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A hard-templating route towards ordered mesoporous tungsten carbide and carbide-derived carbons

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ABSTRACT

Ordered mesoporous tungsten carbide materials are synthesized via a nanocasting approach starting from hexagonal (SBA-15) and cubic (KIT-6) ordered silica templates. A tungsten chloride/sucrose precursor is converted into the desired ceramic by a thermal treatment in hydrogen and argon within the pores of the templates. The resulting materials show high BET surface areas and specific pore volumes of 431 m^2/g and 0.53 cm^3/g, respectively. They can be further converted to carbide-derived carbons (CDC) by metal atom extraction using hot chlorine gas. The ordered structure of the carbide matrix can be fully retained and the BET surface area and pore volume are noticeably enhanced to high values of 1246 m^2/g and 1.63 cm^3/g, respectively.

1. Introduction

Transition metal carbides are of wide interest due to their versatile properties such as high temperature stability, hardness, thermal conductivity, and chemical inertness. Therefore, they are frequently applied as heat shields, hard coatings, abrasives, or cutting tools [1]. If carbides are designed in a porous shape their field of application is further extended to catalytic, electrochemical, or biomedical applications, where they serve as robust support materials [2]. Certain carbides such as molybdenum or tungsten carbide even show intrinsic catalytic activities comparable to those of noble metal compounds like platinum or ruthenium [3]. Thus, they are nowadays widely discussed as new catalytically active materials in fuel cell technology which is an important topic in a century of decreasing oil and coal deposits [4–8]. The efficiency of hydrogen and methanol fuel cells usually depends on the activity of the noble metal catalysts. The main drawbacks of these catalysts are high costs and sensitivity against CO or sulphidic poisoning. In both aspects tungsten carbide (WC) is a potential alternative because it is comparably low in price and shows superior poisoning resistance. WC does not only serve as an independent catalyst but also as promotor for the electrochemical activity of Pt catalysts. Pt/WC co-catalysts show a larger activity compared to pure Pt/C materials due to synergetic effects of WC and Pt [9–11].

Mesostructured tungsten carbides in particular combine the advantage of high specific surface area and pore volume with pores in the mesopore scale (2–50 nm), thus providing both large substrate/catalyst interface and beneficial mass transport towards the active catalytic sites within the material. Both aspects are substantial in catalytic or electrochemical reactions.

In the last decades especially ordered mesoporous materials have attracted considerable attention because they (I) show very uniformly sized pores that can (II) serve as ideal model systems to study the influence of pore size on materials performance and (III) have proven to meet a huge field of different potential applications (e.g. drug delivery, separation, catalysis, electrochemical devices) [12,13]. Two major syntheses routes are common, known as soft- and hard-templating [2]. The well-established soft-templating approaches are based on surfactant-assisted hydrothermal reactions of suitable precursors followed by carbothermal conversions. Recently they have been used to synthesize ordered zmesoporous tungsten carbide/carbon composites from resin/polytungstate precursors [4,14]. However, in soft-templating approaches appropriate precursor–surfactant interactions have to be guaranteed, limiting the variety of possible precursors. Hard-templating concepts, such as the nanocasting principle, enable to increase the variety of possible precursors as well as the variety of possible templates (consequently differing in pore size and geometry) [15,16]. By means of that, mesoporous tungsten carbide/carbon composites were described by Shi et al. using mesoporous silica (KIT-6) as template [17]. Because of the volatility of the applied phosphotungstic acid it was necessary to press the

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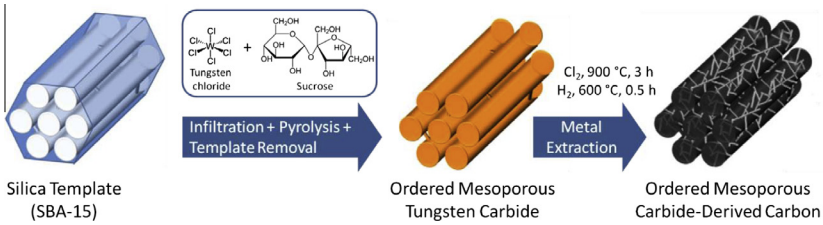

Fig. 1. Nanocasting scheme using the hexagonal ordered SBA-15. A tungsten chloride/sucrose precursor is infiltrated into SBA-15 and converted to WC within its pore network. After template removal ordered mesoporous WC is formed. Metal atom extraction using hot chlorine yield ordered mesoporous carbide-derived carbons (scheme based on Ref. [2]).

