ARC-ASSISTED CO-CONVERSION OF COAL-BASED CARBON AND ACETYLENE

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1. Introdcution

In the past decade, the design and synthesis of three-dimensional (3D) and well-ordered carbons in nano- or micro-meters have drawn much attention because of their potential uses in a wide range of fields [1-6]. It has been well established that the practical and potential applications of these nano- or micro-sized carbon materials depend greatly on their physical and chemical properties, which are closely related to their geometrical micro- and nano-structures as well as their chemical compositions, and these can be tailored by adopting different synthesis techniques and process parameters. Here, we report a novel micro-sized carbon with a spectacular morphology, which is different from the 3D carbon microstructures previously reported. To our knowledge, this kind of self-assembled 3D microcarbons has never been reported in literature.

2. Experimental

The fabrication of novel carbon microstructures was carried out in a conventional arc discharge reactor in a mixture gas of He and C_2H_2 (v:v=5:1). The anode used for arcing was a hollow carbon rod derived from coal that was filled with iron powders (120 μm in size). The weight ratio of iron powder to the hollow anode was *ca.* 5.0 wt%. The detailed process and conditions for making coal-derived carbon rods can be found elsewhere [7,8]. The cathode was a high purity graphite electrode, which was not consumed during the arcing process. The arc discharge experiments were conducted with a current of 50-60 A and a voltage of 40-50 V at 0.060-0.065 MPa. The arcing time was controlled for *ca.* 5-7 min, during which about half of the anode (*ca.* 5-6 cm) was consumed. After the arc discharge was finished, the remaining anode was taken out and examined by scanning electron microscope (SEM, JSM-5600LV).

3. Results and discussion

The SEM examination reveals that three types of carbon with different morphologies are formed on the surface of the residual anode, of which the growth section is schematically shown in Fig. 1. In section (I) that is close to the end of the consumed anode, carbon microtrees grown on the outer surface of the hollow anode are found, while in the middle section (II), a large amount of carbon fibres arrays are found. It is in section (III) near the root of the consumed anode that microcarbons with spectacular ball-like morphology, as shown at the right of Fig. 1, are found, and these ball-like carbons will be focused and discussed in this presentation.

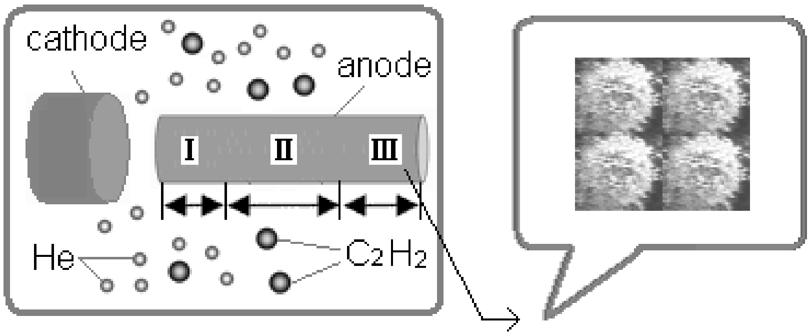

Fig. 1 Schematic illustration of arc-assisted CVD experiments for making novel micro-sized carbons.

Fig. 2 shows typical SEM images of these novel ball-like micro-carbons that look like swabs made of loose cotton wool. From Fig. 2a it can be seen that this new class of micro-carbons is quite uniform in size that varies in a range of 100-150 μm and well aligns in high density on the outer surface of the remaining coal-derived carbon anode. Fig. 2b shows a high-magnification SEM image of one fluffy carbon ball that is randomly selected from Fig. 2a, from which it can be clearly seen that these well-patterned spherical carbons consist of numerous curly carbon fibres that entangle with each other and randomly stretch out along various directions. Obviously, these soft carbon balls have a perfect centrosymmetric structure, implying that their growth process may be a dynamically controlled one. In addition, it is interesting to note that some straight tree-like microcarbons consisting of curly carbon fibres are also formed, as shown in Fig. 2c, which have a hollow core and look like a soft carbon microball being stretched by an unknown force. These tree-like carbons are *ca.* 800 μm long and have a diameter of *ca.* 200 μm. It should be noted that the tree-like carbon also has an obvious perfect centrosymmetric structure, *i.e.* an axis-symmetric structure, which leads one to speculate that the growth of these tree-like microcarbons may follow the same scheme as those spherical ones, and very likely, part of the soft carbon balls might function as the starting building units for these stretched-microcarbons as shown in Fig. 2c. In Fig. 2a the white arrows point to two vertical tree-like microcarbons that are similar to those two shown in Fig. 2c, of which only the top end can be seen simply because they are perpendicular to the outer surface of the anode. Further SEM studies at higher magnification reveal that both ball-like and tree-like soft carbons are made of entangled fibre-like carbons with quite uniform diameters that vary from 1.2 μm to1.5 μm, as shown in Fig. 2d, of which the morphologies are, to some degree, similar to the morphologies of some deep-sea fauna.

