

## Synthesis of Tungsten Carbide Nanocrystal via a Simple Reductive Reaction

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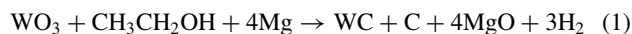
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Tungsten carbide nanocrystal had been prepared by the simple reaction of  $\text{WO}_3$ , Mg, and anhydrous  $\text{CH}_3\text{CH}_2\text{OH}$  in an autoclave at  $600^\circ\text{C}$ . There were two types of tungsten carbide in the samples; one was pure WC, and the other was wrapped by carbon. Transmission electron microscopy (TEM) results revealed that the diameters of WC nanocrystals ranged from 100 to 200 nm, and that the WC nanocrystals were slightly agglomerated. The possible formation mechanism of the as-obtained tungsten carbide was discussed.

Transition-metal carbides had attracted considerable attention because of their unique properties. They had extremely high melting points and high stability at high temperatures, and they were extremely hard and were usually used in cutting tools and wear-resistant parts.<sup>1</sup> Among them, WC was more important alloy materials, but they were brittle, usually together with Co binder material, were used extensively in cutting tools, saw blade tips, cement drills, and many other high wear applications for high hardness and high resistance to both oxidation and corrosion. WC powder was also used as catalysts of hydrocarbon-reforming reactions,<sup>2,3</sup> instead of noble metal such as Pt and Pd.<sup>4</sup> It could be used as promising alternative anodic materials, instead of Pt–Ru electrode,<sup>5</sup> in the direct methanol fuel cell.

Various synthetic methods had been developed for WC powder: direct carbonization ( $1400\text{--}1600^\circ\text{C}$ ),<sup>6</sup> ball milling ( $1000^\circ\text{C}$ ),<sup>7,8</sup> solid state metathesis ( $1000^\circ\text{C}$ ),<sup>9,10</sup> pyrolysis of metal complexes ( $700^\circ\text{C}$ ),<sup>11</sup> plasma-enhanced chemical vapor deposition ( $850^\circ\text{C}$ ),<sup>12</sup> sol–gel ( $900^\circ\text{C}$ ).<sup>13</sup> The relatively mild reductive condition was the main aim sought by many researchers. Recently W, Na, and dry ice were used to prepare WC at  $600^\circ\text{C}$ .<sup>14</sup> Dry ice was attractive as carbon source because it was contamination-free. In view of above-mentioned way, anhydrous ethanol was selected as carbon source.

In this paper, tungsten carbide nanocrystals were synthesized at  $600^\circ\text{C}$  via a solvothermal reaction, in which anhydrous  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{WO}_3$  were used as carbon source and tungsten source, respectively, and Mg as the reductant. The overall reaction equation could be formulated as follows:



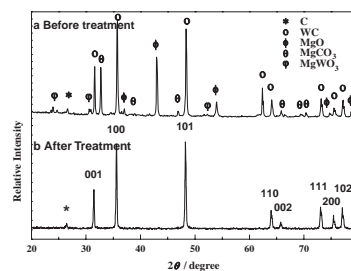
All chemicals were purchased from Shanghai Chemical Corp and used without additional purification. In a typical experimental procedure, appropriate amounts of  $\text{WO}_3$  (1.5 g), Mg (1 g), and anhydrous  $\text{CH}_3\text{CH}_2\text{OH}$  (12-mL) were put into a stainless steel autoclave of 16-mL capacity. Then, the autoclave was sealed and put into an electronic furnace at  $100^\circ\text{C}$ , the temperature of the furnace was increased to  $600^\circ\text{C}$  in 50 min and maintained at  $600^\circ\text{C}$  for 15 h. Then, it was allowed to cool down to room temperature. The dark solid powders were collected and washed by diluted HCl to remove unreacted Mg powder. After that, the

obtained sample was washed with distilled water and ethanol to eliminate by-products, and then it was dried in a vacuum at  $50^\circ\text{C}$  for 10 h.

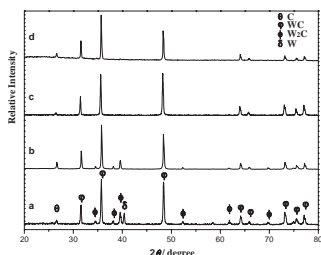
The final products were characterized by X-ray powder diffraction (XRD) [Rigaku (Japan) D/max-rA X-ray diffraction equipped with graphite monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ )]. The morphology and structure of the as-synthesized WC powder were observed by high-resolution transmission electron microscopy (JEM2100).

Figure 1 showed XRD patterns of the products obtained before and after the treatment. After refinement, the lattice constant  $a = 2.8999 \text{ \AA}$ ,  $c = 2.8299 \text{ \AA}$  were very close to the reported value of hexagonal WC ( $a = 2.906 \text{ \AA}$ ,  $c = 2.837 \text{ \AA}$ , JCPDS Card No. 51-0939). The strong reflection peaks suggested that the as-prepared products were well crystallized. The weak peak at  $26.46^\circ$  could be attributed to the (002) reflection of carbon (JCPDS, No. 26-1077). No peaks of any other phases such as  $\text{W}_2\text{C}$  and W were detected.

