

# Application of Organic Carbon Sources in Preparing a Core-shell Structure

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**Abstract**—To synthesize a core-shell structure for preparing nano-sized WC powder, four kinds of organics were adopted as carbon sources and their carbonization characteristics were investigated. The results showed that organic type severely affected the structure and quality of the product. Using starch as carbon source, the carbonization with tungsten source were tightly contacted and formed a typical core-shell structure with a core that was 20-40 nm and a shell that was 10-20 nm in size. The formatting mechanism of the core-shell structure was also explored.

**Keywords**-core-shell structure; WC; organic carbon source; nanopowders

## I. INTRODUCTION

Tungsten carbide (WC) is widely used in many industrial applications, such as in the tool and catalysis industries, because of its high hardness, high toughness, high melting point, and excellent wear and corrosion resistance [1-3]. Furthermore, the hardness and the strength of cemented carbides increase remarkably when the grain size is reduced to the nanometer range. The toughness also improves substantially [4-7]. Hence, the preparation of nano-sized WC powders has become a popular research subject.

WC preparation usually adopts solid-state carbon or gas as carbon source [8-10]. If gas is used as a carbon source, then a long time is needed to penetrate into the inner oxide. When using a solid-state carbon source, the contact area is reduced with the tungsten oxide if the carbon particles are too large. This phenomenon will cause the carburizing process to become difficult, which will slow down the reaction speed. Sintering will accompany the carbide reaction, resulting in particle growth. Ultimately, nano WC powders are not obtained. Therefore, the current study focuses on designing an advanced reaction system that can increase carbonized reaction rate.

In our previous work, a series of WC, WC-Co, and WC-Co-VC nano-sized powders was prepared using a core-shell structure precursor [11-13]. The precursor was synthesized using hydrothermal method, which adopts organics as carbon sources. In the core-shell structure, the carbon clings tightly to the core surface, which can increase the contact areas between reactants, decrease the atom diffusion distance, and increase the reaction rate [14-15]. Thus, this method can obtain nano-sized WC particles.

Therefore, the organic carbon source severely affects the core-shell structure, which consequently affects the quality of the final products. In this work, four kinds of commonly used organics were acquired as carbon sources, and the effect on the quality of the core-shell structure and the final product was studied. The optimized scheme and the formation mechanism of core-shells were explored.

## II. MATERIALS AND METHODS

### A. Experimental

All of the reagents used were of analytical grade, and purchased from Chengdu Kelong Chemical plant. A typical experiment similar to our previous work was conducted. Glucose ( $C_6H_{12}O_6$ ), soluble starch ( $C_{12}H_{22}O_{11}$ ), acetate fiber [ $C_6H_7O_2(OH)_{3-m}(OOCCH_3)_m$ ], and phenol resin ( $(C_7H_6O_2)_n$ ) were used as carbon sources, and ammonium metatungstate [AMT,  $(NH_4)_6(H_2W_{10}O_{40} \cdot 4H_2O)$ ] was used as W source. The sources of W and C were mixed with their solutions in a capacity Teflon-lined autoclave. The autoclave was then sealed into a stainless steel tank and maintained at 200 °C for 8 h without stirring or shaking. After a reaction was achieved, the autoclave was naturally cooled to room temperature. The puce powders were collected by separating the reaction liquid using a high-speed centrifuge. Then, the carbide reaction was placed in a vacuum furnace using the puce powders at 950 °C for 1 h with a temperature rate increase of 10 K min<sup>-1</sup>.

### B. Characterization

The transmission electron microscopy (TEM) images were operated at a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 20kV. High-resolution transmission electron microscopy (HRTEM) images were taken with a FEI Tecnai-G2F20 using an accelerating voltage of 20kV. 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 2 $\theta$  range of 30-90°. The average particle size of the powder was estimated by Scherrer equation ( $D = k\lambda / (\beta \cos \theta)$ ), where D is the particle size, k is a constant taken to be 0.9,  $\lambda$  is the X-ray wavelength (0.15406 nm),  $\theta$  is the Bragg angle, and  $\beta$  is the full width at half maximum (FWHM) of an XRD line which has been corrected from the instrumental broadening [16]

