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Customizable local superhydrophobic micro channels by BNNTs growth

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ABSTRACT

The local superhydrophobic micro channels were fabricated by BNNTs growth with the method of ball milling assisted with B ink annealing. Both the ball milling and annealing processes in the preparation were optimized to obtain high quality and density of BNNT films. The structure of anode plate is designed to synthesize BNNTs selectively under control. Besides, the customizable growth by the calculation of flow model in COMSOL as well as surface treatment were achieved to further reduce the hydro-resistance. This study exhibits the predictability and controllability of BNNTs growth in customizable microstructures.

1. Introduction

Owing to the outstanding physical and chemical properties, boron nitride nanotubes (BNNTs) have been at the forefront of nanoscience, nanomaterials and nanotechnology research for decades [1]. BNNTs are similar to carbon nanotubes (CNTs), with III–V group elements B and N instead of C in the structure [2–3]. These two nanotubes both possess superhydrophobicity as micro scale on length and nano scale on diameter [4–6]. For microscale and nanoscale structures, the characterization of superhydrophobicity of these materials always inspires the fabrication of novel advanced interfaces. For instance, in the flow field of direct methanol fuel cell (DMFC), superhydrophobic coatings on the micro channels of anode plates could effectively reduce the adhesion of water. This is beneficial for CO_2 to be released, and enhance fuel efficiency [7]. As previously reported, superhydrophobic anode plates of DMFC have been produced by several methods, such as chemical etching, functional group grafting or coating treatments [8,9]. However, these methods would dramatically affect the electrical properties of anode plates. Besides, the strength of coating layers, which are used under high temperature and certain flow impact pressure in DMFC, is quite challenging. BNNT films prepared directly on the stainless steel substrates with superhydrophobicity have been confirmed to be excellent coating layers with intensive strength [10,11]. In this paper, we introduce a customizable local superhydrophobic micro channels by BNNT growth to satisfy the special requests in DMFC. Specially, the superhydrophobic BNNT films with high density and quality was controllable achieved on the side walls of flow channels by enhanced roughness as well as local B ink solution method, while the anode planes without BNNTs kept the original electrical properties. In addition, BNNT films with chemical inertness could also build up erosion resistant coatings for anode flow field.

2. Experiment

Both ball milling and annealing processes were carried out to synthesize BNNT films. Amorphous boron powder (B, 99%) and ferric nitrate ($Fe(NO_3)_3$, 98.5%) were used as staring material and catalyst for ball milling process, respectively. The weight ratio of balls to B powder to $Fe(NO_3)_3$ was 80:1:0.08, together with nitrogen (N_2) at a sealed pressure of 50 kPa. This process was conducted at room temperature. The high active mixed powder after ball milling was then dispersed into ethanol solution to form B ink solution. The channels of anode plates were local controllable painted with B ink solution, and followed by annealing process. The requested temperature for this process was 1100 °C, with nitrogen source gas N_2/H_2 (15%) for 1 h.

3. Characterization methods

The morphologies of raw materials and annealed samples were investigated by a scanning electron microscope (SEM, Tescan VEGA 3 SBH) and a transmission electron microscope (TEM, JEOL). The chemical elements were confirmed by an energy dispersive X-ray spectroscopy (EDX, NORAN system 7). The scanning tunneling

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microscope (STM, Being BY1000) was employed to examine the roughness and the morphology of anode plates. The wettability of films was measured by contact angle system (CA, Powereach JC2000C1). The flow mode of annealing process was performed by theoretical simulation in COMSOL Multiphysics.

4. Results and discussion

Fig. 1a,b shows TEM and SEM images of a typical product after the heating of the milled powder in mixed nitrogen source atmosphere under 1100 °C. The high density of cylindrical BNNTs synthesis using milling-assisted method was reported in our previous paper [10]. Here, milled B as precursor and $Fe(NO_3)_3$ as catalyst were used instead of raw B and Li_2O to synthesis BNNTs. The local B ink solution method was used to achieve controllable location growth. Fig. 1a shows that the BNNTs are bamboo structures with diameter from 40 nm to 80 nm range. The arrow in Fig. 1a means Fe particles on the tip of tube [12]. This can be explained by vapor–liquid–solid(VLS) mechanism of nanotube growth [13]. The high yield of BNNT film could be identified in Fig. 1b. The side wall of micro channel where B ink painted was covered by BNNTs. The length of nanotubes could beyond 5 micrometers on average.