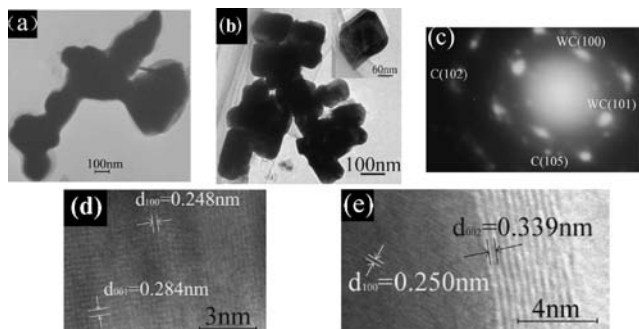
The influences of system pressure, reactive temperature, and reactive time on the formation of the WC powder were also investigated. The system pressure was the key factor for the formation of WC powder. We increased the system pressure by increasing the amounts of liquid ethanol. The experimental results indicated that; the higher was the volume of filling anhydrous ethanol, the easier was the formation of WC. When the filling degree of anhydrous  $\text{CH}_3\text{CH}_2\text{OH}$  was increased to 75 or 90%, more pure tungsten carbide phase could take shape and no other tungsten compounds appear (see Figure 2). Apart from this, the volume of anhydrous ethanol less than three-fourths was investigated such as 30 and 50%, there were more than a sort of tungsten compound including ditungsten carbide and tungsten formed. Therefore, it could be seen that the system pressure played a key role from the experimental results. The experiments also showed not only the system pressure but also the reaction time had main effect on the formation of tungsten carbide. The reaction would be incomplete if the reaction time was shorter than 13 h. The experimental data also bore out: if the reactive temperature was lower than  $500^\circ\text{C}$ , single-phase WC could not be obtained.



**Figure 1.** XRD patterns of the products obtained before (a) and after (b) the acid treatment.



**Figure 2.** XRD patterns of the products at different ethanol filling degrees: a 30%, b 50%, c 75%, d 90%.

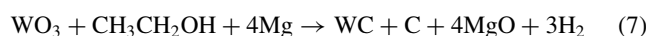
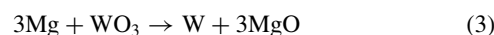


**Figure 3.** (a) Typical TEM morphology of WC, (b) Typical HRTEM images of tungsten carbide samples (the inset was single WC), (c) SAED pattern of a randomly selected tungsten carbide particle, (d) HRTEM image of a part of tungsten carbide particle, (e) Typical HRTEM image of mixed-phase of tungsten carbide and carbon.

Further structural characterization of tungsten carbide samples was made in detail by TEM and SAED. TEM results revealed the existence of carbon in the sample, which corresponded with the XRD pattern. Figure 3a showed TEM morphology of WC, in which tungsten carbide nanocrystals were wrapped by a layer of carbon film. But not all tungsten carbide nanocrystals were covered by carbon. Figure 3b showed the products free of carbon. They mainly composed of WC cakes (the inset was a single WC cake), and the diameters of WC nanocrystals ranged from 100 to 200 nm observed through HRTEM. Not only TEM but also HRTEM results displayed tungsten carbides slightly agglomerated possibly owing to their high surface energy. Figure 3c was SAED pattern of a randomly selected WC particle, which was composed of two sets: carbon and tungsten carbide. Figure 3d showed HRTEM image of single-phase tungsten carbide. The interlayer spacings were about 0.284 and 0.248 nm, which were close to those of expected from WC (001) and (100) reflection planes. And Figure 3e showed HRTEM images of mixed-phase of tungsten carbide and carbon, where the right interlayer spacing was about 0.339 nm corresponding with carbon (002) plane, and the left was HRTEM images of tungsten carbide. These HRTEM results further proved that tungsten carbide nanocrystals were well crystallized.

For probing into the possible formation mechanism of tungsten carbide, we designed and did a series of contrastive experiments. When tungsten powder was used instead of tungsten oxide and when graphite replaced anhydrous ethanol, single tungsten carbide phase could not be obtained even above 600 °C. A conclusion could also be drawn from the experimental data; at the current reaction temperature (600 °C), Mg could re-

duce anhydrous ethanol to C through a thermal reduction process,<sup>15</sup> and  $\text{WO}_3$  could also be reduced to W. The fresh C atoms and W atoms had higher activity than commercial graphite and tungsten powder, which made the formation of WC nuclei at lower temperature. Obviously, this was a vapor–solid process.<sup>16</sup> In the vapor–solid process, once the initial nucleation was started, the growth of the WC nanoparticles would continue by aggregation of the nuclei of WC until W atoms were exhausted. Subsequently, with the WC nanoparticles as substrates, excessive carbon (in this experiment, the quantity of carbon decomposed from ethanol was in excessive.) would deposit on the surface of them. The chemical reactions contained in the whole process could be formulated as follows:



In summary, WC nanocrystals were prepared successfully from cheap, easily available raw materials at the mild temperature of 600 °C. This synthetic route was very simple and easy to control and can be extended to synthesize other transition-metal carbides.

Financial supports from National Natural Science Foundation of China and the 973 Projects of China (No. 2005CB623601) are greatly appreciated.

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