Preparation of polyacrylonitrile based carbon nanofibers by electrospinning with different additives from direct coal liquefaction residue

Tongxin Qiao, Haoxing Wang, Yingjie Yang, Xiangna Lu, Guixia Fan, and Peng Li*

School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China
*Corresponding author’s e-mail: lipeng1987040@126.com

Abstract. Direct coal liquefaction residue is of valuable materials for preparation of carbon materials due to its high carbon content and aromatic structures. In this work, extract, extraction residue, and oxidized extraction residue from direct coal liquefaction residue were employed as additives for preparation of polyacrylonitrile based carbon nanofibers by electrospinning, followed by air stabilization and carbonization processes. The results show that the additives were evenly dispersed in the carbon nanofibers, and the diameters of nanofibers were smaller than that pure polyacrylonitrile based carbon nanofibers. After the extraction residue was pre-treated with hydrogen peroxide, the morphology of nanofibers became more smooth and uniform.

1. Introduction
Direct coal liquefaction residue (DCLR), a coal by-product but also a valuable carbon resource from direct coal liquefaction process [1], is of high carbon content and rich in condensed and heteroatom-containing aromatic structures. Direct utilization of CLR was investigated by gasification [2] and combustion [3]. However, high ash and sulphur content in CLR is considered as the precursors of environmental contaminator when CLR was used directly as fuels. For example, the nitrogen and sulfur are emitted as relevant oxides (NOx and SOx) during coal combustion, causing serious environmental pollutions [4]. The mineral materials in CLR would be transferred into the atmosphere as the toxic substance or hazardous particles during combustion, such as fine particular matter (PM2.5), causing serious health problem [5, 6]. Therefore, efficiently and environmental friendly utilization of the direct coal liquefaction residue from direct coal liquefaction process is an important research topic. The DCLR can be used as raw materials for acquiring valuable polycyclic aromatic hydrocarbons (PAHs) [7, 8], and it was also a good precursor for preparation of carbon materials, such as carbon microfiber [9], mesoporous carbons [10], carbon nanofibers/carbon foam monolithic composite [11], hierarchical porous carbons [12].

Electrospinning is one of the efficient approaches to prepare nanofiber materials, due to the wide source of raw materials, simple operation process and low cost [13]. Mooste [14] et al. reported that non-precious metal cathode catalysts prepared from polyacrylonitrile (PAN) based composite fibers have great advantages in low-temperature fuel cell applications. Jayawickramage [15] investigated the mixture of PAN and lignin for preparation of carbon nanofiber by electrospinning. It was concluded that heat and activation treatments can exhibit strong specific surface area, electrical conductivity and mesoporosity of nanofibers. Moreover, good performance of the nanofibers was also detected when it was used as the supercapacitor electrode.
In this work, we prepared the spinning solution by adding the modified direct coal liquefaction residue as the additives to PAN for electrospinning, to achieve the efficient utilization of coal liquefaction residue, and also provide a reference for decreasing the cost of PAN based carbon nanofibers.

2. Experiment

2.1 Materials
The DCLR was obtained by liquefying Shenmu-Fugu subbituminous coal at 455 °C under 19 MPa of hydrogen in a pilot-scale direct coal liquefaction unit operated by Shenhua Group Corporation Ltd., China. It was pulverized to < 74 μm followed by desiccation in a vacuum at 80 °C for 24 h prior to use. The DCLR was conducted into a Soxhlet extractor, followed by solvent extraction with isometric acetone/CS₂ mixed solvent, to afford the extract (E) and extraction residue (ER). The ER was oxidized by using hydrogen peroxide at 40 °C for 6 h, followed by filter and dried, to prepare oxidized ER (OER). All the reagents used in the experiments are analytical grade, and all the organic solvents were distilled with a Büchi R-300 rotary evaporator prior to use.

