

Preparation of porous carbon fibres : A review

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Abstract. Porous carbon fibres(PCF) was extensively applied to energy storage, environment pollution control and healthcare due to their superior electrical conductivity, diverse aperture,high specific surface area and super electrochemical stability.This paper reviewed the methods of preparing porous carbon fibres.The preparing PCF technology mainly included template methods(hard templates,soft templates, dual-templates), electrospinning technology and polymer blend technology. The working principles of different pore-forming techniques were summarized.The contributions of different preparation techniques to improve material properties such as electrochemical properties,adsorption performance,drug sustained-release materials and catalytic activity in practical applications were described.The different preparation methods had their superiorities and places needed improving.It was proposed that develop more advanced template methods to prepare PCF with reasonable cost, zero environmental pollution, high efficiency and easy removal.

Keywords:Porous carbon fibres;Template methods; electrospinning technology; Polymer blend technology

1. Introduction

Porous carbon fibres (PCF) were synthesized by activation and carbonization of organic precursor fibres. It was the third generation of carbon adsorption materials after powdered activated carbon and granular activated carbon. Porous carbon fibres with well-developed pores, superior thermodynamic and chemical stabilities, favorable ability to conduct electric, stabilized physical and chemical properties and tunable microstructures played a significant role in energy storage and environmental pollution control. The fiber shape of PCF made it easier to treat than powdered or granular activated carbon. Compared with activated carbon, PCF fiber had diminutive diameter, great specific surface area, huge contact area with the adsorbed matter, and large amount of adsorption. The adsorption quantity of PCF fiber was about 10 times than activated carbon, and simultaneously showed the excellent adsorption property in low concentration of gas. The nanopores were divided into three classes, macropores (pore diameter $> 50\text{nm}$), mesopores ($2\text{ nm} < \text{pore diameter} < 50\text{ nm}$), and micropores (pore diameter $< 2\text{ nm}$) according to the pore diameter distribution. The pore size could be adjusted by optimizing process parameters. In addition, PCF had certain mechanical properties, not easy to grind a loss and pulverization, and not caused secondary pollution. The studies indicated that the attrition rate of PCF was 1/14 of the granular activated carbon after several adsorption and desorption cycle experiments. PCFs were the popular materials because of the characteristics as follows, low cost, excellent electronic conductivity, abundant raw materials, excellent chemical and thermal stability, well-controllable porosity, etc[1].

2. Preparation of porous carbon fibres

There were many methods to prepare PCFs including template methods, electrospinning technology and polymer blend technology etc.

2.1 Template methods

The template methods could control an effective area whether the chemical reaction in liquid or gas phase. The advantages of template methods were that it could precisely control the pore size distribution, order pore structure, large specific surface area, interconnected net holes and construct

the diverse morphologies for PCFs[2]. Template methods were generally divided into hard templates, soft templates and dual-templates.

2.1.1 Hard template

The hard template method was an effective method to synthesize PCFs. The principle of hard template method was that solid materials with a certain pore structure and morphology skeleton were filled with carbon precursors as hard templates. PCFs were obtained through the process of template removal after chemical or electrochemical reaction inner or outer surface of the material [3]. There were many methods to synthesize porous carbons by using silica materials, MgO, CaCO₃, Fe₂O₃, KCl, zeolites, molecular sieve or metal carbides [4] as hard templates. The processes for synthesizing porous carbons by means of hard template involved four steps: (i) synthesized an ideal hard template, (ii) mixed carbon sources and the hard template, (iii) carried out a high temperature pyrolysis in a certain atmosphere and (iv) removed the hard template by acid or alkali rinsing.

Lithium-sulfur (Li-S) battery called the most promising storage device had an extremely high energy density. However, the development impeded because of poor electronic conductivity, serious shuttle effect and enormous volume expansion. Yang[5] prepared hierarchical porous carbon from glucose as carbon precursor and CaCO₃ nanoparticles as hard template. MTC-2/S electrode exhibited better electrochemical properties, such as the reversible capacity was 1475 mAh/g in the first cycle and remained at 844 mAh/g after 50 cycles.

2.1.2 Soft template

The soft templates such as copolymer surfactants, organic molecules, and supermolecules feature with the functional groups[6] could provide the interaction forces including hydrogen bonds, hydrophobic and hydrophilic actions and electrostatic interactions[7]. The difference with the hard template method was that the PCFs were formed through hydrogen bonding, hydrophilic/hydrophobic or ionic coordination between the template and the carbon precursor[8].

Ana[9] invented 3D graphitic carbons with nanometric scale by using soft template. Compared with other similar 2D graphene oxide and reduced graphene oxide, the porous structured graphitic carbons showed stronger metal-free catalytic activity in the aerobic oxidation of benzylamine. Zheng[10] synthesized a novel hydrothermal mesoporous biochar (HMC-800) with the 286.3 m²/g specific surface area and 0.249 cm³/g pore volume for adsorbing tetracycline from wastewater using polyethylene-polypropylene glycol as soft-template agent and biomass batatas as carbon precursor. The adsorption performance demonstrated that it had the 55.0 mg/g adsorption capacity.