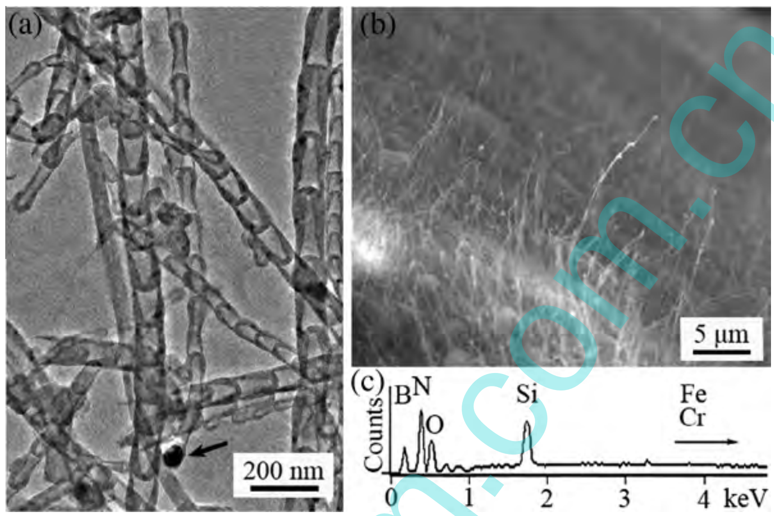

Fig. 1. TEM image (a), SEM image (b) and EDX spectrum (c) of BNNTs. The BNNTs were synthesised by local B ink solution method on the side wall of micro channels.

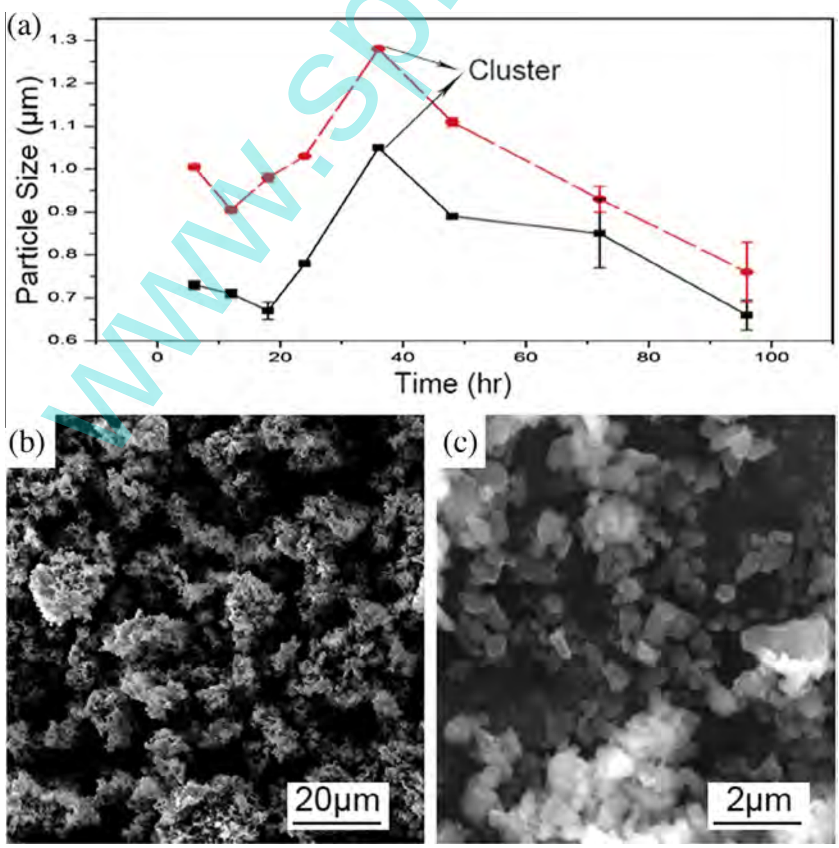

Fig. 2. (a) B particle size distribution curves under different ball milling parameters; (b) SEM image of unmilled B; (c) SEM image of milled B with 18 h.