### III. RESULTS AND DISCUSSION

The puce powders were prepared with four kinds of organics, through HRTEM, as shown in Fig. 1. When glucose was adopted as a carbon source, the great product mass had a core-shell structure. However, some of the generated carbon formed films and became freely suspended on the face of the solution. Thus, the generated carbon was not wholly coated on the surface of the tungsten oxide particles, as shown in Fig. 1a. When the starch solution was adopted as a carbon source, the products had a typical core-shell structure that was complete, compact, and uniform. The core diameter was 20–40 nm, and the shell thickness was approximately 10–20 nm, as shown in Fig. 1b. When acetate fiber was used as a carbon source, the sample had the characteristics of a core-shell, but the core was a coarse particle with a surface that was disorganized and twisted with many trips. Moreover, the shell was not complete. The size of the products was inhomogeneous, as shown in Fig. 1c. When phenol resin was used as a carbon source, the products also had a core-shell structure. However, the coating layer growth had an obvious orientation, which had not closely grown on the core surface. Therefore, the coating layer was not complete, and the particles were not uniform, as shown in Fig. 1d.

Using the above powders as precursor, the samples were obtained through carbothermal process at 950 °C for 1 h. And the XRD diffraction of the samples shows in Fig. 2. The result indicates that only the sample prepared using soluble starch as carbon source was pure WC (JCPDS 89-2727). The average crystalline size of the product was 80 nm, as calculated from the XRD peaks using Scherrer equation. This result was attributed to that the carbon source and the tungsten source were tightly contacted in the precursor, which would be in favor of finishing reaction and obtaining nano-sized WC powders at mild condition. When three other kinds of organics were used as carbon source, the major diffraction phase was WC. Some was the default phases, such as W and W<sub>2</sub>C. As shown in Fig. 2c, the product was composed of WC, W and W<sub>2</sub>C, and it contained some WC<sub>1-x</sub>. The results indicate that the carbonation reaction is not complete, possibly due to the precursor. It was an incomplete core-shell structure because the core-shell did not coat tightly as it needed a long time and a high temperature to finish the carbon reaction [17].

The change of the organic-self in the hydrothermal process was investigated, and four kinds of organic solutions were sealed into the autoclave at 200 °C for 8 h. TEM images of the four kinds of organics after a hydrothermal reaction are shown in Fig. 3. The generated carbon particles of glucose aggregated to form a loose cluster spherical structure. The generated carbon particles of the starch solution also formed a loose cluster spherical structure. Compared with the two results, the generated carbon particles of starch were smaller than those of glucose. Thus, the core-shell structure formed with starch and AMT was complete, unlike that of glucose and AMT. The results are shown in Figs. 1a and 1b. Fig. 3c presents a TEM image of an acetate fiber after a hydrothermal reaction. The products were small strips that were intertwined to form a cluster structure. However, the production of phenol resin did not form a cluster structure, which was similar to many broken chips. When using acetate fiber and phenol resin as carbon

source, the generated carbon was coarse and had a proper shape. Therefore, they cannot get close to the coat on the surface of the metal oxide nucleus, which is similar to that of starch, to completely synthesize and comprise the core-shell structure.

A model is discussed in this article to determine the mechanism for the formation of a core-shell structure. Fig. 4 is the TEM image of the product that the hydrothermal AMT solution generated at 80 °C for 10 min. The image shows that the particles present an algal structure that has a large surface and high surface energy. In the hydrothermal process, metal salt was first hydrolyzed. Many metal oxide particles underwent nucleation and precipitation. The nuclei with high surface energies had a tendency to agglomerate for the surface energy to decrease. The solution starch was then carbonized, which generated many small carbon particles. The carbon particles preferred to be deposited on the nucleus surface that had low energy. The part of the nucleus surface that was coated with carbon particles would stop agglomerating. However, the part of the nucleus surface that had high energy would continue to agglomerate until a smooth spherical surface with low energy was formed. The carbon particles were then deposited on this part of the surface. Finally, the carbon particles formed a complete and composite core-shell structure. When acetate fiber and phenol resin were used as carbon sources, the generated carbon were under ordination. Therefore, part of the coated nucleus had limited growth, but the uncoated part easily grew. Finally, the core was coarse, and the generated carbon did not form a coated shell.