2.1.3 Dual-template

Dual-template usually consisted of hard and soft templates. The hierarchical porous structure was prepared utilizing the space restriction of the two templates to tune the carbon precursor. The hard and soft templates played different roles in the preparation of PCs. The hard template could adjust macroporous structure, while the soft template were assembled into mesoporous structure[11]. Dual-template could be divided into three categories of hard and hard templates, soft and soft templates, as well as hard and soft templates.

Qiao[12] prepared hierarchically porous chitin microspheres (HCM) by dual-template using micron-size CaCO₃ as hard template and chitosan as soft template. Glycine was grafted on the HCM, which was used for the treatment of heavy metal ions. The static batch experiments indicated that the original adsorption capacity still maintained 70% after five adsorption/desorption cycles. Deng[13] prepared nitrogen-doped ordered hierarchically porous carbon (NHMC) by means of surfactant-templating organic resol self-assembly with F127 as soft template and SiO₂ nanosphere as hard template. The catalyst showed high onset potential of 0.91 V and half-wave potential of 0.76 V as well as high limiting current by four-electron pathway for oxygen reduction reaction.

2.2 Electrospinning technology

The electrospinning technology had been known since 1900 when it was first introduced by Cooley. Electrospinning was capable of producing fibres at the nanoscale, but it was not until the 1990s that the field of nanotechnology realized the potential of using fibres. The electrospinning machine structure was shown in fig.1[14]. The basic apparatus included a high-voltage power supply, an injection pump, a syringe with a metal needle and a conductive collector. Electrospinning worked by injecting a polymer solution or melted polymer through a nozzle at high voltage. High voltage created electrical charge and polarity in the polymer solution. The charged polymer formed a Taylor cone under the action of an initial high-voltage electrostatic field. When the charge repulsion force was greater than the surface tension, many small liquid streams were ejected from the surface of the Taylor cone at high speed. The polymer nanofibres were finally deposited on the conductive collector after solvent evaporation and jet solidification [15]. The experimental conditions of polymer, needle diameter, working voltage and receiving distance affected the morphology of porous carbon nanofiber. The porous carbon fibres in the form of non-woven were deposited on the substrate. Electrospinning could add micro or nanoparticles to polymer solution in order to obtain composite fiber materials possessing multiple functionalities.

Electrospun carbon nanofibres were attractive materials to be applied in different fields such as air purification, water remediation, sensing and healthcare. The fibers had the characteristics of abundant available pore size, large specific surface area, high adsorption capacity, fast adsorption rate for various analytes, convenient preparation and fast regeneration, which could be used as adsorbents for different pollutants such as carbon oxides, nitrogen oxides, methane, metal ions, dyes, drugs, antibiotics.

The major challenges of pharmacotherapy were side effects of high concentration of drug. Cellulose nanocrystals were modified by polyamide physical adsorption and added to electrospun cellulose acetate matrix. Tranexamic acid could be detained in the cavity of PAMAM and its release rate was controlled well at the presence of MCNC. Electrospun cellulose acetate modified CNC perfectly controlled the release rate of tranexamic acid and increased the final release of gatifloxacin[16]. Ni-Zn batteries played an important role in energy storage systems. However, the percentage of active materials were very low because Ni-based cathode electrodes were generally composed of non-capacity contribution additives and heavy current collectors. Cui synthesized one-dimensional electrospun carbon nanofibres functionalized with ternary NiCo₂S₄ nanoparticles by electrospinning technique. The Ni-Zn batteries had a high capacity of 0.32 mAh cm⁻² and good magnification performance. After 2000 cycles, the capacity of the battery remained at about 83% of the initial capacity[17].

