

C_3N_4 as a precursor for the synthesis of NbC, TaC and WC nanoparticles

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Abstract

While there already exist some routes to prepare carbides, highly efficient and facile routes are still desired to meet the increasing demand on carbides. By a facile solid-state reaction process using graphite-like phase of C_3N_4 (g- C_3N_4) as the carbonizing reagent, we synthesized three technologically important carbides including cubic NbC and TaC, and hexagonal WC nanoparticles at relatively low temperature (1150 °C). The products were characterized by power X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The results show that g- C_3N_4 is a highly efficient carbonizing reagent and the oxides Nb_2O_5 , Ta_2O_5 and WO_3 are completely converted into the corresponding carbides at 1150 °C, which is significantly lower than that reported for the commercial preparation of the carbides, typically >1600 °C. The NbC, TaC and WC nanoparticles are found to have an average particle size of 4, 35 and 60 nm, respectively. An important feature of this solid-state reaction process is that g- C_3N_4 plays double roles as both efficiently reducing and carbonizing reagent.

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1. Introduction

Transition metal carbides are important materials because they possess some desired properties such as thermal stability, corrosion and wear resistance, electronic, magnetic and catalytic characteristics [1–5]. NbC and TaC powders, for example, are important additives in the manufacturing of hard materials, and also display surprisingly interesting electron transport properties [6–8]. WC is extremely hard, inert and refractory material, and shows excellent catalytic properties similar to those of platinum [9,10]. Traditionally, transition metal carbides have been made by high-temperature powder metallurgical techniques [11]. These methods are energy intensive and result in large grains of low specific surface area, which limits their promise in ceramic and catalytic applications. The high temperatures (over 1600 °C) required for producing these carbides are ascribed to the inefficient nature of heat transfer and the high incongruent melting temperature. Other synthesizing meth-

ods, such as rapid metathesis reactions [12], gas–solid reactions [13,14], carbothermal reduction assisted by microwave [15], electrochemical and solution state methods [16–19], have been recently reported. These methods, however, suffer various drawbacks, such as high-energy consumption and additional costs, poor crystallized, low yields and inconvenient manipulations to some extent. Therefore, new and efficient solid-state routes are still desired to synthesize transition metal carbides.

In this context, we design a facile solid-state reaction assisted by carbothermal reduction process to prepare fine NbC, TaC and WC nanoparticles at 1150 °C. Here, we choose graphite-like phase of C_3N_4 (g- C_3N_4) as a precursor with another one being oxides Nb_2O_5 , Ta_2O_5 and WO_3 , respectively. The obtained products were characterized with X-ray diffraction (XRD), SEM, energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The results indicate that this facile solid-state reaction is highly efficient, and the oxides completely converted into the corresponding carbides. This solid-state reaction mechanism between g- C_3N_4 and oxides can be ascribed to a two-step process: a carbothermal process and a carbonizing process.

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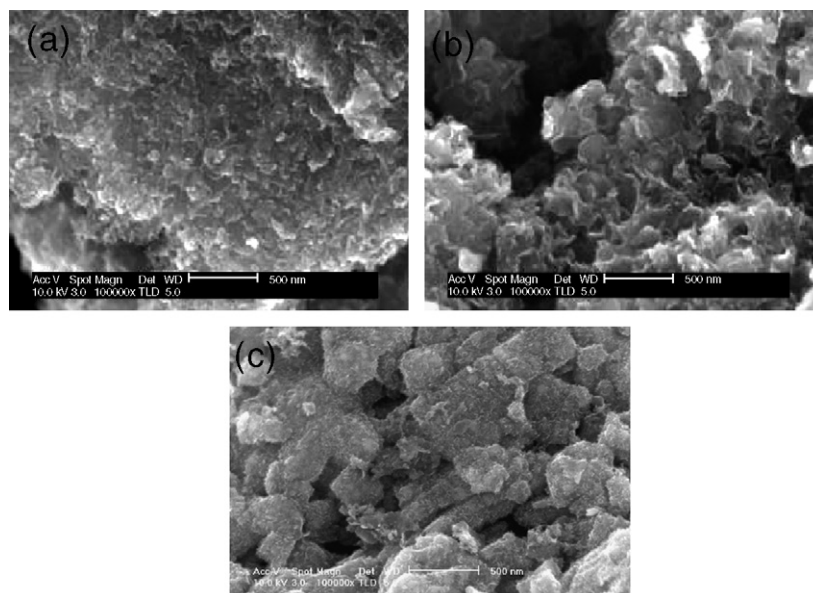


