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Synthesis of Tungsten Carbide from Bacterial Cellulose

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Here we present preliminary experiments for the synthesis of carbide material using bacterial cellulose as carbon source. We used bacteria cellulose available as Nata de Coco and infiltrated it with tungsten trioxide (WO_3) nanoparticles. This composite was heat treated at 1300 °C in nitrogen atmosphere. The XRD pattern confirms the synthesis of tungsten carbide (WC) in the carbonaceous material, though a significant amount of metallic tungsten remained unreacted. SEM images shows that WC particles are present only at the surface of the carbon, which may be a consequence of improper infiltration or collapse of carbon matrix during heat treatment.

Introduction

Carbide materials are advantageous in different industrial applications due to their unique properties such as high melting point, high chemical resistance, low thermal expansion coefficient, low friction coefficient and high hardness [1]. For the synthesis of carbide materials, carbothermal reduction reaction (CRR) has been the most popular among several other synthesis techniques [2]. The CRR process involves two main steps: (i) thermal reduction of a metal oxide nanoparticle to the corresponding metallic element in the presence of carbon in an inert atmosphere; and (ii) reaction of the metallic element with excess carbon to produce metal carbide [3]. In industrial production, the resources used as carbon precursor include petroleum-based carbon, such as carbon black, petroleum coke and asphalt, coal products, graphite mining and other mineral resources [4–7]. Importantly, they are all of non-renewable nature and their extraction demand large and often non-environmentally friendly operations. Hence, the development of a sustainable, environmentally-friendly source of carbon that leads to products of the same quality than those currently available is desired.

The use of renewable Bacterial cellulose (BC) as a carbon source is explored here. The structure of bacterial cellulose consists of a randomly-oriented matrix of nanometer-scaled cellulose fibrils. These fibrils are synthesized by bacteria capable of directly transforming sugars into cellulose. The resultant cellulose is highly pure and features up to 90% crystallinity [8]. This makes bacterial cellulose an advantageous choice over plant cellulose in terms of strength, purity and easiness of production. Particularly, the extraction of biomass from plants and purification of cellulose to remove hemicellulose and lignin is not required in BC production. The use of a bioreactor to produce BC also eliminates the need for forestry operations to produce cellulose. While the fabrication throughput of BC may appear low, it must be compared to the growth rate of plants, with the advantage that pure BC can be directly obtained. The bacteria strain *Gluconoacetobacter xylinus* (previously known as *Acetobacter xylinum*) is commonly

used for this purpose although other species, such as *Acanthamoeba*, *Achromobacter*, and *Zoogloea* [9], also exhibit cellulose-synthesizing capability.

In this work, we present initial results for the synthesis of carbide using bacterial cellulose. The rationale is that a BC scaffold provides a pure nano-scaled matrix that can facilitate the required carbothermal reduction of metallic oxides. Here we focus to synthesis tungsten carbide by infiltration of tungsten trioxide (WO_3) nanoparticles in the cellulose matrix followed by a heat treatment in inert atmosphere.

Materials and Methods

Materials

Commercially available bacterial cellulose was purchased in Amazon.com as Jubes® Nata de Coco. Nata de Coco is a popular desert in the Philippines and consists of bacteria-free BC cubes immersed in flavored syrup. Tungsten trioxide (WO_3) nanoparticles of 25-65 nm diameter were purchased from US Research Nanomaterials Inc, USA. Ultra-pure water obtained by filtration and distillation was used as solvent and washing agent throughout this work. Isopropyl alcohol (IPA) was purchased from Sigma.

Experimental Procedure

BC cubes from Nata de Coco were washed repeatedly in ultra-pure water to eliminate the flavored syrup. In parallel, a WO_3 nanoparticle dispersion was made by mixing 40 mg of particles in 5 ml of IPA and using a vortex mixer (Thermo Scientific, Maximix M16710-33Q) to achieve a dispersion. After washing, the cubes were directly immersed in the WO_3 dispersion and manually shaken gently for 30 minutes. After this the cubes were taken out of the dispersion and directly introduced in a tube furnace (TF1400, Across International, USA). The heat treatment was performed using a heating rate of 5 °C/min under a constant flow of nitrogen gas. The heating protocol consisted of a dwell time of 30 minutes at 300 °C to eliminate excess oxygen from the tube, followed by a heating ramp to a dwell time of 3 hours at 1300 °C. The furnace was then cooled to room temperature with natural cooling.

