high-temperature synthesis (SHS), alternating-current discharge, high-frequency plasma.^{1–5} In addition, various techniques have been applied to obtain TaC films including pulsed-laser deposition, physicochemical vapor deposition and direct-current magnetron sputtering.^{6–8} Recently, much efforts have been made to synthesize TaC or prepare TaC films at lower temperatures, controlling morphology or simplifying reaction procedures. For example, TaC whiskers have been synthesized via a carbothermal reduction process.⁹ TaC films have been prepared at low temperatures (350–650 °C) by chemical vapor deposition with Ta complexes as precursors.¹⁰

In this paper, we report a simple low-temperature chemical route to synthesize cubic TaC nanorods. The reaction was carried out in an autoclave at 650 °C and can be described as follows:



All manipulations were carried in a dry glove box with Ar flowing. In a typical procedure, an appropriate amount of anhydrous TaCl₅ (0.01 mol), C₄Cl₆ (0.0025 mol), and Na (0.065 mol) were put into a glass-lined stainless autoclave of about 50 mL-capacity. The autoclave was sealed and maintained at 650 °C for 8 h, and then cooled to room temperature. The product was washed with absolute ethanol, dilute hydrochloric acid, and distilled water in turn to remove NaCl and other impurities. After drying in vacuum at 60 °C for 4 h, the final black powder product

was obtained. The yield of TaC from the raw materials is about 90%.

X-ray powder diffraction (XRD) measurement was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg Kα X-ray as the excitation source. Thermogravimetric analysis (TGA) profile was collected with a Shimadzu-50 thermoanalyzer apparatus under airflow.

Figure 1 shows the XRD pattern of the as-prepared TaC sample. All the peaks can be indexed as cubic TaC. After refinement, the lattice constant, $a = 4.443 \text{ \AA}$, is obtained, which is very close to the reported value for TaC ($a = 4.446 \text{ \AA}$, JCPDS card, No.770205). The broadening of the XRD peaks may originate from the small grain sizes of the TaC sample, which is confirmed by the TEM results.

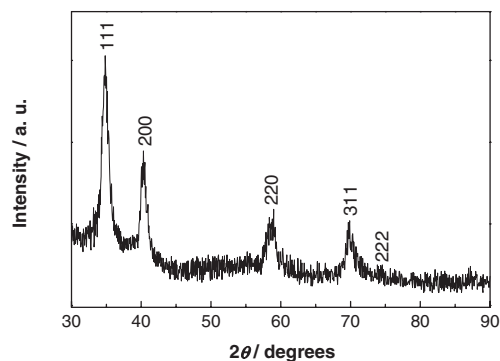


Figure 1. XRD pattern of the as-prepared TaC sample.

The composition information of the TaC sample could be obtained from the XPS spectra (not shown). The Ta 4f and C 1s core-level regions were examined. The binding energies of Ta 4f_{7/2} and Ta 4f_{5/2} are observed at 23.2 and 25.2 eV, respectively. The major signal of the C 1s electron is found at 282.9 eV. The binding energies for Ta 4f and C 1s are consistent with the reported value for TaC.^{10,11} A minor peak of C 1s at 284.6 eV is also observed, which could be attributed to a small amount of graphitic carbon on the powder surface. The quantification of the peak intensities reveals that the atomic ratio of C to Ta is 0.99:1.0, which agrees well with the chemical stoichiometric relation of TaC.

The morphology of the as-prepared TaC sample was observed from TEM. Figures 2a, 2b, and 2c show TEM images of the TaC sample. It can be seen that TaC crystallites are com-

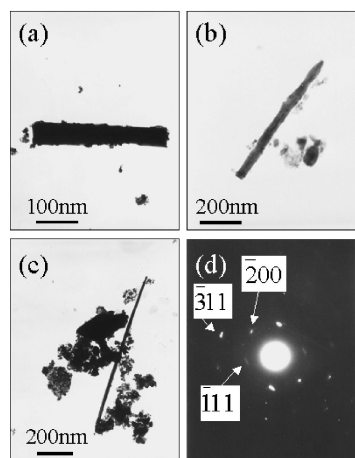


Figure 2. (a), (b) (c): TEM images of TaC nanorods; (d): selected area electron diffraction pattern of the TaC nanorods.

posed of nanorod crystallites with a typical size of about 40×800 nm. Some uniform particles with an average size of about 40 nm are also found to exist in the TaC sample. On the basis of the TEM observations, the TaC nanorods account for about 40% of the total product. Figure 2d reveals the corresponding selected area electron diffraction (SAED) pattern of the TaC nanorods, which indicates that the nanorods were of a cubic TaC single crystalline structure.

