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RESEARCH ARTICLE

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Synthesis of tungsten carbide nanocrystals and their electrochemical properties

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Abstract Tungsten carbide (WC) nanocrystals have been prepared by a solvothermal method with Mg as the reductant and WO_3 and anhydrous ethanol as the precursors. The effects of time and temperature on the synthesis of WC were investigated and a probable formation mechanism was discussed. The obtained WC nanocrystals were characterized by X-ray diffraction, transmission electron microscopy, energy dispersive spectroscopy and electrochemical methods. Hexagonal close-packed WC was successfully synthesized when the temperature was as low as 500°C. The content of carbon was more than that of W, indicating that the composition of the treated sample was C and WC only. The diameters of WC nanocrystals were ranged from 40 nm to 70 nm and the nanocrystals were dispersed on carbon films. The electrochemical measurements reveal that WC nanocrystals obviously promote Pt/C electrocatalytic ability for the oxygen reduction reaction.

Keywords solvothermal method, nanocrystal, tungsten carbide, electrocatalysis, oxygen reduction reaction

1 Introduction

Polymer electrolyte membrane fuel cells, such as proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC), have been considered as the most advanced low-temperature green power sources. Pt-Ru alloys as electrocatalytic materials show a high and stable activity for hydrogen. It has a very high catalytic activity for the oxidation of methanol [1–3]. However, the high loading of these expensive noble metals is required, which makes for the high-cost of fuel cells. Pure platinum is not a very good anode catalyst for methanol electro-oxidation at room or moderate temperature, because it is easily poisoned due to the CO poisoning at the Pt surface in the course of the methanol oxidation [4]. There is an urgent necessity to replace these noble metals with non-noble materials or reduce their usage [5, 6]. WC shows catalytic properties similar to platinum group metals. There had been many attempts to utilize tungsten carbide as an electrocatalyst because of its platinum-like catalytic behaviors in the past decades [7, 8]. Carbides of IV B-VI B group metals with catalytic properties similar to those of platinum group metals are widely considered [9, 10], which exhibit platinum-like catalytic characteristics and have been reported as potential materials for replacing platinum group metals. The surface of the WC could be modified by forming different phase structures *via* proper post-processing of oxidation to change the surface electronic structure and catalytic property [11, 12]. The surface electronic structure of WC is similar to that of Pt, which is used as a catalyst in many chemical reaction fields. Because the catalytic activity is uninfluenced by almost any CO concentration and 10^{-6} mol/L H_2S, WC exhibits better tolerance to poisoning species and stability for electrochemical oxidation [13, 14]. In electrocatalysis, WC has been mainly employed as the electrocatalyst for hydrogen evolution, water electrolysis and methanol oxidation. Therefore, there is a strong need to develop low-cost alternatives, such as WC or WC-base composites, for heterogeneous catalysis and electrocatalysis. In addition, WC has good conductivity, which can be used as electrodes in electrochemical catalysis and fuel cell [15, 16].

WC nanoparticles have been synthesized by different routes, such as temperature programmed reduction methods (TPRS) [17], halide decomposition methods (Bayer A G) [18], carbothermal reduction process (Patent RCR, World Brand Lab) [19], carbon coated precursor processes [20] and solvothermal methods [21].

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In this work, WC nanocrystals are prepared by a facile ethanol-thermal method in a high-pressure stainless steel autoclave at a temperature as low as 500°C. The obtained WC nanocrystals are characterized by X-ray diffraction (XRD), transmission electron microscopy, energy dispersive spectroscopy (EDS) and electrochemical methods.

2 Experimental

2.1 Synthesis of WC nanocrystals

All the chemical reagents in this work were of analytical grade purity and used without further purification. Mg was used as reductant and anhydrous CH_3CH_2OH and WO_3 were used as the carbon source and tungsten source, respectively. A detailed procedure is as follows: WO_3 (1.5 g), Mg (1.0 g) and anhydrous CH_3CH_2OH (20.0 mL) were added into a high-pressure stainless steel autoclave of 60 mL capacity, and the autoclave was sealed and put into an electronic furnace at 100°C. The temperature of the furnace was increased to 600°C in 50 min and maintained at 600°C for 15 h, and then it was allowed to cool down to room temperature. The dark solid powders were collected and washed by diluted HCl to remove the remaining Mg powder. Subsequently, the as-prepared products were immersed in hot and high concentration NaOH solution for removing the tungstate for 12 h. After that, the products were washed with distilled water and ethanol to eliminate by-products, and then it was dried in a vacuum at 50°C. In order to study the influence of temperature and synthesis time, the temperature was controlled at 500°C, 550°C and 650°C for 15 h, and at 600°C for 8 h, 12 h, 15 h, respectively.