Fig. 1. SEM micrographs of the obtained carbides: (a) NbC; (b) TaC; (c) WC.

2. Experimental

The $\text{g-C}_3\text{N}_4$ was firstly prepared by the reaction of $\text{C}_3\text{N}_3\text{Cl}_3$ and Li_3N according to a facile mechanochemical method reported in the literature [20,21]. In the standard synthesis, firstly, the as-synthesized $\text{g-C}_3\text{N}_4$ and oxide Nb_2O_5 (The molar ratio is 4:1 for $\text{g-C}_3\text{N}_4$ to Nb_2O_5 . Here we used excess of the $\text{g-C}_3\text{N}_4$ to ensure the complete conversion of Nb_2O_5 to NbC.) were mixed together, and then pressed to a pellet. The pellet was put into a silica ampoule with the volume of 15 cm^3 . Secondly, the ampoule with the pellet was evacuated to $1 \times 10^{-5}\text{ Pa}$ and sealed. In succession, the ampoule was heated to 1150°C at the rate of 5°C min^{-1} . Then the whole system was kept at 1150°C for 1 h. At last, the ampoule was cooled naturally to room temperature and black powder was found after cooling. By the similar methods, TaC and WC can be also synthesized by the reaction of $\text{g-C}_3\text{N}_4$ and oxides Ta_2O_5 , WO_3 , respectively.

The overall crystal structures of the products were analyzed using a Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. 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 X-ray spectroscopy, transmission electron microscopy (Philips CM12 at 100 kV) and high-resolution TEM (Philips CM12 at 200 kV).

3. Results and discussion

It can be seen from Fig. 1a that irregular particles composed of many nanocrystallites are obtained. The EDX data (Fig. 2a) on the sample indicate that only elements Nb, C and O are detected.

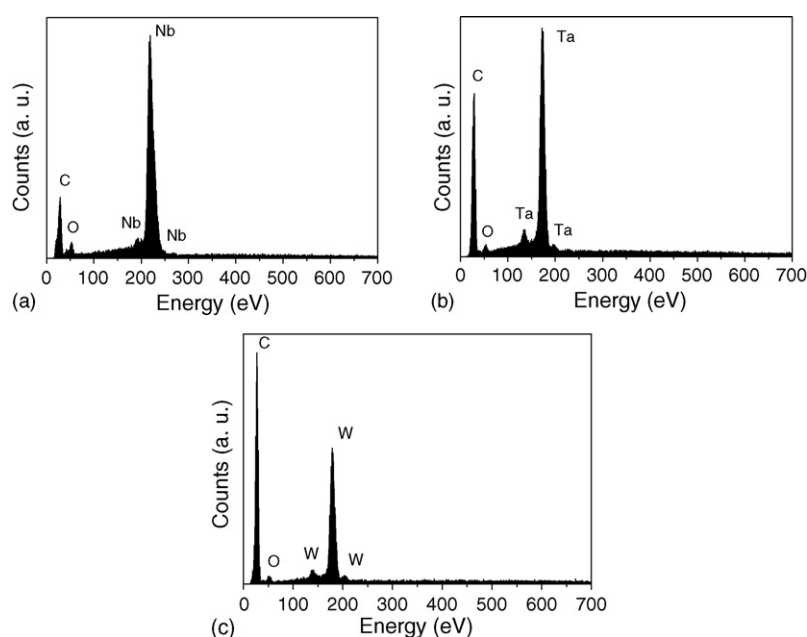


Fig. 2. EDX measurement of the obtained carbides: (a) NbC; (b) TaC; (c) WC.