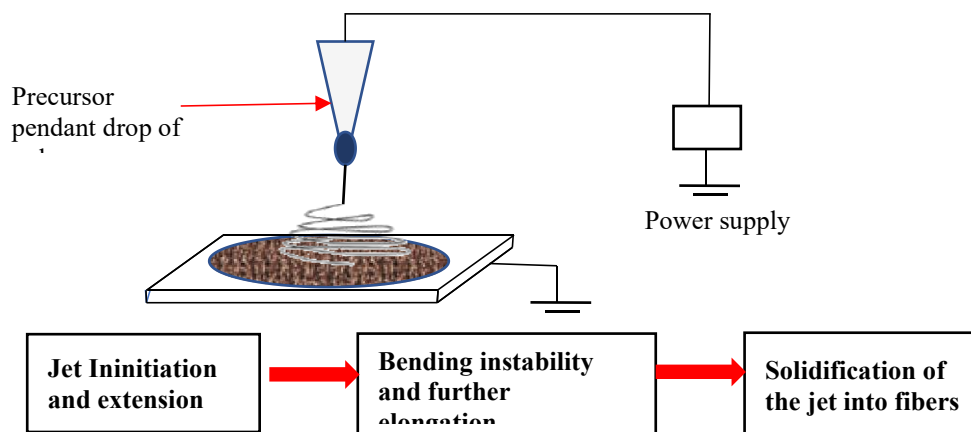


Fig.1 The schematic of basic principle of electrospinning

2.3 The polymer blend technology

The blending polymers had different thermal decomposition capacities. One was pyrolytic polymer (TDP) such as PE and PMMA and the other was carbon precursor polymer (CPP) such as PF and PAN. When the blending polymers were heated to a certain temperature, TDP was broken down and CPP was converted to carbon. So the porous carbon fibres were synthesized. The morphological structure of the porous carbon fibres could be adjusted according to the different type and proportion of blending polymers.

The preparation of porous carbon fibres with polymer blend technology was shown in figure. 2^[18]. The process was that CPP and TDP were blended. CPP in the blend was controlled as continuous phase and TDP as dispersed phase, so that TDP could be dispersed in the CPP matrix in granular form. In the spinning process, due to the tensile action along the fiber axis, the dispersed phase would also be oriented along the fiber axis. TDP as dispersed phase could be dispersed in CPP as continuous phase granularly. The phase (TDP) was decomposed completely and CPP was converted into carbon by pre-oxidation and carbonization, leaving holes in the fiber parallel to the fiber axis^[19]. The incompatible blend fibres presented a “sea island” structure. When TDP was used as sea component the nanocarbon fiber (CNFS) could be obtained. On the contrary, if TDP was used as force island component, porous carbon fiber (PCFS) could be obtained.

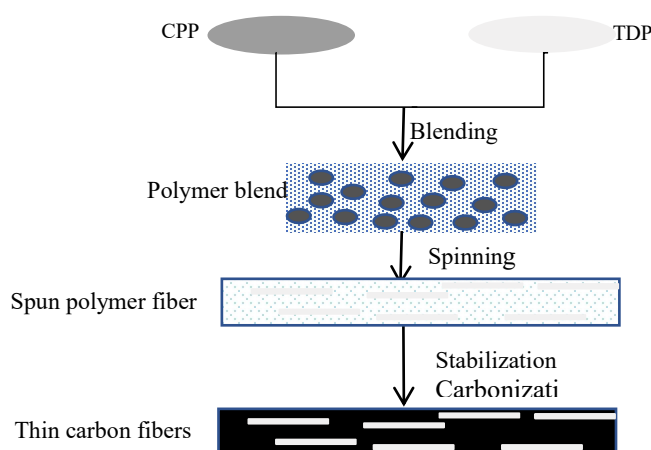


Fig.2 Schematic flow of carbon nanofibers preparation using the polymer

Electrospun polystyrene (PS) fibre mat had high sorption capacity and oil-water selectivity, so it was considered as a potential oil absorbent. However, the mechanical properties were poor because of lacking of inter-fibre bonding. In a study, coaxial or multi-nozzle side-by-side spinning (rather than mixed spinning) was used as a means of “incorporate” PU[20]. Uniaxial tensile strength tests showed that the addition of PU in the blend improved the mechanical properties of the pad.

3. Conclusions and future perspectives

The preparation strategy of PCFs were reviewed in this paper. Despite significant progress has been made in this area, the preparation of porous carbon still had many problems that require further research. The synthesis and removal of hard template were complex, which increased the costs and commercialization barrier. The properties of PCFs largely depended on the properties of the template. The porous carbon were usually composed of macro and mesopores, and had relatively low specific surface area. Therefore, the development of environmentally friendly hard templates and chemical activators was the crucial to obtain carbon materials with high specific surface area, high pore volume and high micro-porosity. Although removing the soft templates after carbonization were unnecessary, the disadvantages were low specific surface area and low specific capacitance

because of the mesopore-dominated framework. Moreover, it was scarcely possible for large-scale production because the synthesis of soft template was complicated and expensive. The dual-template fabricated the hierarchical porous structure by the dual space restriction of the two templates. Because of the unique microstructure, the double template method can provide a variety of templates for preparing carbon materials, but the template content was low. Electrospinning provided a high relative surface area of nanofibres that went beyond any conventional spinning method currently available. Electrospinning technology had great application prospect, but there was still a big bottleneck which the preparation of high orientation fiber and industrialization was extremely difficult. The effect of high orientation fiber preparation by collection cylinder with high speed rotation was not ideal. The polymer blend technology not only carried out industrial production but also in small batch production. There were many kinds of mixtures by polymer blend technology, therefore, it had great potential. However, the method had strict requirements on compounds such as similar solubility, polarity, crystallinity, surface tension, viscosity. Therefore, it was essential and urgent to actively design and develop more advanced template methods to prepare PCF with reasonable cost, zero environmental pollution, high efficiency and easy removal.

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