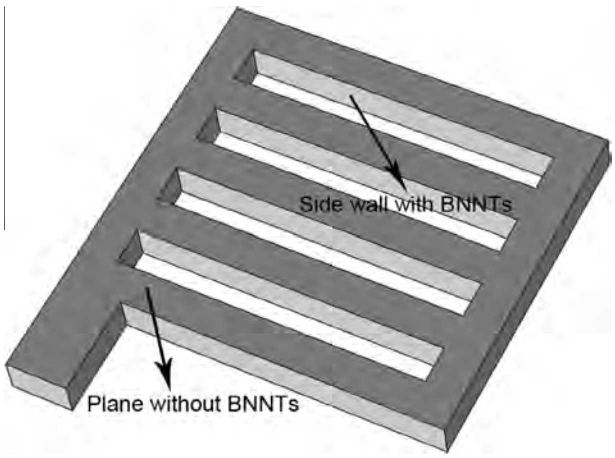

Fig. 3. Schematic design of customizable local superhydrophobic micro channels for DMFC anode plate.

The EDX result confirms that the sample consists of B (40% atoms percent) and N (39% atoms percent), along with O (under 10% atoms percent) and other metal impurities mainly from ball milling process as well as stainless steel anode planes. The proportion of B and N is consistent with structure of BNNTs, and the oxygen impurity is reasonable by annealing method from air during operation. Because of local ink of sample, part of uncovered substrate may affect the result of EDX, which shows higher Si, Fe, Cr etc. compared to previous results in our paper before [14]. In the following CA measurements, results present that the impurities did not impact hydrophobic properties of BNNTs, thus the composition of impurities could be neglected in this condition.

The ball milling assisted with B ink annealing method was used to synthesis BNNT films [15–17]. The ball milling aim to obtain fine B particles at nanoscale with increased surface area and chemical activity. In general, B particles could reduce to hundreds of nanometers. Fig. 2 shows the B particle size distribution curves under different ball milling parameters, indicating a dynamic process of ball milling. The solid line indicates B particle size as function of ball milling duration at 200 rpm while the dot line means milling at 300 rpm. The particle size continuously decreased with the increase of milling time to the minimum of 0.67 μm until 18 h at 200 rpm. With extended milling time, the attractive force between micro B particles would take the place of grind force as dominating force, forming agglomerations and resulting in observably increase in particle size. However, when B particle size came to certain degree, grind force would take over the leading role, deagglomerating the as-packed B particle, which in turn would reduce B particle size. The particle size distribution curve at 300 rpm illustrates similar results to certify the dynamic balance regularity. While it is also worth noting that the B particles milled at 200 rpm possess smaller size than that at 300 rpm. From the experimental results, high milling speed and long milling time seem to be more intensive, but do not guarantee the best outcome, since the optimum milling parameters require a reasonable milling speed and time in order to attain perfect B particles. In view of the above results, we milled B powder at 200 rpm for 18 h in the following experiments.

Fig. 3 illustrates the schematic design of customizable local superhydrophobic micro channels for DMFC anode plate, which was used as a substrate for BNNTs growth, and made of quality low-carbon stainless steel in the actual experiments. During the experiments, it was found that the yield of BNNTs on the side walls of channels could be improved by surface roughness treatment. The side walls were rubbed with fine sandpaper to achieve appropriate roughness where grow BNNTs (Fig. 4). It is supposed that certain roughness in nanoscale would increase reaction interface area, and thus more catalysts and B powder were seized on the side walls while the anode plate surface being smooth, and the attachment of these particles is difficult. It is also noteworthy that the roughness treatment should be controlled in nanoscale, since excessive roughening may deform the flow channels, which related to the efficiency of DMFC.