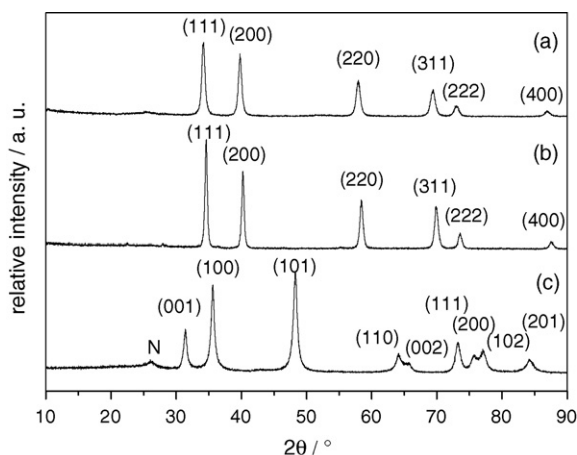


Fig. 3. XRD pattern of the obtained carbides: (a) NbC; (b) TaC; (c) WC. The observed peak N denotes the carbon byproduct.

Trace amount of O element probably comes from the O_2 and H_2O absorbed on the surface of the sample. The X-ray diffraction pattern (Fig. 3a) shows that the sample was cubic NbC. The indexed pattern agrees well with ICDD-PDF#38-1364. The corresponding broadening peaks are due to the size effect of the sample grains, as confirmed by further TEM observation. The TEM micrograph (Fig. 4a) reveals the sample is composed of well-crystallized nanoparticles with the average size of 4 nm. The high-resolution TEM image shown in the inset of Fig. 4a clearly exhibits the lattice fringe spacing for (2 2 0) plane of

cubic NbC ($d_{220} = 0.158$ nm), giving further evidence the prepared sample is NbC.

The route reported here is applicable to synthesize other carbides. By similar methods, both TaC and WC were synthesized by the reaction of g- C_3N_4 and metal oxides Ta_2O_5 and WO_3 , at $1150^\circ C$, respectively. As shown in Fig. 1b and c, both products are irregular aggregates consisting of many nanocrystallites. The corresponding EDX analysis (Fig. 2b and c) indicates that these two samples mainly consist of Ta, C and W, C, respectively. Trace amount of O element is detected in these two samples probably due to the surface contamination by the O_2 and H_2O in air. Fig. 3b and c shows their experimental patterns, respectively. The patterns are indexed to the corresponding cells of carbides with lattice constants in good agreement with their known values. The reference patterns are as follows: ICDD-PDF#35-0801 and ICDD-PDF#25-1047 for TaC and WC, respectively. The broadening peaks of the patterns can be also observed, mainly due to the size effect of the sample grains, consistent with the TEM observations. TEM images (shown in Fig. 4b and c) show that TaC and WC are composed of well-crystallized particles with average size of 35 and 60 nm, respectively. HRTEM clearly indicates the plane spacing for the respective carbides: $d_{111} = 0.257$ nm for cubic TaC (inset of Fig. 4b) and $d_{001} = 0.284$ nm for hexagonal WC (inset of Fig. 4c). These values are consistent with the known data in the corresponding ICDD-PDF reference patterns, further confirming the results of XRD measurements. These particles with nano-scale size can be more useful in the ceramic and catalytic