2.2 Preparation of carbon nanofibers
The PAN (2 g) with none additive was ultrasonically dissolved in 20 mL of N,N-dimethylformamide (DMF) to afford the spinning solution labelled as P-N. Then PAN (1.8 g) with additive of E (0.2 g), ER (0.2 g), and OER (0.2 g) from DCLR were also separately dissolved in DMF (20 mL), to afford the spinning solutions labelled as P-E, P-ER, and P-OER, respectively. The mass ratio of additive to PAN is 1/9. Then, 5 mL of the solution was transformed into a syringe with a needle diameter of 0.5 mm. The solution was spun into nanofibers through a positively charged needle by using an electrospinning apparatus at 18 kV and a negatively charged aluminum foil at -3.00 kV to collect the fibers with a spinning distance of 15 cm, injection speed of 0.1 mm/min, and room temperature. The carbon nanofibers precursors were collected from the aluminum foil, then placed in an air atmosphere at the heating rate of 2 °C/min up to 250 °C, holding for 1 h. Finally, carbon nanofibers were obtained by carbonizing at 450 °C for 2 h under Ar.

The surface of the carbon nanofibers and their precursors were characterized by a Nova Nano SEM450 Ultrasonic Field Emission Scanning Electron Microscope (SEM) provided by FEI.

3. Results and discussion

3.1 SEM analysis of carbon nanofibers and their precursors

As shown in Table 1 and SEM images of P-N, P-E, P-ER, and P-OER in Figure 1, it is clear that the pristine carbon nanofibers show regular fibrous morphology with diameters mostly in the range of 251.8-426.9 nm, by adding E, ER, and OER from DCLR as additives in to PAN. Carbon nanofibers precursors with smaller diameters were obtained by adding E and OER, but larger diameters by adding ER. That is because both of the E and OER were well dissolved in DMF as well as PAN to form a homogeneous solution, thereby having good spinnability during electrospinning. The ER from DCLR has larger average molecular mass and poor solubility in DMF. In contrast to the P-ER, the diameters of the nanofibers of P-OER were more uniform, indicating that oxidation can improve the spinnability of ER with PAN.
As displayed in Table 1 and Figure 2, the surface of the nanofibers became more smooth after carbonization treatment, and the diameters of the carbon nanofibers were also reduced. The diameter of carbon nanofibers has smaller diameters with additives than that pure PAN. Carbon nanofibers with smaller diameter and more smooth surface were prepared with additive of E than that of ER. The P-ER had the smallest average diameter and most regular fibrous morphology than the others, indicating the oxidation treatment shows positive effect on the morphology and diameter of carbon nanofibers.

3.2 Raman spectroscopy analysis of carbon nanofibers

| Sample | $D$ peak (cm$^{-1}$) | $G$ peak (cm$^{-1}$) | $2D$ peak (cm$^{-1}$) | $I_D/I_G$ |
|--------|---------------------|---------------------|---------------------|-----------|
| PA     | 1360                | 1581                | 2725                | 1.1227    |
| PC-R   | 1359                | 1574                | 2720                | 1.0963    |
| PC-O   | 1356                | 1578                | 2718                | 1.0715    |
| PC-E   | 1360                | 1584                | 2719                | 1.0486    |
According to the Raman spectroscopy fitting analysis, the Raman spectrograms and $I_D/I_G$ values of P-N, P-E, P-ER, and P-OER were illustrated in Table 2 and Figure 3. After incorporating the modified raw materials, the graphitized degree of carbon nanofibers is significantly improved. There are two possible reasons: one is that participation of modified raw materials reduces the proportion of carbon atoms in the disordered structure. The other is that some components in the modified raw materials promoted the high-temperature carbonization process. In addition, the appearance of 2D peak indicates that graphene exists in the nanofibers after carbonization.

4. Conclusions

The E, ER, and OER from DCLR were successfully added into the PAN, thereby forming the uniform nanofibers. Adding DCLR’s components into PAN as additives can obviously improve the morphology of carbon nanofibers, and the oxidation treatment provided positive effect on the morphology and diameter of carbon nanofibers.

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