Composites Science and Technology 72 (2012) 1651–1655

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

An easy soft-template route to synthesis of wormhole-like mesoporous tungsten carbide/carbon composites

Liaoyuan Xia [a,b,*], Mingqiu Zhang [b], Minzhi Rong [b,*], Kunkun Guo [c], Yunchu Hu [a], Yiqiang Wu [a], Tibor Czigany [d]

[a] College of Material Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, PR China
[b] Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China
[c] College of Materials Science and Engineering, Hunan University, Changsha 410082, PR China
[d] Department of Polymer Engineering, Budapest University of Technology and Economics, Budapest H-1111, Hungary

ARTICLE INFO

Article history:
Received 21 December 2011
Received in revised form 11 June 2012
Accepted 8 July 2012
Available online 15 July 2012

Keywords:
A. Hybrid composites
A. Nano composites
A. Wormhole-like mesostructure
E. Sol–gel methods

ABSTRACT

Wormhole-like mesoporous tungsten carbide/carbon (WC/C) composites can be prepared by an easy method that combines emulsion processing with triblock copolymer self-assembly strategy, followed by a high-temperature carbothermal reduction. X-ray diffraction, transmission electron microscopy, X-ray spectroscopy, thermogravimetric analysis and N_2 sorption techniques were employed to characterize the mesoporous WC/C composites. The results show that the resultant materials have a wormhole-like mesostructure containing nanoscale (~40 nm) tungsten carbide particles, and high surface areas (up to 314.9 cm^2/g). It is proposed that a general assemble procedures are responsible for the wormhole-like mesoporous WC/C composites.

1. Introduction

Tungsten carbide (WC), as a special type of carbide material, has received considerable attention because of its widely application in such fields as metal working, drilling, and mining industries under severe conditions, which is due to its superior properties of high melting point, hardness, fracture toughness, and resistance to wearing, and oxidation [1–4]. More importantly, WC can be used as potential catalysts for various chemical and electrochemical reactions, such as a methanol oxidation [5–7], oxygen reduction [8,9], nitrophenol oxidation [10,11], hydrogen evolution [12,13] and biomass conversion [14]. This important application is attributed to its platinum-like catalytic behavior, stable in acidic and basic solutions, relatively low cost and high resistance to poisoning [5,15–20]. However, some critical problems are limited to develop the highly efficient WC catalyst. On the one hand, the WC alone shows much lower catalytic activity than that of noble metal and instability in some environments. On the other hand, the WC prepared by direct carburization of tungsten species at high-temperature usually has low surface area, which thereby restricts its applications as catalysts in the related fields.

In this regard, an efficient solution is to form mesoprous tungsten carbide/carbon (WC/C) composites. As we know, the catalytic performances of a catalyst are strongly relying on the dispersion and accessibility of the active sites. Therefore, nano-structured carbon [21–23], active carbons [8,9,24], especially mesoporous carbon [25,26] have been widely used as catalyst supports to improve the catalytic activity and durability of the WC, which is attribute to their particular structures and high surface area. Up to now, much effort has been focused on preparation of the mesoprous WC/C composites by using various methods, such as impregnating method [8,25], hydrothermal reaction [7,22,27] and template-replicating [26,28], in which carbon reacts with tungsten or tungsten oxides under reductive environments, which is the most universal approach. For instance, Meng and Shen [8] developed an intermittent microwave heating (IMH) method to prepare W_2C/Vulcan XC-72 carbon composites, but the W_2C particles easily aggregated each other on the carbon support. More recently, Ganesan et al. [7] and Wang et al. [22] synthesized mesoporous WC phase by a surfactant-assisted hydrothermal reaction route. However, the resultant materials showed relatively small pore diameters and low surface areas, compared to common mesoporous materials by similar surfactant routes. Normally, the hard-template method is also regarded as an effective way to prepare ordered mesoporous WC/C

* Corresponding authors. Address: Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China. Tel./fax: +86 02084114008.
E-mail addresses: xly1516@126.com (L. Xia), cesrmz@zsu.edu.cn (M. Rong).

0266-3538/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2012.07.007

composites [21,26,28]. Nevertheless, the synthesis procedures are rather multi-steps, high-cost, time-consuming, and a collapse of the mesostructure regularity would usually occur during the removal of the hard templates. Although the excellent progress has been made in the preparation of the WC/C composites, as far as we know, until now there is only a little literature regarding the synthesis of mesoporous WC/C composites by a soft-template method [29,30], because it is difficult to find proper precursors for the self-assembly of precursors and surfactants through a sol–gel process [28]. Thus, it is still a great challenge to provide a facile soft-template route for a mass of fabrication of the mesoporous WC/C composites with well-defined mesostructures and well-dispersed behavior for the practical applications.

In this work, for the first time, we demonstrate a simple soft-template method to prepare the mesoporous WC/C composites with wormhole-like mesostructures, small-sized (~40 nm) and finely dispersed tungsten carbide particles, and high surface areas. The materials have great potential for applications in fuel cell electrocatalyst, sensors and organic synthesis reactions.

2. Experimental section

2.1. Chemicals

All chemicals were used as received without further purification. Poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide) triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, M_w = 12600) and ammonium tungsten oxides hydrate (ATOH, used as tungsten source) were bought from Aldrich. Phenol, formalin solution (37%), melamine, hydrogen chloride (HCl, 37%), sodium hydroxide and ethanol were obtained from Guangzhou chemical company. Deionized water was used in all the experiments.