2.2 Characterization of WC nanocrystals

The X-ray diffraction (XRD) patterns were recorded on a MSAL-XD2 Diffractometer using Cu-Kα radiation (Cu Kα, λ= 0.154056 nm, 40 kV, 20 mA). The morphologies of the samples were observed on a Philip TECNAI-10 transmission electron microscopy (TEM) operating at 120 kV. The component analysis was conducted on an Oxford Inca 350 energy dispersive spectrometer (EDS).

2.3 Electrochemical performance measurement

The products, absolute alcohol and Nafion solution (5%) were mixed and dispersed by ultrasonication for 15 min, and then the dispersed solution was dropped on polished graphite disk electrodes. All electrochemical measurements were performed in a three-electrode cell on CHI600B electrochemical workstation. A platinum foil (2.0 cm^2) and SCE were used as counter and reference electrodes, respectively. All the potentials were relative to SHE in this study.

3 Results and discussion

3.1 X-ray diffraction analysis

Figure 1 shows the XRD patterns of WC nanocrystals prepared by heating at different temperatures for 15 h. The structural evolution was observed by XRD during the period of increasing the temperature from 500°C to 650°C. XRD analysis results indicate that amorphous carbon and WC coexist in the sample at all the studied temperatures, and $MgWO_4$ starts to form and some WO_3 remains at 500°C. With the increase of temperature, all WO_3 is reacted completely. The reaction procedure is finished and the diffraction peaks of $MgWO_4$ disappear completely. Meanwhile, pure tungsten carbide phase is observed and no other tungsten compounds appear at 650°C. Simultaneously, the peak intensity of WC becomes stronger and sharper with increasing temperature from 500°C to 650°C. The XRD results illustrate that the increase of temperature results in enhancing the activity of C and W atoms, making the solid phase reaction of forming WC nanocrystals complete, and increasing the crystallinity of the WC nanocrystals. The system pressure plays a key role in the formation of WC powder, which makes the synthesis temperature of WC nanocrystals much lower than that of solid phase reaction (1900°C) at normal pressures [22].

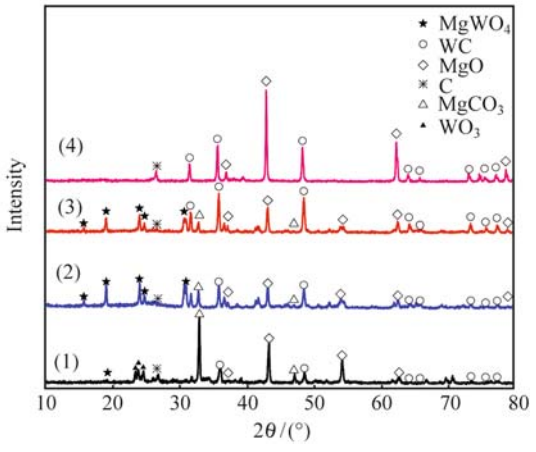

Fig. 1 XRD patterns of WC nanocrystals prepared by heating at different temperatures for 15 h. (1) 500°C, (2) 550°C, (3) 600°C, (4) 650°C

The effect of reaction time on the formation of the WC powder was also investigated. Considering the safety of high-pressure stainless steel autoclave and the little change of the XRD peak intensity between 600°C and 650°C, we have adopted 600°C of the reaction temperature for studying the influence of reaction time. The XRD patterns of the WC nanocrystals prepared by heating at 600°C for different times are shown in Fig. 2. The results indicate that not only the system pressure and reaction temperature, but

also the reaction time, have important effect on the formation of WC nanocrystals. The reaction is still incomplete even when the reaction time is as long as 15 h. However, the WC phase can be observed at the reaction times from 8 h to 15 h and WO_3 has been reacted completely. As the reaction time increases to 15 h, the diffraction intensity of WC phase increases markedly. These experiments results show that Mg can reduce the WO_3 to W atoms in a comparatively short time, and W atoms with high activity are continuously obtained until the reaction is over. From Figs. 1 and 2, it can be seen that the formation of WC phases is obviously dependent on the system pressure, reaction temperature and reaction time. The optimum conditions for synthesizing WC nanocrystals are at 600°C for 15 h.