Characterization

The crystallinity and the composition of the carbonaceous material were determined using a Cu-K α X-ray diffractometer (XRD, Rigaku Ultima IV, Japan). The morphology of the sample was investigated using scanning electron microscopy (SEM, Hitachi SU6600, Japan). Energy dispersed x-ray spectroscopy (EDS, Oxford Instruments, USA) available in the SEM was also used for elemental analysis of the sample.

Results

After the heat treatment of the white and spongy, nanoparticle infiltrated Nata de Coco, a dark grey, solid and light weight material was obtained. Albeit a significant amount of shrinkage, the cubic shape of the original Nata de Coco was retained with an

irregular deformation on the cube. The material was hard, as comparatively greater effort was needed to crush it to powder for the sample preparation for XRD characterization.

The XRD pattern of the heat treated sample is presented in Figure 1. The XRD pattern is indexed with hexagonal tungsten carbide (WC) which corresponds to the International Centre for Diffraction Data (ICDD) PDF number 01-072-0097. A strong presence of WC can be observed in the diffraction pattern along with less-intensity peaks corresponding to tungsten hemicarbide (W_2C , ICDD PDF no. 01-071-6322). A significant amount of metallic tungsten (W, ICDD PDF no. 01-089-4900) is still present in the sample. The presence of amorphous carbon can also be inferred from the slight hump between 20° - 30° in the X-axis.

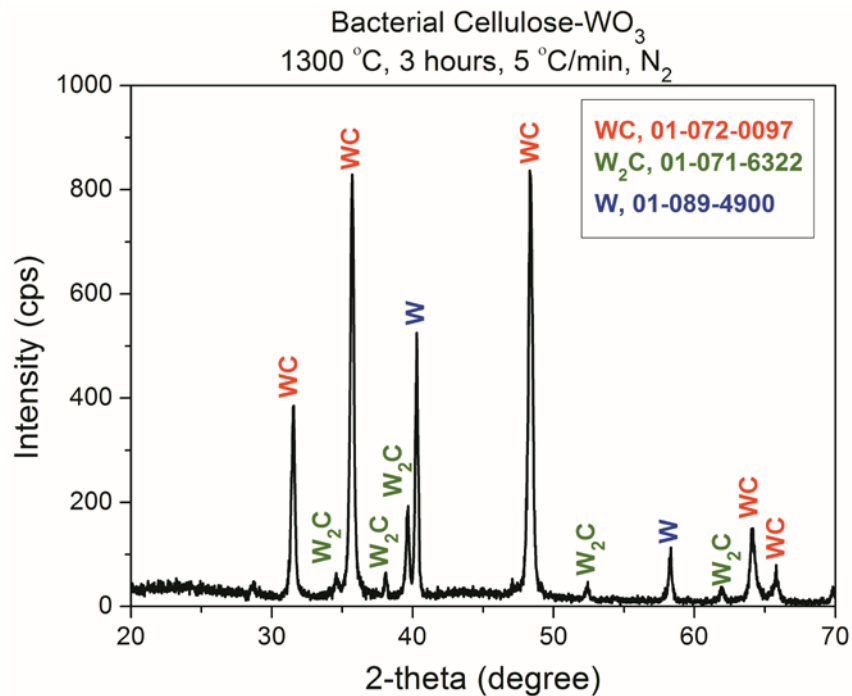


Figure 1: XRD pattern of carbonaceous material obtained from WO_3 infiltrated bacterial cellulose at $1300^\circ C$

Results obtained using SEM are shown in Figure 2a. Carbide particles seem to have formed only on the surface of the sample. The distribution of carbide particles is also non-uniform. Figure 2b shows a detail of carbide particles on the surface. The synthesized carbide features particle size ranging from tens of nanometers up to $1.5\ \mu m$. The molar ratio of W:C calculated from the EDX analysis of the particles enclosed by the rectangles in figure 2b is shown in Table I. This ratio is around 1, which confirms that the particles are WC.