The novel micro-sized carbons are also characterized using energy dispersive X-ray spectrum (EDS), which shows that carbon is the only element in these novel carbons.

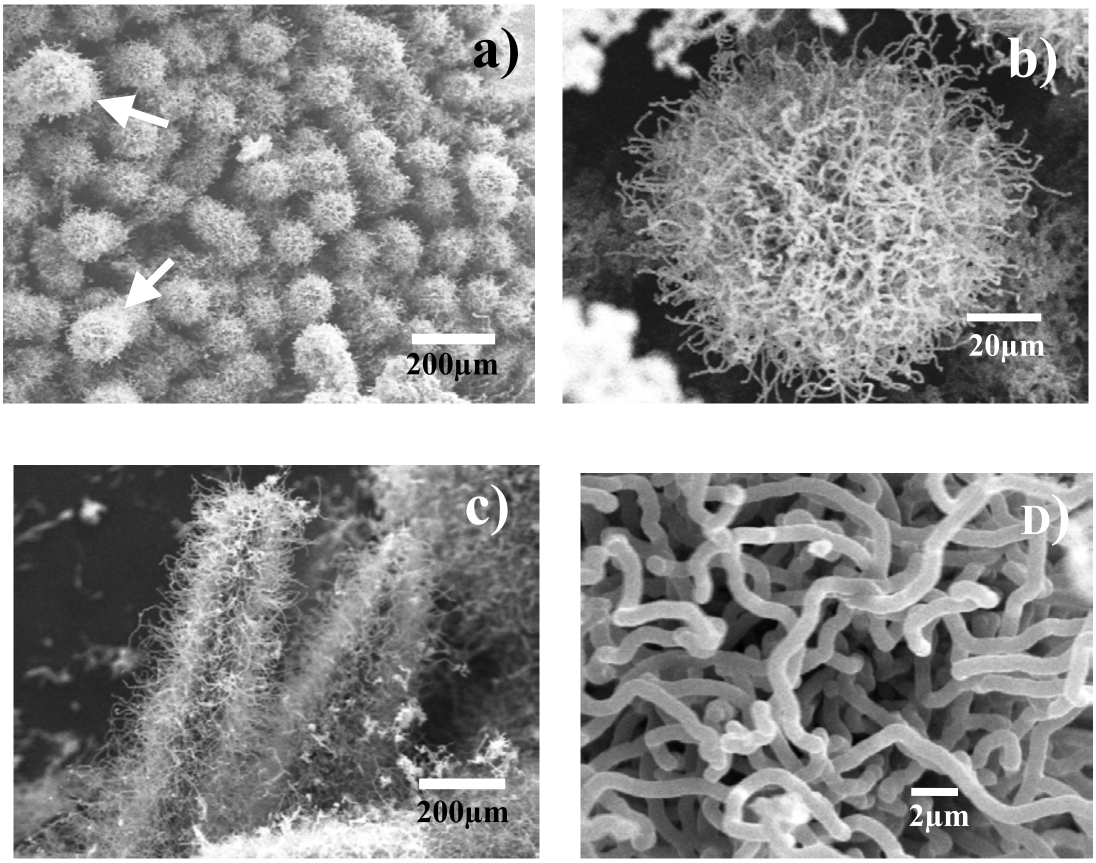

Fig. 2 SEM images of novel microcarbons with two types of spectacular morphologies; a) low-magnification SEM image of spherical microcarbons, showing they are quite uniform in diameter and in a well-ordered pattern; b) high-magnification SEM image of a typical fluffy carbon microball with a diameter of *ca.* 100 μm; c) SEM image of two straight rod-like microcarbons consisting of curly carbon fibres, which seems to have a hollow core and looks like a soft carbon microball being stretched out by an unknown force; d) High-magnification SEM image of soft carbon balls, showing that the carbon balls consist of microsized worm-like curly carbon fibres with a tidy surface.

X-ray diffraction (XRD) studies of these novel microcarbons are also conducted and the typical XRD pattern is shown in Fig. 3, in which two diffraction peaks corresponding to graphite can be clearly seen in a region of $5^{o}<2\theta<80^{o}$, and these two peaks can be assigned to graphite (002) and (100), indicating the presence of graphitic crystallite. It is surprising to note that besides the peaks corresponding to graphite, no other signals are detected in the XRD pattern, this means that the obtained microcarbons are pure carbon materials, which is in good agreement with the EDS results.

At this moment, the formation mechanism of this novel form of microcarbons is not clear. We have made a number of similar experiments with and without iron catalysts or with graphite electrode as anode instead of coal-derived rods with an aim of working out the mechanism involved in the formation process, and found no such novel microcarbons without catalyst or with graphite as anode. This clearly implies that for the growth of