

## Soft-templated Synthesis of Carbon Micron-Buds

Jiangtao Li\*, Ruijuan Song, Jingjing. Li, Pengna Li, Liuchang Wang, Yuan Jia, Limei Song and Xiaohui Yang

The Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, School of Chemical Engineering, Xi'an University, Xi'an, 710065 China.

**\*Correspondence:**

Jiangtao Li, The Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, School of Chemical Engineering, Xi'an University, Xi'an, 710065 China, E-mail: lijiantao-968@126.com.

Received: 02 October 2018; Accepted: 20 October 2018

**Citation:** Jiangtao Li, Ruijuan Song, Jingjing. Li, et al. Soft-templated Synthesis of Carbon Micron-Buds. Chem Pharm Res. 2018; 1(1): 1-3.

**ABSTRACT**

Using coal tar pitch based amphiphilic carbonaceous materials (ACMs) as the precursor and amphiphilic triblock copolymer F127 as the only soft template, hollow Carbon Micro-Buds (CMBs) were synthesized. The concentration of F127, cF, and the mass ratio of F127 to ACM, r, are the key parameters of controlling the shape of the as-prepared products. CMBs with diameters of about 1  $\mu\text{m}$  were prepared under the condition of  $c_i = 53.4 \text{ g/L}$  and  $r = 2$ . CMBs were amorphous materials.

**Keywords**

Triblock copolymer Plutonic F127, Soft-templated, Carbon Micron-Buds.

**Introduction**

Oxidized carbonaceous materials, which are called amphiphilic carbonaceous materials (ACMs), can be dissolved in basic aqueous solution and some polar organic solvents and then form carbonaceous gel easily [1]. The raw materials of ACMs are cheap, including mesophase pitch, coal tar pitch, petroleum green coke, green needle coke and so on [2]. Due to their amphiphilic property, ACMs have been used for the preparation of hollow carbon microbeads [3], ultrafine carbon powders [4], amorphous carbon nanoparticles [5], Ti(C, N, O) nanoparticles [6], vesicular carbon with mesopores of 2-4 nm in width [7], mesoporous carbon particles [8] and carbon aerogels [9]. Although most of the mesopores of these porous materials are disordered, it is a simple and inexpensive approach to use ACMs as the precursor of carbon spheres and porous carbons, which have been expected to find extensive applications in catalysis, adsorption and electric conductive materials [8,10].

For the preparation of carbon materials with ordered mesopores, amphiphilic triblock copolymer Plutonic F127 has been used as the typical soft template coupled with mesoporous  $\text{SiO}_2$  as the hard template [11-15], or only the hard template, KIT-5, is used [16-19]. It is worthy of note that mesoporous carbon materials have not

been prepared if only P123 is used [20]. Here, we develop a facile procedure for synthesizing CMBs, using F127 as the only template and ACMs as the precursor.

**Experimental  
Synthesis of CMBs**

Coal tar pitch were purchased from the Wuhan Steel Co., Ltd. in China. ILs was purchased from Nanjing Will Co., Ltd. in China. ACMs were synthesized by oxidation of coal tar pitch with the mixture of concentrated nitric acid and sulfuric acid (v/v = 3/7) at 30°C. The details of this preparation have been described in earlier report [21]. In a typical synthesis, F127 (53.4 g/L in terms of the concentration of F127, cF) and ACM (the mass ratio of F127 to ACM is 2) were added to 150 ml of solution of aqueous ammonia and stirred until dissolution at 30°C, followed by a stirring for 3 h and the addition of 10 ml of ethanol under stirring. Subsequently, the solution was aged at 90°C for 24 hrs and filtrated. The residue was dried at 100°C in a vacuum drying device and the resulting mixture of F127 and ACM was denoted as F-ACM. The heating rate of carbonizing the mixture of F127 and ACM is 1°C /min before 450°C and 3°C /min afterward. After carbonized at 800°C for 6h under  $\text{N}_2$  flow, the carbonized products were obtained and denoted as CMBs.

**Material characterization**

The morphology and the structure of CMBs were examined by high resolution transmission electron microscopy (TEM, JEOL

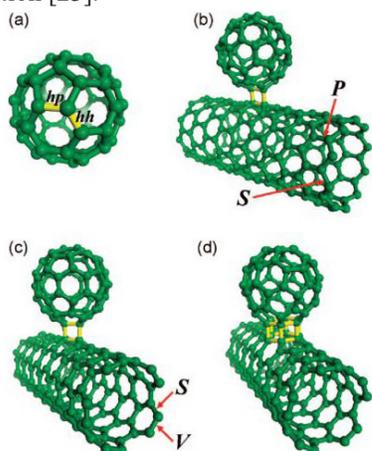
JEM3010, operated at 160 kV) and field emission scanning electron microscopy (FESEM, 6700F, operated at 5 kV).

## Results and Discussion

### Formation mechanism of CMBs

ACM molecules and F127 micelles can form ordered lyotropic liquid crystals via S010 multiple hydrogen bonding interactions in solution of aqueous ammonia, in which the hydroxyl groups on ACM are hydrogen donors and the hydrophilic group on F127 are hydrogen bonding acceptor. The macroscopic morphologies of ordered lyotropic liquid crystals are various, depending on the stacking of the micelles of F127 [22]. The CMBs were synthesized from sphere and cylinder.