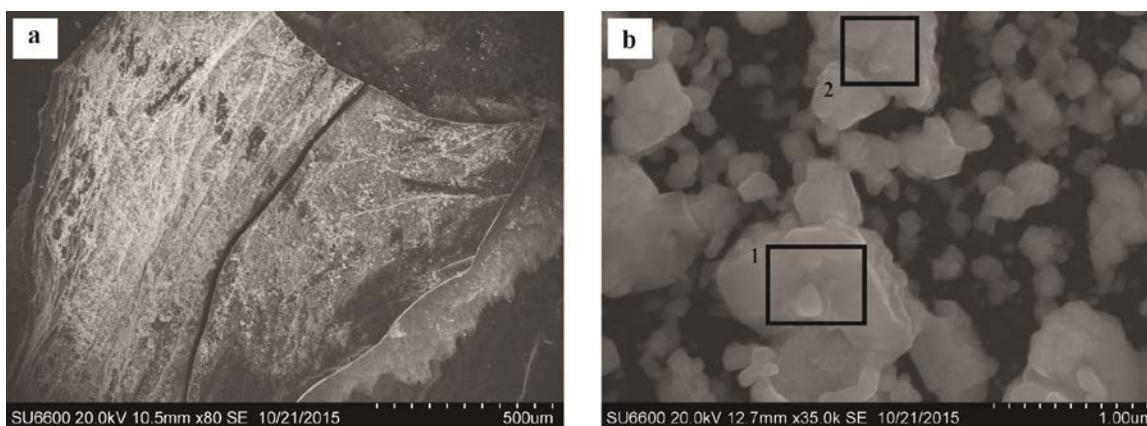


Figure 2: SEM images of (a) carbonaceous material obtained from WO_3 -infiltrated bacterial cellulose at $1300\text{ }^\circ\text{C}$; (b) particles of tungsten carbide scattered on the surface of the sample.

Table I: Elemental analysis of the particles obtained from the EDX of the particles contained in the rectangles of Figure 2b

Spot Number	Composition (%)		W : C molar ratio
	W	C	
1	94.5	5.5	1.12
2	94.3	5.7	1.07

Discussion

It is known that BC can hold up to 90% of its volume as water [10]. During heat treatment water evaporates which causes a significant amount of shrinkage in the cellulose matrix. Further shrinkage originates during the carbonization of cellulose. From the XRD and EDX analysis, it is confirmed that tungsten carbide was formed during the heat treatment of the WO_3 infiltrated BC. This process is expected to happen as follows. The bacterial cellulose turns into an amorphous carbon upon heat treatment in the temperature range $300\text{-}600\text{ }^\circ\text{C}$. At this point the infiltrated WO_3 nanoparticles become surrounded by the amorphous carbon and get reduced to metallic tungsten (W) at a temperature more than $750\text{ }^\circ\text{C}$ [11,12]. Once the reduction of WO_3 is completed at temperatures around $900\text{ }^\circ\text{C}$, the reaction between the resultant W and the surrounding carbon starts around $1000\text{ }^\circ\text{C}$ to form WC. During the reaction, the surrounding carbon diffuses into the W utilizing the thermal energy and forms a hexagonal lattice structure of WC. Deficiency in carbon diffusion into the W results in a metastable form W_2C [13]. The W_2C can be further carburized into WC at higher temperature to obtain WC to be the sole material in the sample [14].

In the SEM images, it has been shown that the carbides were formed only on the surface of the carbon derived from BC. Our hypotheses are first that most of the WO_3 nanoparticles could only infiltrate a couple of microns into the cellulose network. Although the pore size of the BC matrix is expected to be far larger than the diameter of the particles used here, the nature of the particle dispersion requires further study. If only clusters of particles are obtained, these may not be small enough to navigate into the

matrix. The effect of the dispersion solvent, IPA in this case, also requires further study in order to optimize the wetting of the cellulose and facilitate transport of the nanoparticles. An alternative hypothesis is that the particles could have been pushed out from the inner matrix during water evaporation and deposited on the surface. Assuming the particles were well dispersed to begin with and able to reach the inner volumes of the matrix, an alternative drying method such as critical point drying needs to be established to obtain a more homogeneous material. In any scenario, the carbon:WO₃ ratio needs to be optimized to guarantee a reaction that leads only to WC and minimizes the residues of other materials such as W and amorphous carbon.

Conclusion

Here we have demonstrated the synthesis of tungsten carbide (WC) using BC as a carbon source. WC was synthesized by infiltrating the bacterial cellulose with WO₃ nanoparticles followed by a heat treatment at 1300 °C in inert atmosphere. This process compares advantageously to current process because the use of non-renewable carbon precursors can be replaced by BC which can be easily reproduced by microbial fermentation. Also use of pure form of cellulose can eliminate the formation of impurities in the sample during heat treatment, which eliminates the use of acidic environment for purification. Though the presence of WC was dominant in the heat treated material, a significant amount of metallic tungsten (W) was also present as shown by the XRD pattern. Ongoing work is on optimizing the heat treating protocol to eliminate the W₂C from the matrix and obtain WC as the sole material in the sample. Furthermore, the extent of nanoparticle infiltration in the BC matrix requires further study towards obtaining homogeneous materials.

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