The possible formation mechanism of TaC nanorods can be proposed here. In our experiment, the overall reaction may proceed via a coreduction route. According to free energy calculations, our synthetic route is highly exothermic ($\Delta H^\circ = -1950.3$ kJ/mol). During the reaction process, with the temperature increasing, C_4Cl_6 will be reduced by Na through dechlorinating to free C_4 chains. The newly formed free C_4 chains are so active that they connect with each other to produce carbon chain clusters. $TaCl_5$ will also be reduced by Na to activated Ta particles. The coreduction of $TaCl_5$ and C_4Cl_6 generates a great deal of heat and results in an instantaneous high local temperature, which may be sufficient to melt the reaction by-product NaCl (melting point: $801^\circ C$). The molten NaCl provides a liquid medium in which the diffusion coefficient is higher than that in the solid medium. As a result, the newly formed activated Ta particles disperse in the liquid environment and diffuse easily to the surface of carbon chain clusters where Ta reacts with carbon in site to form TaC nanorods. Meanwhile, the vaporization of $TaCl_5$ (boiling point: $233^\circ C$) and C_4Cl_6 (boiling point: $215^\circ C$) during the reaction process can bring about high pressure in the autoclave (according to the ideal gas law, the highest pressure can be about 1.57 MPa), which may favor the formation of crystalline TaC nanorods.

The oxidation behavior of the as-prepared TaC sample was studied below $1000^\circ C$ by the thermogravimetric analysis (TGA) carried out in air at atmospheric pressure. Figure 3 shows the TGA curve of the TaC sample. It indicates that a small weight loss step occurs around $100^\circ C$, this can be attributed to the evaporation of absorbed water on the surface of the sample. The onset of the oxidation of the TaC sample is found to begin at about $300^\circ C$. This initial oxidation temperature is much lower than that of TaC whiskers with diameter of about $0.3 \mu m$, which is stable in air up to $550^\circ C$.¹² The lower thermal stability of TaC

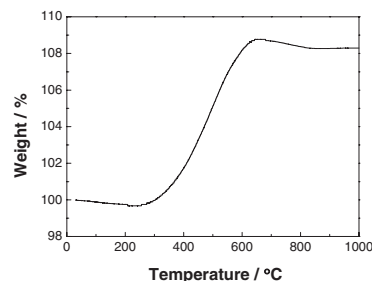


Figure 3. TGA curve for the as-prepared TaC sample.

sample may be due to its nanometer structure. It is known that the ratio of the surface to volume of nanocrystals is much larger than that of the bulk materials and there exist a lot of vacancies and dangling bonds exposed on the surface of nanocrystals. The high surface area and reactivity lead to the onset of oxidation for nanocrystalline TaC at a much lower temperature. Figure 3 reveals that the weight gain increases slowly below $400^\circ C$. This may be due to the produced oxide layer coating on the surface of grains, which could inhibit the oxidation of TaC. With the temperature increasing further from $400^\circ C$, the weight gain shows a significant increase and reaches a maximum value at about $670^\circ C$. This may originate from the fact that the formed protective oxide layer is destroyed and the oxidation rate increases rapidly again. Above $670^\circ C$, a small weight loss step is observed, which may be induced by the oxidation of a small amount of residual carbon in the sample.

In summary, nanocrystalline TaC has been successfully synthesized at $650^\circ C$ by using $TaCl_5$, C_4Cl_6 , and Na as the reactants. The TGA result showed that the onset of oxidation of TaC nanocrystals occurred at $300^\circ C$. An atomic ratio of C to Ta of 0.99:1.0 was determined from X-ray photoelectron spectra.

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

References

- 1 H. Preiss, D. Schultze, and P. Klobes, *J. Eur. Ceram. Soc.*, **17**, 1423 (1997).
- 2 J. Canteloup and A. Mocellin, *J. Mater. Sci. Lett.*, **11**, 2352 (1976).
- 3 T. Takahashi and K. Sugiyama, *J. Electrochem. Soc.*, **121**, 714 (1974).
- 4 H. Xue and Z. A. Munir, *Int. J. Self-Propag. High-Temp. Synth.*, **5**, 229 (1996).
- 5 E. M. Larson, J. Wong, J. B. Holt, P. A. Waide, G. Nutt, B. Rupp, and L. J. Terminello, *J. Mater. Res.*, **8**, 1533 (1993).
- 6 R. Teghil, L. D'Alessio, G. De Maria, and D. Ferro, *Appl. Surf. Sci.*, **86**, 190 (1995).
- 7 B. Wendler, *Mater. Sci. Eng., A*, **163**, 215 (1993).
- 8 G. Hakansson, I. Petrov, and J. E. Sundgren, *J. Vac. Sci. Technol., A*, **8**, 3769 (1990).
- 9 M. Johnsson and M. Nygren, *J. Mater. Res.*, **12**, 2419 (1997).
- 10 Y. H. Chang, J. B. Wu, P. J. Chang, and H. T. Chiu, *J. Mater. Chem.*, **13**, 365 (2003).
- 11 Q. Y. Zhang, X. X. Mei, D. Z. Yang, F. X. Chen, T. C. Ma, Y. M. Wang, and F. N. Teng, *Nucl. Instrum. Methods Phys. Res., Sect. B*, **127**, 664 (1997).
- 12 N. Ahlen, M. Johnsson, and M. Nygren, *Thermochim. Acta*, **336**, 111 (1999).