The annealing treatment is a crucial process to form final BNNT films products, and proper growth parameters would help the as-prepared samples possess a good performance. The velocity of N_2/H_2 (15%) gas in annealing process contributes significantly to BNNTs growth. The experimental results indicate that in terms of a small velocity magnitude, the provided nitrogen source is not sufficient for BNNTs growth due to the low dissolution and

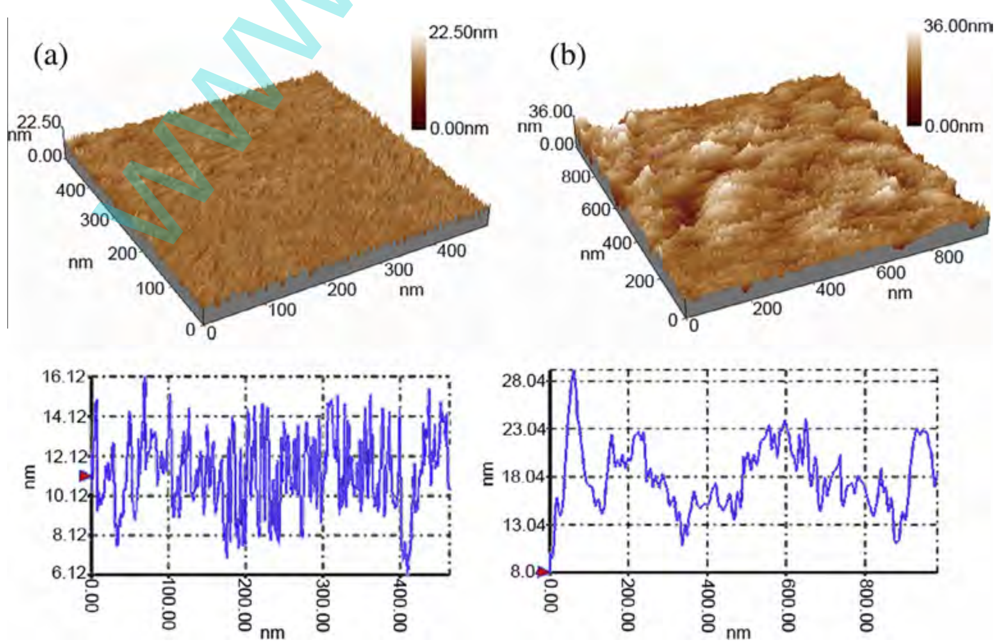

Fig. 4. STM images and profile analysis of (a) raw stainless steel channel and (b) stainless steel channel after roughening.

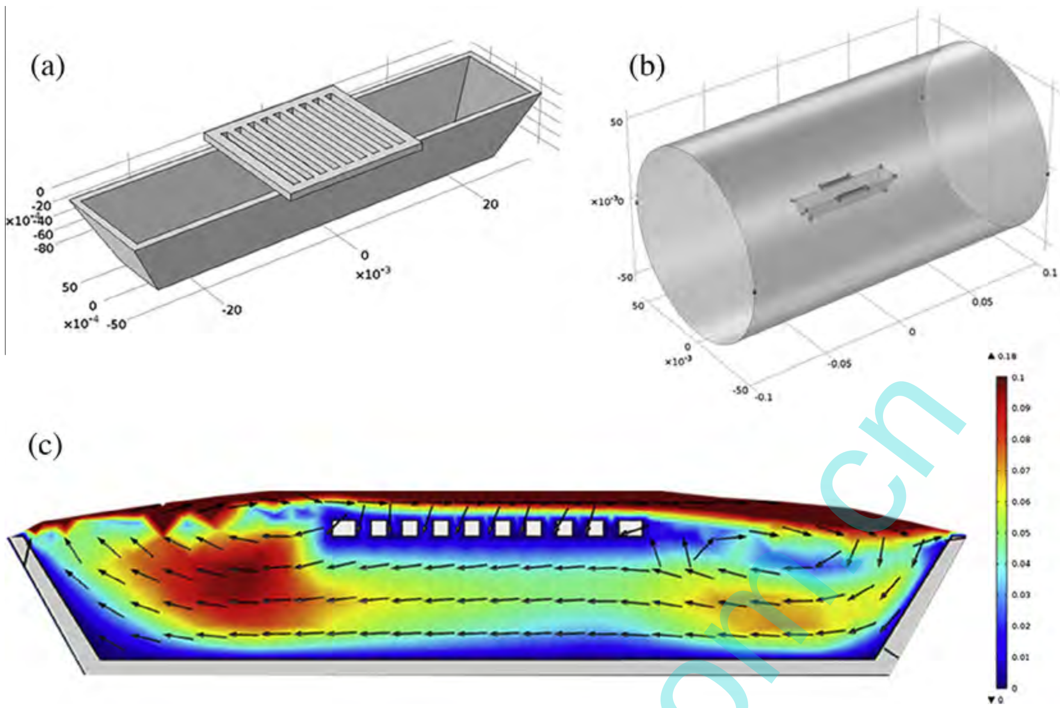

Fig. 5. COMSOL simulation with (a) a comb-substrate on the boat; (b) 3-D model; (c) velocity magnitude and direction on the cross section (inlet velocity: 0.2 m/s).

