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One-step synthesis porous tungsten carbide films with excellent hydrophilicity

Feng Teng [1], Peng Zhang [1], Guozhi Zhang, Chengshi Gong, Caitian Gao, Xiaowei Fu, Jiangtao Wang, Zhenxing Zhang, Xiaojun Pan *, Erqing Xie **

School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, People's Republic of China

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ABSTRACT

Tungsten carbide porous films have been prepared by hot filament chemical vapor deposition with carbonized tungsten filaments as precursors. The structural properties and morphologies of the nanofilms were characterized by XRD, SEM and Raman. There are many nanocones and channels in the surface. A possible formation mechanism of the structure was proposed. And the contact angle measurements show that the films exhibit excellent hydrophilicity, especially the film after the treatment by hydrogen has a contact angle of 8.6°. The high roughness and chemical composition on the surface are responsible for its hydrophilicity. Therefore, this film maybe has potential as electrocatalyst and electrocatalyst support.

1. Introduction

Tungsten carbide (WC) has attracted considerable attention for its catalytic and electrocatalytic applications since the discovery of its Pt-like characteristics as reported by Levy and Boudart [1]. It is well known that WC exhibits certain activity for various electrochemical reactions [2,3]. The low cost and insensitivity to catalyst poisons make it a viable candidate to replace noble metal catalysts. Besides, high corrosion resistance and superior electronic conductivity render WC suitable as an electrocatalyst support for various electrochemical applications [4,5]. Conventionally, several routes have been adopted to synthesize WC, such as the direct carbonization of tungsten at high temperature, solid-state metathesis and mechanical milling [6]. However, there is little study on the synthesis of WC nanostructure [7]. It remains a big challenge to synthesize nanostructured WC with controlled morphology. Moreover, the hydrophilic properties of the material used as catalyst are very important. If the hydrophilicity of WC is bad, its application in the liquid phase will be seriously limited. It is known that the wetting behavior of solid is mainly affected by both chemical composition and surface roughness [8,9]. The hydrophilicity, with the application in self-cleaning [10], antifogging [11], and biocompatibility can be realized by the capillary effect on the surface of two-dimensional (2D) [12] or three-dimensional (3D) [13] materials. So, the hydrophilicity of WC can be tuned by introducing some 3D nanostructures on the surface. But, to our best knowledge, there is almost no report on the wetting properties of nanostructured WC.

In this study, porous WC films were prepared by hot filament chemical vapor deposition (HFCVD) with carbonized tungsten filament as precursor. The morphologies, structures and crystalline of the films were measured. And the wettability mechanism of the WC films was discussed in detail.

2. Experimental

WC films were synthesized by HFCVD, which was mentioned in our previous work [14]. Before the experiment, the tungsten filament was carbonized in a mixture of methane and hydrogen as a precursor. The silicon wafer was used as the substrate and ultrasonically cleaned orderly in acetone and alcohol for 10 min. The chamber was pumped down to 1.0×10^{-3} Pa after the substrate had been placed under the filament. The WC film (Film A) was deposited for 5 min with hydrogen (H_2) and methane (CH_4) as feed gas. The volume ratio of methane to hydrogen was 1.5% with the total flow rate of 200 standard cubic centimeters per minute (SCCM) and the pressure was maintained at 3000 Pa. After deposition, the film was treated for 1 h in a hydrogen environment with the flow rate of 100 SCCM and the pressure was maintained at 1000 Pa, and the obtained film was called Film B. To be comparable, another film (Film C) was deposited for 5 min with only hydrogen as feed gas at a flow rate of 100 SCCM and the pressure was maintained at 1000 Pa during the deposition process.

* Corresponding author. Tel.: +86 15117233439.
** Corresponding author. Tel.: +86 9318912616; fax: +86 9318913554.
E-mail addresses: xjpan@lzu.edu.cn (X. Pan), xieeq@lzu.edu.cn (E. Xie).
[1] This authors contributed equally to this work.

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The surface morphologies of the samples were examined by scanning electron microscopy (SEM, Hitachi S-4800). The components and structure of crystals were measured respectively by Raman spectroscopy (JY-HR800 micro-Raman) and X-ray diffraction analyzer (XRD, PANalytical X'Pert). The contact angle measurements were taken at room temperature using a Krüss DSA100 goniometer. One droplet of 5 μL waters was dispensed on the surface using a computer-controlled automated syringe, and the average value of the three measurements from different positions of the sample was adopted as the contact angle.