### IV. CONCLUSION

In the synthesis of nano-sized WC powders, the carbon source is very important. The above experiments show that the structure and state of the organic affect the coating layer quality. The results indicate that starch is the best carbon source to prepare a core-shell structure and to obtain pure WC powders with size of 80 nm at mild condition. Starch is a polymeric compound with dextrose as its basic unit, and has the advantages of being abundant, low cost, biodegradable, renewable, and obtainable from many plants. These characteristics will provide an economic advantage for the application of this method to prepare nano-sized tungsten carbide tools.

### ACKNOWLEDGMENT

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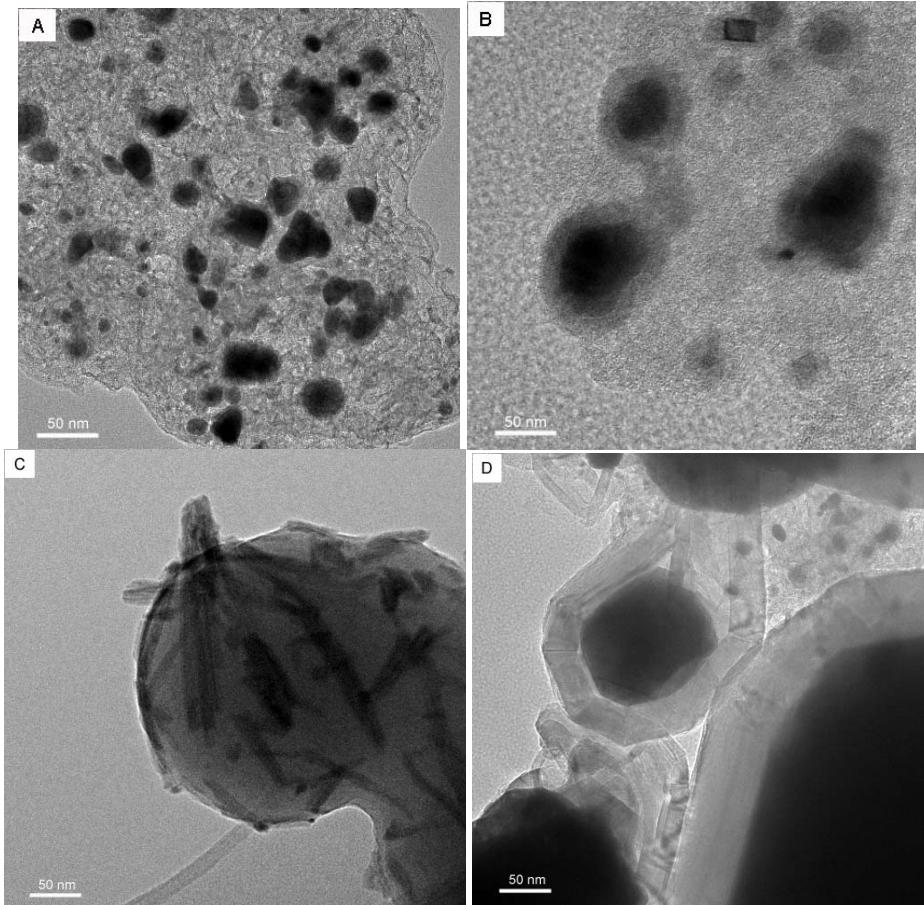