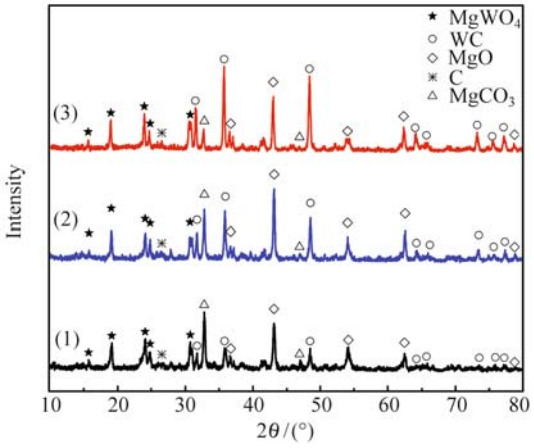

Fig. 2 XRD patterns of the WC nanocrystals prepared by heating at 600°C for different time. (1) 8 h, (2) 12 h, (3) 15 h

Figure 3 shows the XRD patterns of the WC nanocrystals prepared by heating at 600°C for 15 h before and after the acid and alkali treatment. After acid and alkali treatment, the XRD pattern indicates that the as-prepared product consists of only the hexagonal close packed WC and carbon. The diffraction planes of WC phase are consistent with JCPDS card No. 12070-12-1, and the lattice parameters are $a = 0.2906$ nm and $c = 0.2838$ nm. The average grain size of the WC nanocrystals is calculated from the half-width-at-full-maximum (HWFM) by using the Scherrer formula:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where D, K, λ, β and θ are average grain size, a constant that varies with the method of taking the breadth (0.89), the wavelength of incident X-rays (0.154056 nm), the breadth of the peak of a specific phase (HWFM) and the center angle of the peak, respectively. The average grain size of the WC nanocrystals obtained from XRD is approximately 66 nm.

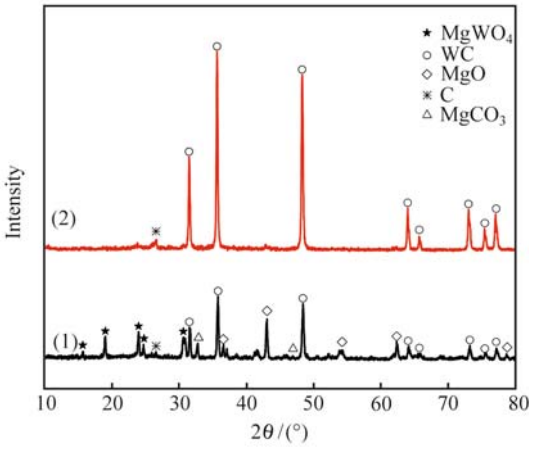

Fig. 3 XRD patterns of the WC nanocrystals prepared by heating at 600°C for 15 h before (1) and after (2) the acid and alkali treatment

The X-ray analysis shows that the WC is synthesized by ethanol-thermal method through a stepwise mechanism. The reaction pressure, temperature and time are the main influencing factors. First, WO_3 is reduced to lower valence tungsten oxides by Mg at low temperatures and then further reduced to metallic tungsten with increasing the temperature. When the temperature and reaction time are increased, the reduced metallic tungsten combines with carbon to form WC. Obviously, this is a vapor-solid reaction. In the vapor-solid process, once the initial WC nucleation is completed, the growth of the WC nanoparticles will continue by aggregation of the nuclei of WC until W atoms are exhausted [21, 23]. The possible formation mechanism of the WC nanocrystals is deduced as follows:

$$Mg + CH_3CH_2OH \rightarrow Mg\,O + 2C + 3H_2 \quad (1)$$

$$CH_3CH_2OH \rightarrow 2C + 2H_2 + H_2O \quad (2)$$

$$Mg + CH_3CH_2OH + WO_3 \rightarrow MgWO_4 + 2C + 3H_2 \quad (3)$$

$$Mg + MgWO_4 + C \rightarrow W + MgO + MgCO_3 \quad (4)$$

$$2W + C \rightarrow W_2C \quad (5)$$

$$W_2C + C \rightarrow WC \quad (6)$$

and the total reaction :

$$2Mg + WO_3 + CH_3CH_2OH \rightarrow MgCO_3 + WC + MgO + 3H_2 \quad (7)$$

3.2 Microstructure and component analysis

The microstructure, size and content of WC were determined by TEM and EDS, respectively. Figure 4 shows the TEM image (a) and EDS spectrum (b) of WC synthesized by heating at 600°C for 15 h. Black WC crystals dispersed on the membranous carbon can be observed under the TEM. The average particle size is about 40–70 nm. The EDS analysis shows that the contents of C and W are 83 wt% and 17 wt%, respectively, in agreement with the XRD results.