diffusion rates of reacting gases in catalysts, causing a low yield of BNNTs with short length. Meanwhile, as for a large one, no increased production was found. The redundant ingredient gases would take the defects on the walls of BNNTs as growth points for further secondary growth, leading to the formation of other morphologies BN materials, such as BN nanosheets. An appropriate velocity in the channels can not only make B particles in contact with reacting gases adequately, but also release the residual as well as the exhaust gases instantly. Here, the stationary laminary flow was modeled by finite element simulations in COMSOL Multiphysics to optimize the annealing process. The calculated model of a comb-substrate on the boat was first established in 3-dimension (Fig. 5a), and the boat was estimated right on the center of the horizontal furnace (Fig. 5b). This suspended boat could be realized in the actual experiments with assistant tools. The ratio of the length of furnace to that of boat is too large, and as a result, the turbulent flow at inlet would develop into a laminar flow when it flow into the center zone, for which the calculated model could be simplified by just cutting out the center zone. From the actual experiments, we could extract that 0.2 m/s of inlet velocity is evaluated to be the best for this model, and thus the perfect velocity for B react with N to form BNNTs is calculated to be 0.025 m/s.

The ethanol solution was introduced in annealing process, which served as a dispersant, ensuring a good dispersion of ball milled B powder and $Fe(NO_3)_3$ as well as an entire contact between reactants and catalysts. Besides, ethanol solution would volatilize rapidly in the heat process, leaving large quantities of pores in the mixed powder, resulting in a well contact even between the bottom powder on stainless steel substrates and the reacting gases. However, the velocity direction of reacting gases plays an important role in the enhancement of nitriding efficiency. As the pressure driven flow would slide from a smooth substrate, the velocity direction is in parallel with the substrate, making the gases get into the pores in difficulty. In regard to the substrate specially carved for DFMC, the pressure induces a circular flow, and the gases would go across the comb-substrate by channels in a special direction to form local turbulence instead of flowing above the surface (the arrows in Fig. 5c), which increases the yield to a large extent. This property guarantees the local BNNTs growth on the side walls of channels even when the B ink solution was painted all over the surfaces of plate, keeping the original electric property of native stainless steel, which is coincident with the experimental results.

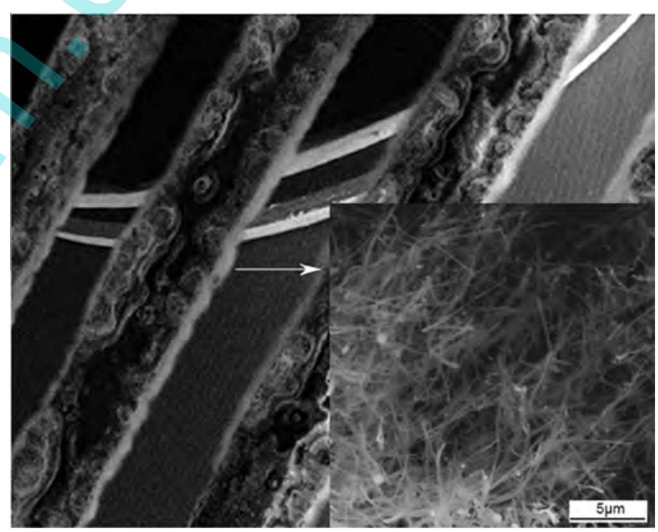

Fig. 6. SEM images of flow channel with local superhydrophobic BNNT film coated.

Fig. 6 presents that the quality of synthesized BNNTs on the side walls of flow channels is much better than that on anode plate surfaces. As previous literatures reported, BNNT films behave in a superhydrophobic manner [18–19]. However, for anode plate, this property is hard to verify due to the small gap between micro channels. Instead, we also prepared BNNT films on the uncarved anode stainless steel substrates by the same method, serving for the characterization of wetting properties on BNNT films.