In the covalent bonding between  $C_{60}$  and a SWCNT, our DFT computation shows that a single C-C covalent bond between  $C_{60}$  and the SWCNT is unstable and can spontaneously break. At least two C-C covalent bonds are required via the cycloaddition reaction to stabilize the CNB (Figure 1b). Two possible ways for the cycloaddition reaction were considered: (1) a pair of parallel C-C bonds form a quadrilateral ring, namely, the [2+2] cycloaddition (Figure 1b,c), and (2) a hexagonal face of  $C_{60}$  and a hexagonal ring in the SWCNT are connected together to form six C-C covalent bonds, namely, the [6+6] cycloaddition (Figure 1d). It is well-known that there exist two types of C-C bonds in  $C_{60}$  fullerene, one between two hexagonal faces and another between the hexagonal and pentagonal faces (labeled as the hh and hp bond in Figure 1a, respectively). Also, two types of C-C bonds can be seen in the SWCNT, characterized by the angle between the C-C bond and the tube axis. Among the C-C bonds, 1/3 are either normal (labeled as V) or parallel (labeled as P) to the tube axis in the armchair or zigzag SWCNT, while the remaining 2/3 form a sharp angle with the tube axis (labeled S), as shown in Figure 1b,c. In total, eight possible  $C_{60}$ /SWCNT configurations are available for the [2+2] cycloaddition and two  $C_{60}$ /SWCNT configurations for the [6+6] cycloaddition. We have performed full geometric optimization for all 10 possible  $C_{60}$ /SWCNT configurations. The resulting 10 CNB structures are all stable. The covalent bonding between  $C_{60}$  and SWCNT induces a local distortion of the SWCNT surface where some carbon atoms of the SWCNT are pulled outward from the original wall surface and their bonding is transformed from  $sp^2$ - to  $sp^3$ -hybridization [23].



### Morphologies of carbonized products

SEM images of CMBs is presented in Figure 2 consists of irregular MicronBuds and carbon tube of micronsize. These tubes are composed of primary particles connecting to each other after the formation of carbon gel. After carbonization, the diameter of CBMs is about 1  $\mu$ m.

Scanning electron microscopy (SEM) images of the product at low magnifications suggest that most synthesized CMBs have an 'amorphous particles' and carbon tube (Figure 2a-c). However, careful investigations reveal that much of the particles in fact consists of fullerenes. Their spherical nature has been confirmed by tilting samples within a TEM (Figure 2d). carbon spheres have non-uniform diameter of lower 500 nm.

It is known that non-covalently attached fullerenes are highly mobile on the surface of fibers under exposure to a TEM beam [23], but our TEM observations showed CMBs to be stationary, indicating strong bonding. In order to further examine the nature of the CMBs bond, we attempted both to evaporate and to dissolve the MicronBuds from the surface of the carbon tube. Thermal treatment of the samples at 300-700°C in inert helium or argon/hydrogen atmospheres showed no changes in the observed CMBs structures (Figure 2c). Careful washing of the CMBs in various solvents (hexane, toluene and decaline) also did not result in any significant alteration of the examined samples. Moreover, a mass-spectrometric investigation of the solvent after MicronBuds-carbon tube washing did not reveal the presence of any dissolved MicronBuds, further indicating a strong interaction between the MicronBuds and carbon tube.

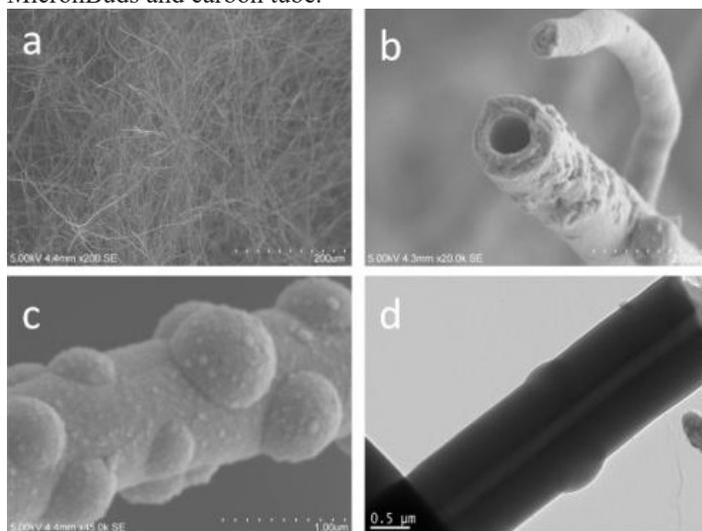


Figure 2: SEM and TEM images of samples.

### Conclusion

We have synthesized CMBs using coal tar pitch based ACM as the precursor and F127 as the soft template. The shape of the as-prepared products can be controlled by tuning the F127 concentration and the mass ratio of F127 to ACM. MicronBuds with diameter of 150-500 nm were obtained when the mass ratio of F127 to ACM is 2 and the F127 concentration is 53.4 g/L. During

the immediate carbonization of F127/ACM aggregates, ordered mesopores structure within the carbon skeleton was destroyed, due to the crosslinking reaction and decomposition of functional groups.

