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Biotemplating fabrication, mechanical and electrical characterizations of NbC nanowire arrays from the bamboo substrate

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In this work, NbC nanowire arrays were successfully synthesized via a facile and cost-effective biotemplate method. Natural bamboo chips were used as both the carbon source and the template for formation of catalyst particles, which significantly simplify the synthesis process of NbC nanowire arrays. Based on the structural, morphological, and elemental analyses, a fluoride-assisted vapor–liquid–solid growth mechanism was proposed. *In situ* nanoscale three-point bending measurements demonstrated that the Young's modulus of NbC nanowires was in the range from 281 to 453 GPa with an average value of 338 ± 55 GPa. The resistivity of NbC nanowires was further investigated by *in situ* electrical property characterization using a multipoint measurement inside a transmission electron microscope. The resistivity of NbC nanowires was calculated to be 5.02 mΩ cm.

1. Introduction

Transition metal carbides (TMCs) have been studied extensively as high-temperature-resistant composites [1], coatings [2], cutting tools [3], superconducting devices [4], energy storage electrodes [5], and catalysts [2,6,7], due to their elevated melting points, excellent mechanical properties, high resistance to oxidizing acids, and good electrical and thermal conductivities. NbC, as one of TMC, is known to possess a unique combination of valuable properties. It exhibits a high toughness (3–6 MPa m$^{1/2}$), high hardness (20–22 GPa), high melting point (3873 K) and Young's modulus (400–500 GPa) [8,9], excellent chemical stability, together with superior wear resistance. It has been used as wear resistant [10], medical [11] and chemical materials [12].

In the past decades, one-dimensional (1D) TMC nanostructures such as nanowires [13] and nanorods [14] have drawn extensive attention because of their size-dependent optical, electronic [13–15], mechanical [13,14,16], and field emission properties [17], opening up unprecedented opportunities for constructing nano-devices with new functionalities. However, there are only few routes for synthesizing 1D NbC nanostructures. Moreover, 1D NbC nanostructures' mechanical and electrical properties are still lacking in literature. This limits their applications in constructing NbC based nanocomposites and nano-devices. To date, various techniques including carbon nanotube confined reaction [18], chemical vapor deposition [19], carbon thermal reduction [20–22], and pyrolysis of polymeric precursors [23] have been developed for the preparation of 1D carbide nanostructures. In our recent studies, a facile and cost-effective biotemplating method has been developed to synthesize 1D TMC nanostructures [13,14,24].

In this paper, we demonstrate, for the first time, that NbC nanowire arrays can be fabricated by a facile biotemplate method. Using *in situ* atomic force microscopy (AFM) and transmission electron microscopy (TEM), the Young's modulus and the resistivity of individual NbC nanowires were measured, providing critical parameters for practical applications.

2. Experimental section

Dried bamboo chips (wide: 2.5 mm; length: 0.7 mm; thickness: 0.2 mm) were immersed in ethanol solution of acetone with 0.2 mol/L concentration. After stirring for 0.5 h, bamboo chips were dried at 80 °C for 30 min, then at 110 °C for 2 h in an oven. 0.375 g of NaF, 2.372 g of Nb_2O_5 and 0.259 g of $Ni(NO_3)_2$ $6H_2O$ were dissolved into 20 ml ethanol to form a Nb–Ni–F emulsion under ultrasound irradiation. Bamboo chips were dipped in the Nb––Ni–F emulsion. After stirring for 2 h, the bamboo chips were dried at 90 °C for 30 min in a preheated oven and finally cured at 110 °C for 1 h. The bamboo substrates were then inserted into a sealed graphite crucible and then heated to 1250 °C at a heating rate of 5 °C/min and maintained at that temperature for 1 h under a constant Ar gas flow (350 sccm). After deposition, the furnace was cooled to room temperature.

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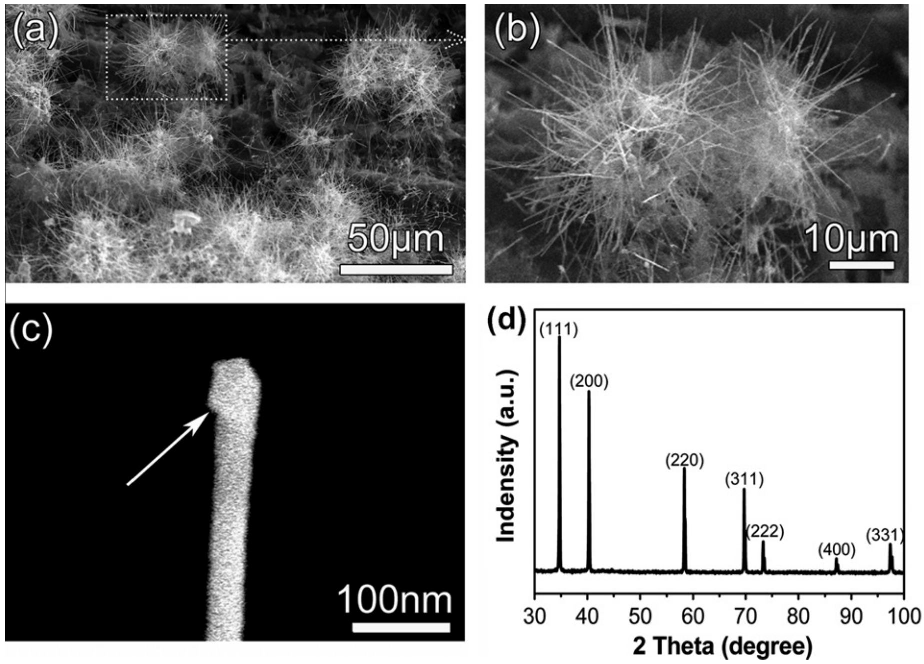

Fig. 1. (a) SEM image of NbC nanowire arrays on the bamboo substrate; (b) partial enlargement SEM image in (a); and (c) an individual NbC nanowire. (d) XRD pattern of NbC nanowire arrays.