3. Results and discussion

Fig. 1 shows the XRD patterns and Raman spectra of WC films. The (100) direction peak of WC crystal at $2\theta=35.7^\circ$ can be obviously observed. Another two XRD peaks at about 60.1° and 71.8° are from silicon carbide (SiC), which was formed at the interface of WC and silicon substrate. The XRD peak at about 55.7° results from the tungsten trioxide (WO_3). The formation of WO_3 was caused by the oxidation of metallic tungsten when the films were exposed in air, and the metallic tungsten came from the hydrogen treatment of WC. Compared with the Film C, the XRD peak of WO_3 in Film B is lower, indicating that the content of WO_3 in Film B is less than that in the Film C. In Fig. 1d, peaks at 1350 and 1580 cm^{-1} could be ascribed to the D and G peak of amorphous carbon, respectively. That means that amorphous carbon exists in the WC films. Through the Raman spectra of Film A, B and C, we can conclude that the content of amorphous carbon was reduced because atom hydrogen (H) plays an important role in etching amorphous carbon in CVD [15,16]. The SEM images of WC films are shown in Fig. 2. Fig. 2a shows the low resolution image of Film A, the WC film deposited for 5 min with CH_4/H_2, in which many nanochannels can be observed (red circle). Fig. 2d is the high resolution of Film A. Fig. 2b and e shows the morphology of Film B, which was etched for another 1 h by hydrogen after deposited under the same condition as Film A. The low resolution image of Film B (Fig. 2b) shows that the nanochannels became very wide and many nanocones (red circle) were formed because of H etching. Fig. 2c and f are the morphology of Film C, in which nanochannels can also be observed (red circle). And the WC film is covered by a lot of WO_3 nanoparticles, the sparking particles on the surface.

The possible formation mechanism is discussed as follows. Before the deposition, the tungsten wire was carbonized and a WC shell was formed on the surface. During the deposition process, numerous H were generated around the wire when the temperature reached 2200 °C, and reacted with the WC shell, then it transferred the WC to the substrate. Either WC or amorphous carbon was formed on the silicon wafer during the deposition process. The crystalline structure of WC would be destroyed due to the presence of excess amorphous carbon. Many nanochannels could be formed for the restriction of H on the deposition of amorphous carbon. Then, the channels were widened because of the treatment of hydrogen, and many nanocones were formed and bits of metallic tungsten, the source of WO_3, could be formed at the same time. More metallic tungsten was generated with only hydrogen as feed gas. The results are consistent with the XRD pattern and Raman spectra.

The wettability of the films was examined by contact angle (CA) measurement. Compared to 85° for the amorphous carbon film with nanostructure [17], the CA value of the hydrophilic Film A is about 16.7°. But after the treatment of hydrogen plasma, Film B exhibits better hydrophilicity, whose CA value is only 8.6°. This is

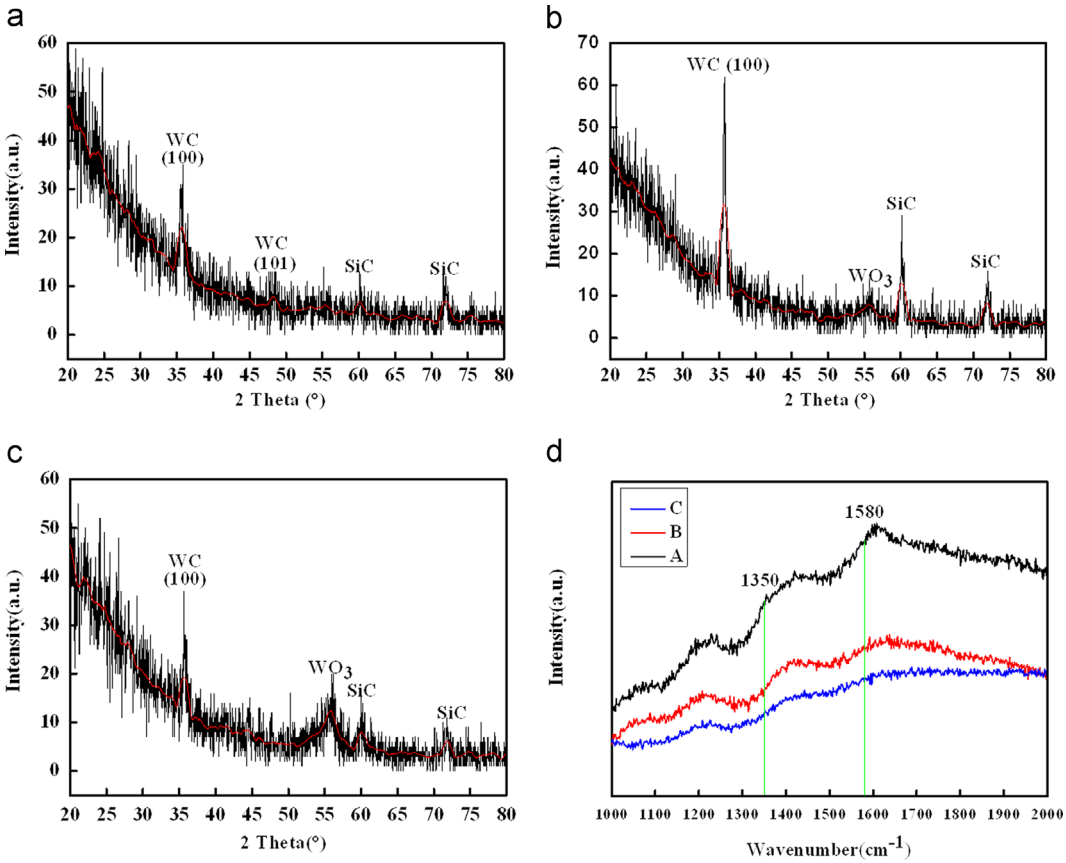

Fig. 1. XRD patterns of WC films (a) film A; (b) film B; (c) film C and (d) is the Raman spectra of WC films.