### Acknowledgment

This work was financially supported by the National Science Foundation of China (No. 21706209), The Industria Research Project of Science and Technology, Department of Shaanxi Province (No. 2017GY-126).

### References

1. Esumi K, Takahashi S, Sugii H, et al. Characterization of organo-carbonaceous gel. *Carbon*. 1993; 31: 1303-1306.
2. Li XK, Liu L, Shen SHD. The influence of starting materials on the structure of ultrafine carbon powders. *Carbon*. 2001; 39: 2335-2338.
3. Esumi k, Eshima Y, Murakami H, et al. Preparation of hollow carbon-microbeads from water-in-oil emulsion using amphiphilic carbonaceous material. *Colloids Surf*. 1996; 108: 113-116.
4. Li XK, Liu L, Shen SHD. Structure of ultrafine carbon powders prepared using a carbonaceous gel. *Carbon*. 2001; 39: 1431-1433.
5. Wu WZ, Zhu ZP, Liu ZY. Amorphous carbon nano-particles prepared by explosion of nitrated pitch. *Carbon*. 2002; 40: 2034-2037.
6. Li XK, Liu L, Sh Ge, et al. The preparation of Ti(C,N,O) nanoparticles using binary carbonaceous titania aerogel. *Carbon*. 2001; 39: 827-833.
7. Li ZJ, Yan WF, Dai S. A novel vesicular carbon synthesized using amphiphilic carbonaceous material and micelle templating approach. *Carbon*. 2004; 42: 767-770.
8. Wang J, Chen MM, Wang CY, et al. Preparation of mesoporous carbons from amphiphilic carbonaceous material for high-performance electric double-layer capacitors. *J Power Sources*. 2011; 196: 550-558.
9. Wang JZ, Chen MM, Wang CY, et al. A facile method to prepare carbon aerogels from amphiphilic carbon material. *Mate Lett*. 2012; 68: 446-449.
10. Esumi K, Onoa R, Sugiia O, et al. Catalytic property of platinum-dispersed carbon prepared using amphiphilic carbonaceous material. *Colloids Surf A*. 1995; 94: 93-96.
11. Li JS, Li HJ, Zhu Y, et al. Dual roles of amphiphilic triblock copolymer P123 in synthesis of  $\alpha$ -Fe nanoparticle/ordered mesoporous silica composites. *Appl Surf Sci*. 2011; 258: 657-661.
12. Li LX, Zou LD, Song HH, et al. Ordered mesoporous carbons synthesized by a modified sol-gel process for electrosorptive removal of sodium chloride. *Carbon*. 2009; 47: 775-781.
13. Wang XX, Li TH, Ji YB, et al. Synthesis and characteristics of continuous mesoporous carbon films by a rapid solvent evaporation method. *Appl Surf Sci*. 2008; 255: 1719-1725.
14. Li LX, Song HH, Chen XH. Pore characteristics and electrochemical performance of ordered mesoporous carbons for electric double-layer capacitors. *Electrochim Acta*. 2006; 51: 5715-5720.
15. Liu N, Song HH, Chen XH, et al. Synthesis of spheroidal ordered mesoporous carbon materials from silica/P123/butanol composites. *Mater Chem Phys*. 2011; 130: 1016-1021.
16. Sang LC, Vinu A, Coppens MO. Ordered mesoporous carbon with tunable, unusually large pore size and well-controlled particle morphology. *J Mater Chem*. 2011; 21: 7410-7417.
17. Xia YD, Mokaya R. Synthesis of ordered mesoporous carbon and nitrogen-doped carbon materials with graphitic pore walls via a simple chemical vapor deposition method. *Adv Mater*. 2004; 16: 1553-1558.
18. Ignat M, Oers CJV, Vernimmen J, et al. Textural property tuning of ordered mesoporous carbon obtained by glycerol conversion using SBA-15 silica as template. *Carbon*. 2010; 48: 1609-1618.
19. Kim TW, Park IS, Ryoo R. A synthetic route to ordered mesoporous carbon materials with graphitic pore walls. *Angew Chem*. 2003; 115: 4511-4515.
20. Yan Y, Yang HF, Zhang FQ, et al. Low-temperature solution synthesis of carbon nanoparticles, onions and nanoropes by the assembly of aromatic molecules. *Carbon*. 2007; 45: 2209-2216.
21. Cheng YL, Li TH, Li FJ, et al. Preparation and characterization of pitch-based carbon nanospheres. *J Coal Sci Eng (Chin)*. 2010; 35: 490-493.
22. Nooney RI, Thirunavukkarasu D, Chen Y, et al. Synthesis of nanoscale mesoporous silica spheres with controlled particle size. *Chem Mater*. 2002; 14: 4721-4728.
23. Smith BW, Luzzi DE. Formation mechanism of fullerene peapods and coaxial tubes: a path to large scale synthesis. *Chem Phys Lett*. 2000; 321: 169-174.