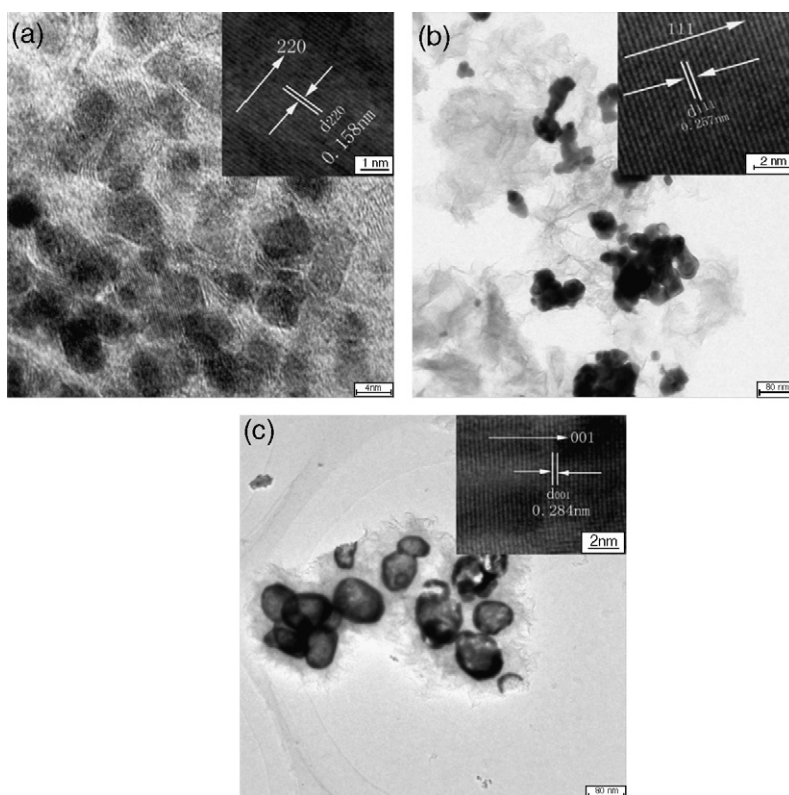


Fig. 4. TEM micrographs of the obtained carbides: (a) NbC; (b) TaC; (c) WC. The inset of each image implies the lattice of the corresponding carbides.

applications because they are easy to machine and are of high surface area.

These results suggest that this route is very effective in converting oxides into carbides. A characteristic in this solid-state reaction is that these obtained carbides are impossibly synthesized by other routes from oxides at the low temperature (1150 °C). The reaction mechanism can be expected to include two steps: a carbothermal reduction process and a carbonizing process. Firstly, g-C₃N₄ decomposes into various carbon nitride species, such as C₂N₂⁺, C₃N₂⁺ and C₃N₃⁺, at temperatures over 550 °C [21]. These highly active species will easily bond the oxygen atoms and reduce the oxides into the corresponding metals. Then, the subsequent carbonizing process between the metal and these carbon-rich species will occur and finally lead to the corresponding carbides. Either process can be the important controlling step to the overall reaction, which can be confirmed by the experimental observations. It is found that Fe₂O₃ cannot be converted into Fe₃C by g-C₃N₄ while Fe can. The possible reason is that Fe₂O₃ is so stable that the active carbon nitride species cannot firstly react with it at moderate temperatures. On the other hand, the Ni₂O₃ can be converted into metal Ni instead of NiC in the final products, which indicates that the carbonizing process is also an important controlling step to the final product.

4. Conclusions

We report a facile and highly efficient solid-state reaction for the synthesis of fine NbC, TaC and WC nanoparticles at the low temperature (1150 °C). g-C₃N₄ chosen as a precursor is proven to be a highly efficient carbonizing reagent, and the oxides Nb₂O₅, Ta₂O₅ and WO₃ are completely converted into the corresponding carbides, respectively. The NbC, TaC and WC are found to have an average particle size of 4, 35 and 60 nm, respectively, suggesting that these nanoparticles can be more useful from viewpoint of technical application. A striking feature of this facile solid-state reaction is that g-C₃N₄ plays double roles in the reaction: carbothermal reduction reagent and carbonizing reagent. This novel route may provide new insights into the synthesis of other transition metal carbides.

Acknowledgements

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