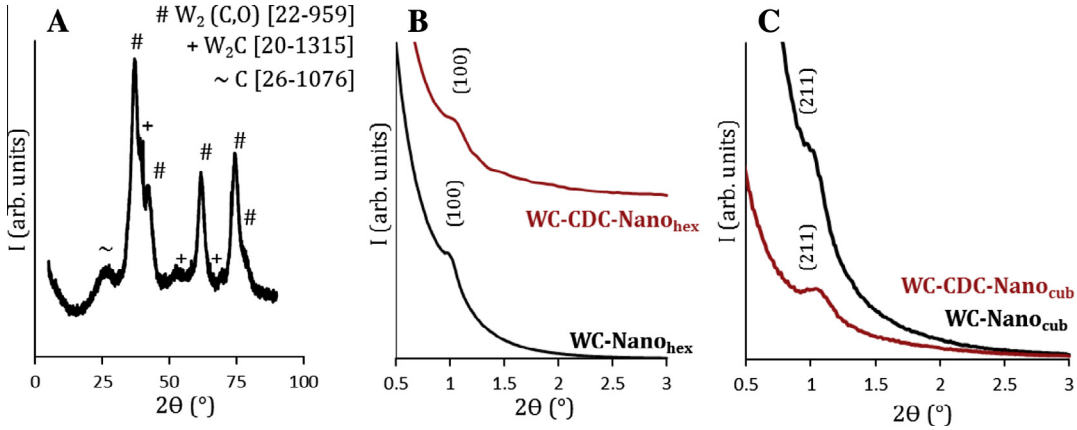

Fig. 2. Wide-angle X-ray diffraction pattern of hexagonally ordered WC-Nano (A) as well as low-angle X-ray diffraction patterns of the hexagonal (B) and cubic (C) ordered mesoporous tungsten carbides and carbide-derived carbons.

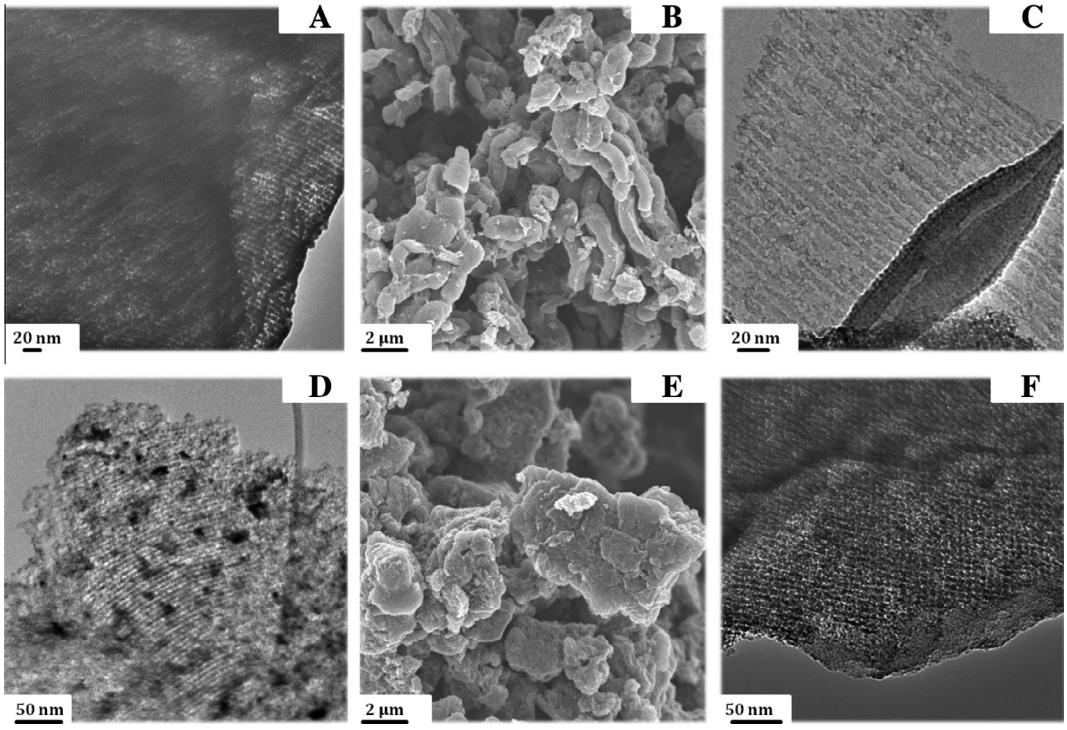

Fig. 3. Transmission electron micrographs (A, D) and scanning electron micrographs (B, E) of ordered mesoporous tungsten carbide with hexagonal and cubic pore structure, respectively. Transmission electron micrographs of the corresponding CDCs are shown in (C, F).

"filled" KIT-6 for the purpose of closing the pore entrances and keeping the precursor within the pore network. These materials exhibit surface areas as high as 138 m^2/g and show a cubic ordering of pores.