2.2. Preparation of phenol–formaldehyde–melamine (PFM) resin precursor

In a typically synthesis, 6.1 g of phenol was melted at 42 °C in a flask, follow by added 1.3 g sodium hydroxide (NaOH) aqueous solution (20 wt%) under stirring. After 30 min, 10.5 g of formalin solution (37 wt%) was added and further stirred for 30 min at 65 °C. Then, 4.1 g of melamine and certain of formalin was added, and the reaction was carried out at 65 °C for 30 min. After 1 h, the mixtures were cooled down to room temperature, and added HCl until the pH value of the solution was close to 7. The final product, a viscous liquid, was obtained by evaporating the water under vacuum at 40 °C.

2.3. Synthesis of wormhole-like mesoporous WC/C composites

Wormhole-like mesoporous WC/C composites were prepared by an easy method that combines emulsion processing with evaporation-induced self-assembly (EISA) route [31], followed by a carbonization treatment at 900 °C in ($N_2 + H_2$) mixture flow. In a typically synthesis, 5.0 g PFM resin precursors were dissolved in 20.0 g ethanol and 10.0 g H_2O solution at 35 °C. Then, 2.0 g of F127 was added and stirred for 30 min. A certain amount (0.5–2.0 g) of ATOH aqueous solution (33.3 wt%) was dropped into the above mixture under vigorous stirring for 30 min. Then, the mixture was cast onto glass dishes, followed by evaporation of mixture solution for 24 h at 35 °C. The resulting sticky films were further thermosetted at 105 °C for 24 h. Last, the brown colored films were placed in an alumina boat and calcined at 900 °C for 3 h under ($N_2 + H_2$) atmosphere in a tubular furnace. Then, the sample was passivated in a flow of 1% O_2/N_2 for 8 h at room temperature.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded by a Rigaku 2200 diffractometer using Cu Kα radiation source (40 kV, 30 mA). Transmission electron microscopy (TEM) observation was conducted on a JEM-2010HR machine operating at 200 kV. The compositions of the samples were determined by using energy dispersive X-ray spectroscopy (EDS). Nitrogen adsorption–desorption isotherms were measured at 77 K on a Micrometrics ASAP 2010 apparatus. Thermogravimetric analysis (TGA) was carried out on a Netzsch TG-209 apparatus at a heating rate of 10 °C min^{-1} under air atmosphere.

3. Results and discussion

Herein, a feasible assembly route for the formation of wormhole-like mesoporous WC/C composites was proposed. As illustrated in Fig. 1, three steps are required for this fabrication strategy. Firstly, a homogenous solution of PFM resin precursor and triblock copolymer F127 surfactant in ethanol/water solvent was prepared. Then, a certain amount of aqueous ATOH solution was uniformly dispersed in the above solution to form W/O emulsion under vigorous stirring and stabilization of F127, in which the ATOH solution acts as the dispersed phase while the ethanol/water solution as the continuous phase. This is because the ATOH is soluble in water, but insoluble in alcohol. As solvent evaporation processing, the ATOH firstly aggregated to form a larger droplet, and then precipitated and well-dispersed in sticky polymer films with solvent evaporation processing. Meanwhile, progressively increasing surfactant concentration (c > CMC) drives self-assembly of PFM precursors with template action of surfactant F127 based on hydrogen bond interaction, and further leads to formation of mesophases consisting of amphiphilic triblock copolymer micelles surrounded by cured PFM. Lastly, the triblock copolymer templates were removed by calcinations and tungsten carbide produced in situ by carbothermal reduction, so that the wormhole-like mesoporous WC/C composites is obtained [32].

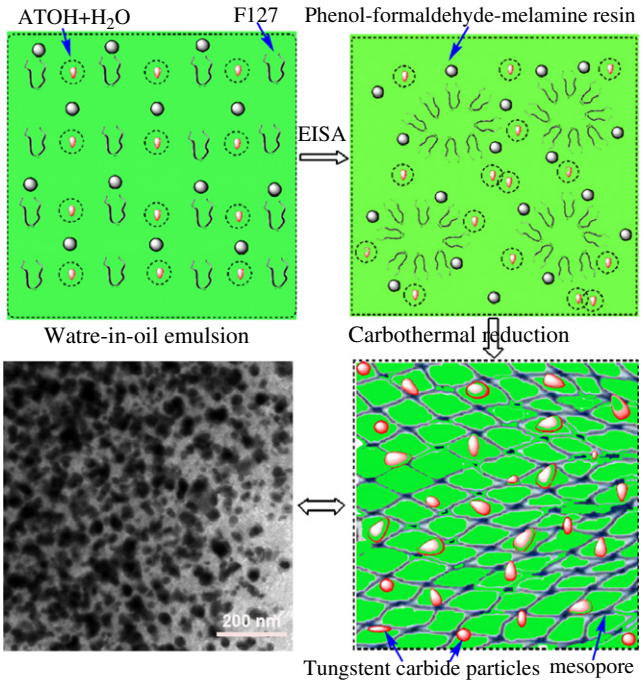

Fig. 1. Possible assemble procedures for the preparation of wormhole-like mesoporous WC/C composites.