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Mesoporous tungsten carbide nanoslices with pure phase and superior electrocatalysis

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ABSTRACT

Tungsten carbide nanoslices with mesoporosity have been prepared by an easy two-step strategy, *i.e.*, a hydrothermal pretreatment followed by a carburization reduction process. The greatest advantage of this strategy is that by changing carburization reduction temperature, the morphology and crystal phase of final products could be effectively adjusted. Structure characterizations of the as prepared monotungsten carbide products showed that they were constructed from irregular nanoslices with rough surfaces containing nanoparticles and mesopores. Methanol oxidation experiments using the monotungsten carbide nanoslice material as electrocatalyst found that, though it was consisted of pure WC, of which the electrocatalytic activity towards methanol oxidation is normally thought to be very low, it showed even higher catalytic activity than that of commercial Pt/C (E-TEK), offering a great possibility to develop totally noble-metal-free electrocatalysts for direct methanol fuel cell in the future.

1. Introduction

Monotungsten carbide (WC), due to its Pt-like catalytic behavior [1], high stability [2,3], high electronic conductivity [4], and especially its resistance to CO and H_2S poisoning [3,5–7], is viewed as one promising catalyst to replace precious metal in direct methanol fuel cell (DMFC) [8]. However, its relative high density results in small specific surface area and low electrocatalytic activity, which inhibits its application in electrocatalysis. In order to solve this problem, scientists have tried various methods that mainly utilize two strategies. One strategy making use of the synergistic effects of WC with other metals, is to composite it with other materials, such as modifying other metals on its surface [9–11] and anchoring it on other carriers [5] *etc.* The other strategy takes the advantage of structure adjustment with main aims of fabricating nanostructured and porous WC materials [4,5,10–16], which was thought may bring possible advantages beneficial to improve the electrocatalytic activity and stability, such as more active sites exposure, efficient mass transportation, increased release of gas bubbles, suppressed agglomeration of catalysts and enlarged interfaces between different components and so on [17–20].

Recent researches often apply both strategies that mentioned above and there are many publications reporting that loading of platinum nanoparticles (PtNPs) onto WC showed better catalytic activity toward methanol oxidation than a commercial Pt/C catalyst, as summarized in Table 1 [21–26]. For example, Li and co-workers demonstrated that a Pt supported nanochain-structured mesoporous tungsten carbide (m-NCTC) catalyst showed superior electroactivity and high resistance to CO poisoning for methanol oxidation compared to Pt/C [27]; J. S. Lee et al. reported a mesoporous WC with hexagonal crystal structure loaded with a small amount of Pt showed higher activity per mass of Pt by a factor of six than that of commercial Pt-Ru/C catalyst [28]. However, there have been few reports about using pure WC as electrocatalyst since it is often thought that WC alone showed low electrocatalytic activity [29,30]. As a result, the application of electrocatalysts in the fields of DFMC and so on still could not get rid of the limitation of precious metal.

Herein, we report mesoporous WC nanoslices with pure phase that showed better electrocatalytic performances than that of Pt/C (E-TEK). To the best of our knowledge, this is the first report that describes the synthesis of this novel nanomaterial (*i.e.*, slice-like nanostructured WC). What's more interesting, the morphology and crystal phase of the WC product could be easily adjusted by tuning its carburization reduction temperature. The facile synthesis, good electrocatalytic activity and excellent stability of the prepared mesoporous WC nanoslice make it a great promising substitute for precious metal catalysts in DMFC in the future.

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Table 1
Electrocatalytic activity of various catalysts for methanol oxidation.

Materials	Electrolyte	Specific activity (mA cm^{-2})	Ref.
WC nanotubes	0.1 M H_2SO_4 +2 mM	0.17 at 1.12 V Vs. Ag/AgCl	[33]
Pt/C	$H_2C_2O_4$ at 50 mV/s	0.17 at 1.30 V Vs. Ag/AgCl	
WC nanochain (NCTC)	0.5 M H_2SO_4 + 1.0 M	no characteristic peaks	[27]
Pt/NCTC	CH_3OH at 50 mV/s	5.35 at 0.67 V Vs. SCE	
Pt/C		3.5 at 0.65 V Vs. SCE	
WC nanorods	0.5 M H_2SO_4 + 1.0 M	no characteristic peaks	[16]
Pt/WC-nanorods	CH_3OH at 50 mV/s	9.68 at 0.65 V Vs. SCE	
20 wt% Pt/C		3.97 at 0.65 V Vs. SCE	
3.5 wt% Pt/WC	0.5 M H_2SO_4 + 1.0 M	185.1 at 0.80 V Vs. Ag/AgCl	[28]
20 wt% Pt-Ru(1:1)/C	CH_3OH at 50 mV/s	114 at 0.75 V Vs. Ag/AgCl	

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of $WO_3•2H_2O$ Precursor

13.2 g $Na_2WO_4·2H_2O$ (AR, Chemical Reagent Ltd, National Drug Group, China) was dissolved in 500 mL deionized water, 2 mol dm^{-3} HCl was then dropwise added into the $Na_2WO_4·2H_2O$ solution under stirring until its pH value had reached 1, which formed a yellow sol. Then 1.0 g $H_2C_2O_4·2H_2O$ (AR, Shanghai Linfen Chemical Reagent Ltd, China) was added into the sol. After being stirred for 30 minutes, the liquid was transferred into a hydrothermal reactor with a volume of 100 ml, and the reactor was put into a stove. The temperature of the stove was first raised to 100 °C at a speed of 10 °C·min^{-1} and then kept at this temperature for 4 h. After that, the stove was cooled naturally down to room temperature and the resultant in the reactor was centrifuged, rinsed with deionized water until its pH value was 7. Then the sediment was dispersed with absolute ethanol and dried at 60 °C overnight to get some yellow powder, which was used as precursor ($WO_3•2H_2O$) in the following experiments.