FIGURE I. EXAMPLE OF A TWO-COLUMN FIGURE CAPTION: (A) THIS IS THE FORMAT FOR REFERENCING PARTS OF A FIGURE

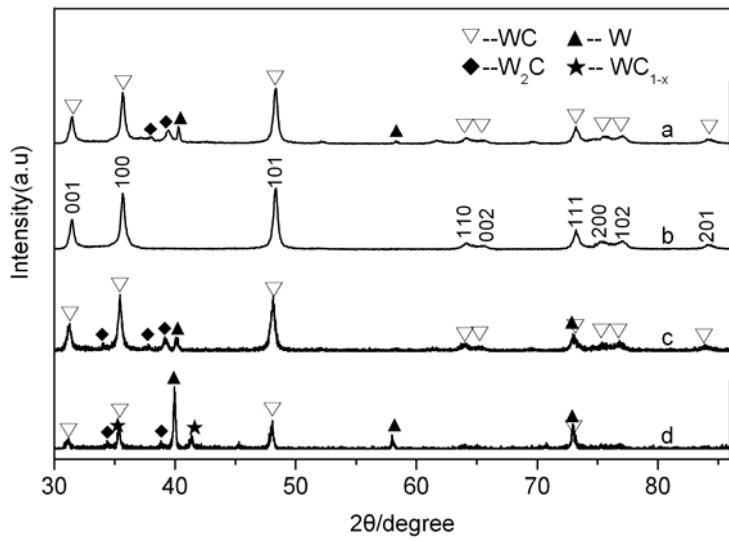


FIGURE II. XRD PATTERNS OF THE CARBONIZED PRODUCTS WITH DIFFERENT ORGANIC CARBON SOURCE: A. GLUCOSE; B. SOLUBLE STARCH; C. ACETATE FIBER; D. PHENOL RESIN

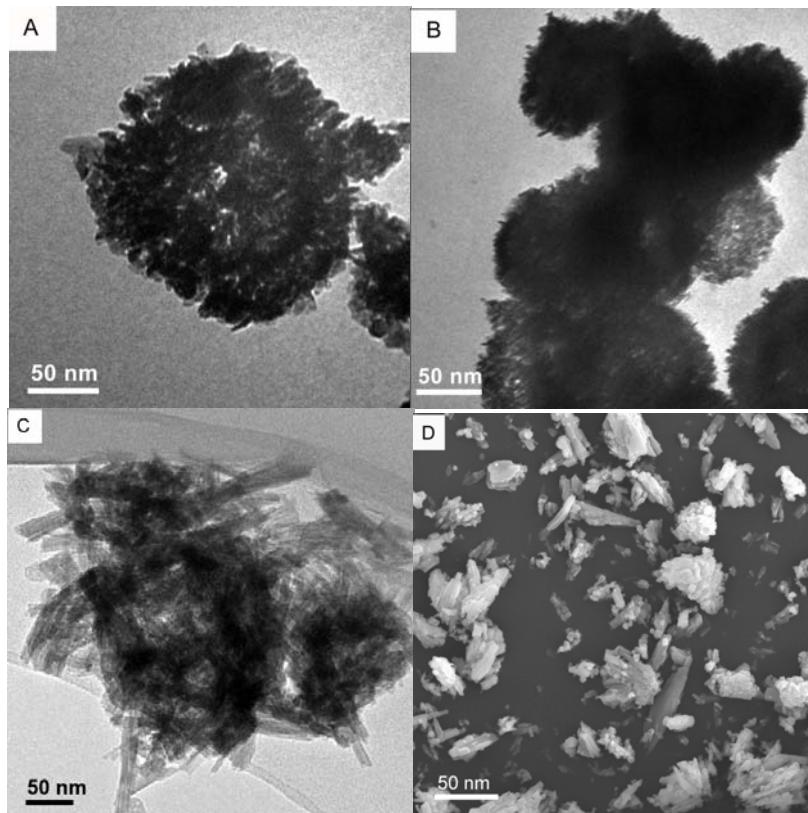


FIGURE III. TEM IMAGES OF THE SAMPLES PREPARED BY DIFFERENT ORGANICS: A. GLUCOSE; B. SOLUBLE STARCH; C. ACETATE FIBER; D. PHENOL RESIN

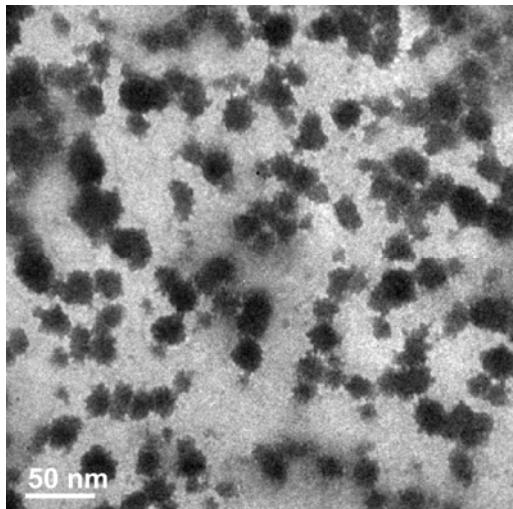


FIGURE IV. TEM IMAGE OF THE AS-PREPARED SAMPLE BY HYDROTHERMAL AMT AT 80 °C FOR 10 MIN