The phase of the as-prepared products was determined by X-ray diffraction (XRD) using an XPert Pro diffractometer with a step size of 0.02 for Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM, Hitachi s-4800) and transmission electron microscope (TEM,FEI Tecnai G2 F30) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector were applied to investigate the microstructure and morphology. A drop of an ethanol solution containing the nanowires was placed on a stan dard atomic force microscope (AFM) reference sample (Veeco Metrology Group) with uniform trenches. In order to avoid nanowire sliding during the bending tests, both ends of the nanowire, which bridged the trench, were clamped by 20 min electron beam-induced deposition (EBID). A Veeco Dimension 3100 AFM was used to perform three-point bending tests by directly indenting the center of a suspended nanowire that bridged the channel with a tapping-mode silicon AFM tip. A total of 15 bending tests were performed to obtain the Young's modulus. The electrical properties of individual nanowires are characterized using a scanning tunneling microscope–transmission electron microscope (STM–TEM) holder (FM2000E, Nanofactory Instruments AB) in a TEM (JEOL 2200FS) with a field emission gun.

3. Results and discussion

The morphologies of the as-prepared products were characterized by SEM. Fig. 1a is the low magnification SEM image of nanowire arrays. The image clearly reveals that an abundance of uniform and straight nanowire arrays grew on the bamboo substrate. The magnified image (Fig. 1b) shows that nanowires have a length of 1–50 μm and a diameter of 30–100 nm. As indicated by the arrow in Fig. 1c, there is a quasi-spherical-shaped catalyst particle at the tip of the nanowire, indicating the top growth mechanism of this nanowire. The XRD pattern of the prepared NbC nanowire arrays is shown in Fig. 1d, in which seven diffraction peaks could be distinguished. The reflections at 34.7°, 40.2°, 58.3°, 69.7°, 73.3°, 87.1° and 97.3° are indexed to the diffractions from the (111), (200), (220), (311), (222), (400), and (331) crystal family planes of cubic NbC (JCPDS 65-0281). No Nb_xO_y, NbO_xC_y and Nb can be detected, suggesting that Nb_2O_5 was successfully converted to NbC.

Further structural characterization using transmission electron microscopy (TEM) is depicted in Fig. 2. Fig. 2a shows a low magnification, bright-field image of an individual nanowire with the growth direction along [010] of cubic NbC nanowire. It reveals that the diameter of the nanowire is less than 100 nm. The TEM results are in accordance with the SEM observations as shown in Fig. 1. As indicated by the black arrow in Fig. 2a, there is a catalyst particle at the tip of the nanowire, indicating a VLS growth mechanism [25] for the NbC nanowire. The EDS spectrum reveals that the catalyst particle contains C, Nb, and Ni. Fig. 2b shows the HRTEM image taken from the nanowire (as indicated by the red[1] arrow in Fig. 2a). The space between two adjacent lattice fringes is 0.22 nm, corresponding well to the {010} planes of NbC. Fig. 2c shows the corresponding indexed fast Fourier transform (FFT) pattern of the NbC nanowire in Fig. 2b, indicating that the NbC NW is a single crystal with the growth direction along [010].

During the VLS growth of NbC nanowires, there must be gas-phase transport of C and Nb to the Ni catalyst particle. In this work, bamboo chips acted as the renewable carbon source. Fig. 3 shows the decomposition product of bamboo cellulose at high temperature. On one hand, during pyrolysis (Eq. (1)), bamboo cellulose undergoes: (1) condensable vapors were condensed into a liquid product (tar), (2) condensable gases, and (3) solid carbon that consists of elemental carbon [26]. On the other hand, cracking of tars (Eq. (2)) occurred under high-temperature calcination (1250 °C), which is believed to be a significant pathway for production of CO, H_2, and several light hydrocarbon gases such as CH_4, C_2H_2, C_2H_6, and C_3H_6 [27]. These hydrocarbon gases resulting from pyrolysis of cellulose served as the carbon source

$$(C_6H_{10}O_5)_n \rightarrow C_3H_6(g) + C_2H_6(g) + C_2H_2(g) + CH_4(g) + CO_2(g) + CO(g) + H_2O(g) + H_2(g) + \mathrm{tars}(l) + \mathrm{char}(s) \quad (1)$$

$$\mathrm{tars} \rightarrow C_xH_y(g) + C_2H_5OH(g) + CH_4(g) + CH_3OH(g) + CH_3CHO(g) + CH_2O(g) + H_2O(g) + H_2(g) + CO_2(g) + CO(g) \quad (2)$$

[1] For interpretation of color in 'Fig. 2', the reader is referred to the web version of this article.