2.1.2. Preparation of tungsten carbide samples

10 g precursor was put into a quartz boat, which was then sent into a tubal stove. A N_2 flow was applied to the stove for 30 min to remove the air in it. Then a mixed flow of H_2 and CH_4 with a volume ratio of 2:3 (H_2 to CH_4) was applied to the stove. Meanwhile, the temperature of the stove was raised to 650 °C at a speed of 10 °C min^{-1} and kept at this temperature for 6 h. Then the stove was cooled naturally, and the gas flow passing through the stove was changed to N_2 until the temperature of the stove was lower than 60 °C. Finally, the powders in the quartz boat were collected and used as samples for further explorations, which is signed as WC_{650}. Tungsten carbide samples with carburization reduction temperature at 700, 750 and 850 °C were also fabricated using the same procedure as that of WC_{650}, which were signed as WC_{700}, WC_{750} and WC_{850}, respectively.

2.2. Characterizations of $WO_3•2H_2O$ precursor and tungsten carbide samples

Crystal phase, morphology and microstructure of the tungsten carbide samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). XRD was performed on X'Pert PRO (PANalytical Netherlands), using Cu target as X-ray source with a step length of 0.04', of which K_α is 0.154056 nm, tube current and tube potential were 40 mA and 40 kV, respectively. SEM was carried out on a field emission scanning electron microscope (S-4700 II Hitachi, Japan). TEM was performed on a high-resolution field emission transmission electron microscope (Tecnai G2 F30 S-Twin, Philips-FEI, Netherlands).

2.3. Electrocatalytic activity measurement

Electrocatalytic activity of the tungsten carbide samples for methanol oxidation was measured using powder microelectrode with a three-electrode system, using CHI660d (Chenhua Ltd, Shanghai China) at room temperature (25 °C). A powder microelectrode was used as the work electrode, which was prepared by the following procedure: first seal a Pt wire with a diameter (D) of 60 μm in a glass tube, and polish the tube with rough sandpaper until the inner sealed Pt wire came out. Then fine sandpaper was used to further polish the tube to show complete cross-section of Pt wire. It is advised that the corrosion length of Pt wire (L) is better controlled in such a range that the ratio of L to D is 0.4-1. Next, the electrode was ultrasonically cleaned and rinsed with distilled water for several times, which was then used to calibrate the L value by using steady-state diffusion limiting current method. In our experiment, L was calculated to be 60 μm. Finally, the catalyst powder was firmly filled in the electrode after it was ultrasonically cleaned and dried, which was then used as work electrode in our experiments. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum plate with an area of 10*10 mm^2 was used as the counter electrode. All the potentials listed in this paper were referenced to SCE.

3. Results and discussion

3.1. XRD

XRD patterns of the $WO_3•2H_2O$ precursor (Fig. 1a) and tungsten carbide samples (Fig. 1b, curve b1-b4 represents XRD patterns of WC_{650}, WC_{700}, WC_{750} and WC_{850}, respectively) are presented in Fig. 1. From Fig. 1a, it can be seen there are five main peaks with 2θ at 16.51, 25.63, 34.15, 34.93 and 35.04°, respectively, which could be accordingly assigned to (020), (111), (200), (002) and (131)

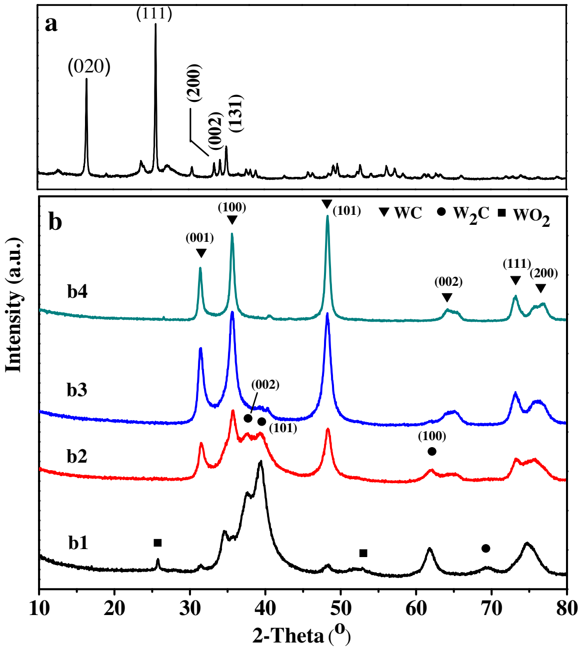

Fig. 1. XRD patterns of (a) the $WO_3•2H_2O$ precursor and (b_1) WC_{650}, (b_2) WC_{700}, (b_3) WC_{750} and (b_4) WC_{850}.