Fig. 7a clearly shows the profile of a deionized water droplet on BNNT film. The contact angle was measured to be 154° on average,

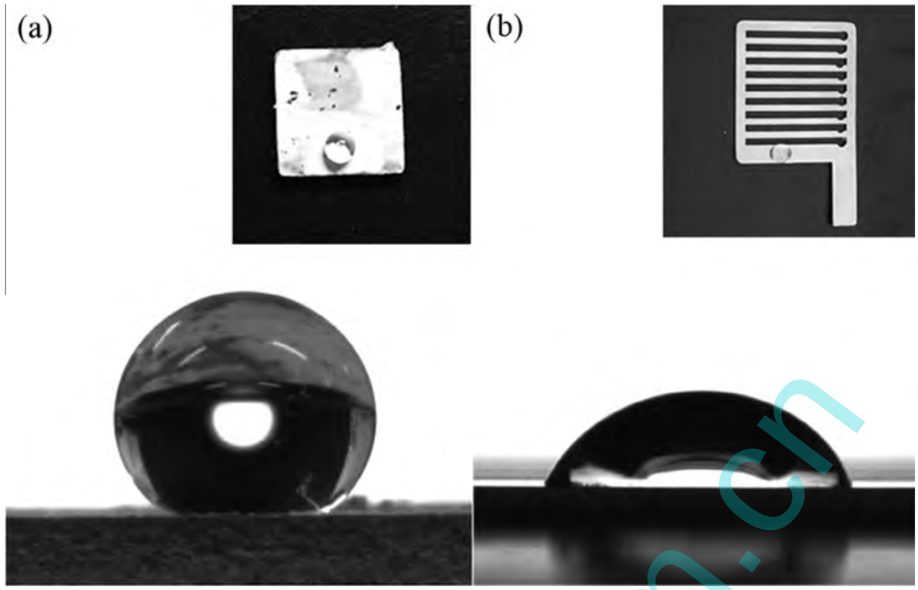

Fig. 7. Photographs of contact angles on BNNTs film (a) and uncovered anode substrate (b). The insets are top view of samples.

indicating the superhydrophobicity of BNNT films. In contrast, the anode stainless steel substrate presents hydrophilic without BNNTs covered (Fig. 7b). It should be notice that the droplets on uncovered substrates show a little lateral spreading due to the metal texturing, thus there are errors with quantitative measurement, but enough to indicate that hydrophilicity of the uncovered substrates.

The superhydrophobic BNNT films coating on anode plates would directly contact with flowing liquid solution, and thus the dynamic property of droplets on BNNT films is crucial to evaluate gas reduction performance. By the as-mentioned fabrication method, low adhesive force between walls and liquid of DMFC could be obtained, which guarantees a smooth flow of methanol solution without gas generation to a large extent. The check experiment was carried out by squeezing a suspended droplet set by a needle (a part of the contact angle system) to the film [20,21]. After removing the needle, the droplet barely stood on the film, only if it was large enough to be dictated by gravity, but yet was easily sliding off from the film, which reveals a low degree of adhesion between BNNT films and water droplets. As a consequence, the channels of DMFC anode plate which request local superhydrophobicity were achieved by BNNT films with high density and quality, and at the same time, the plate itself kept electric conductivity with only less BNNTs.

5. Conclusion

In summary, we demonstrate that local superhydrophobic BNNT films fabricated by ball milling assisted with B ink annealing are a high practical method to obtain customized microstructures. The synthesis of BNNTs exhibits predictability and controllability by calculation of flow model as well as ink pattern. With this method, the BNNT films are produced with high density and quality to achieve local superhydrophobic for certain requirements of different applications. An important fundamental result of flow model simulation in this study is that BNNTs growth in annealing process could be controlled by reacting gases flow. The design of turbulence in the gaps of micro structures induces a significant improvement of high yield BNNTs growth compared to laminar flow zone under the same operation. These results indicate that BNNTs are promising superhydrophobic nanomaterials, the work in this paper direct further and more investigations of practical applications of BNNTs in customizable microstructures.

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