these novel carbon microstructures, the coal-derived carbon anode plays a key role. In other words, the formation of these novel microcarbons is closely related to the chemical and/or physical properties of the coal-based hollow carbon rods that were originally made for preparing carbon membranes, on the surface of which there exist numerous micro-sized pores. In the presence of iron catalyst, the coal-based hollow anode might function as a template for the growth of microcarbons in a well-oriented and patterned way, which is similar, to some degree, to the method widely used for preparing carbon nanotubes arrays from hydrocarbons by chemical vapour deposition (CVD) [1]. In our case, the acetylene in the reaction system might be activated by the arc plasma and then take part in the formation reactions of the microcarbons, in which the active species or precursors released from the vaporization of coal-based carbon rods might also get involved. Because of this, it may be appropriate to term this approach as arc-plasma assisted CVD method.

This kind of microcarbon materials reported here might be of potential application in adsorption, catalysis and composite because of their unique and uniform symmetric structure. The work is in progress now with an aim of exploring the potential applications of these novel microcarbons.

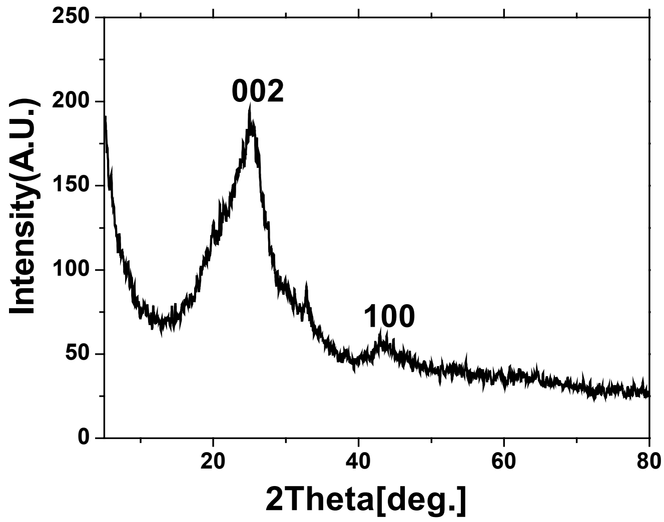

Fig. 3 A typical XRD pattern of the as-prepared micro-sized worm-like and curly carbon fibres.

4. Conclusions

We have demonstrated that micro-sized novel carbons consisting of curly carbon microfibres have been successfully prepared from a mixture gas of acetylene and helium via an arc-discharge assisted CVD process. Furthermore, this arc-plasma assisted CVD approach needs to be further explored and extended to prepare other well-patterned carbon materials.

Acknowledgments

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