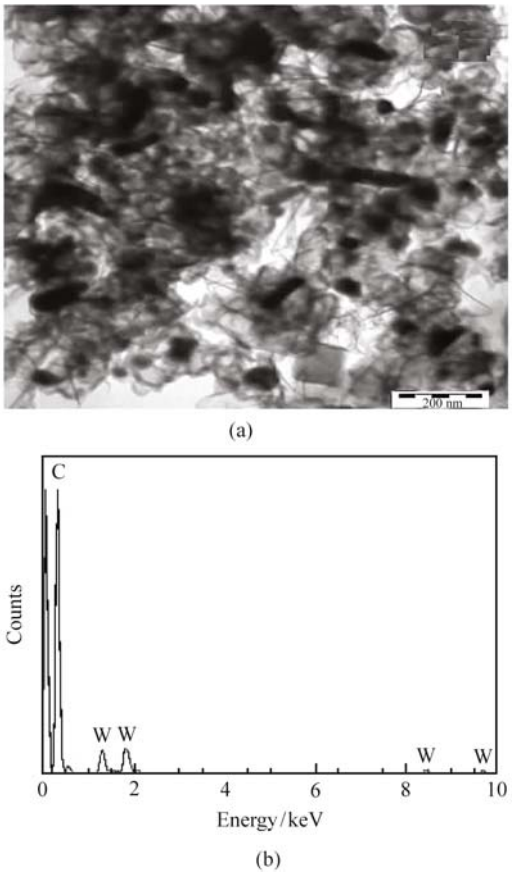

Fig. 4 TEM image (a) and EDS spectrum (b) of WC synthesized by heating at 600°C for 15 h

3.3 Electrochemical properties

Figure 5 presents the cyclic voltammogram of WC in 0.5 mol/L H_2SO_4. It can be seen that hydrogen adsorption/desorption peaks appear from 0 V to 0.1 V (vs. SHE), which is attributed to the adsorption of hydrogen ion by WC in the H_2SO_4 solution, and is an evidence for that WC has the platinum-like property [7, 8].

To the best of our knowledge, there is no report so far on WC prepared by solvothermal method for the utilization in oxygen reduction reactions (ORR). For comparison, we have prepared three electrodes prepared using WC, Pt/C and Pt-WC/C for ORR. As can be seen from the ORR polarization curves of the different electrodes (WC, Pt/C and Pt-WC/C) in 0.5 mol/L H_2SO_4 in Fig 6, the initial onset potentials are 0.790 V, 0.800 V and 0.973 V, respectively. The WC nanocrystals obviously promote the Pt/C electrocatalytic ability for the oxygen reduction reaction with a positive shift of 173 mV of onset potential, compared to that of the traditional Pt/C electrocatalyst. The peak current densities for WC, Pt/C and Pt-WC/C are 0.70 mA/cm^2, 8.98 mA/cm^2 and 9.80 mA/cm^2, respectively, indicating that WC possesses the synergetic catalysis effect with pt/C catalyst for oxide reduction reaction.

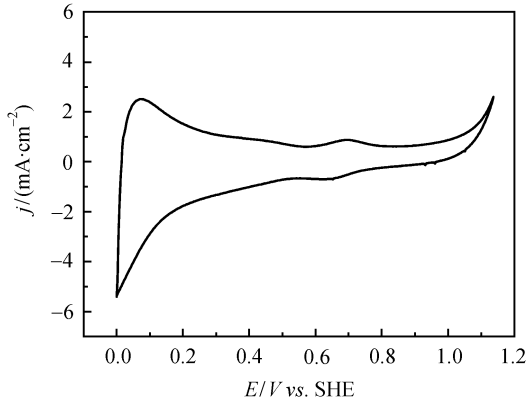

Fig. 5 Cyclic voltammogram of WC in 0.5 mol/L H_2SO_4 at 298 K
Scan rate: 50 mV/s; WC loading: 40 μg

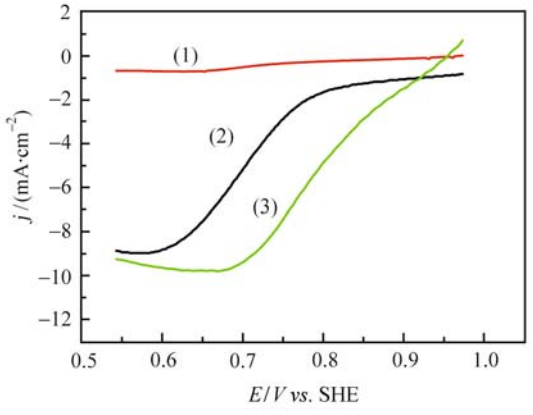

Fig. 6 Oxygen reduction reactions (ORR) of the different electrodes in 0.5 mol/L H_2SO_4 at 298 K
Scan rate: 50 mV/s; (1) WC loading: 40 μg, (2) Pt loading: 40 μg, (3) Pt-WC: 40 μg, 20 μg Pt + 20 μg WC

4 Conclusions

WC nanocrystals have been prepared successfully at relatively low temperature by a solvothermal method, which was simple, controllable and dependent mainly on the reaction temperature and time. A possible synthesis mechanism has been proposed and may be applicable to the synthesis of other metal carbides. The electrochemical measurements show that WC has the platinum-like property and possesses the synergetic catalysis effect with pt/C catalyst for oxygen reduction reaction.

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