

Preparation of mesoporous carbon nanofibers from the electrospun poly(furfuryl alcohol)/poly(vinyl acetate)/silica composites

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Reagents and materials

Furfuryl alcohol (FA, 98.0%) was purchased from Aladdin Industrial Inc., China. Poly(propylene oxide)-*b*-poly(ethylene oxide)-*b*-poly(propylene oxide) triblock copolymer Pluronic F127 was supplied by Sigma-Aldrich. Tetraethyl orthosilicate (TEOS, SiO₂% = 28.4), oxalic acid (99.5%), ethanol (99.7%), acetone (99.5%), hydrofluoric acid (HF, 40.0%), sulfuric acid (98.0%), toluene (99.5%), cetyltrimethylammonium bromide (CTAB, 99.0%) and poly(vinyl acetate) (PVAc, M_w 40,000) were provided by Sinopharm Chemical Reagent Co., China. All reagents were used without further purification. Deionized water was used throughout this work.

Preparation of poly(furfuryl alcohol)/poly(vinyl acetate)/silica sols

Two different routes were applied in this part.

(i) 1.0 g of PVAc was mixed with 10 mL of acetone in a three-necked flask first. After the polymer was fully dissolved, 1.0 g of F127 was added into the solution. Then, 0.02 g of oxalic acid was added, playing the role of both hydrolysis catalyst of TEOS and polymerization catalyst of FA. The system temperature was raised and then held at 45 °C for the following reactions. A total amount of 5 mL of TEOS was added dropwisely into the system. After magnetically stirred for 1 h, 4 mL of FA was also added slowly into the mixture. The reactions were conducted at 45 °C for 48 h. After complete cooling, a brown and viscous liquid was obtained, as the poly(furfuryl alcohol)/poly(vinyl acetate)/silica sol.

(ii) 20 mL of TEOS, 16 mL of FA, 4.0 g of F127 and 0.08 g of oxalic acid were mixed and magnetically stirred in a three-necked flask at 70 °C for 48 h. The product was treated with ethanol to dissolve and remove the unpolymerized FA molecules. The insoluble part was dried under vacuum at 60 °C for 12 h, thus the poly(furfuryl alcohol)/silica composite was obtained. Then, 6.03 g of this composite was mixed with 10 mL of acetone and 1.0 g of PVAc. After magnetically stirred for 2 h, the poly(furfuryl alcohol)/poly(vinyl acetate)/silica sol was formed.

Preparation of PFA/PVAc/silica nanofibers

The composite sol was moved to a plastic syringe, which was equipped with a metallic nozzle. During electrospinning, a high voltage of 18 kV was applied to the nozzle. The sol was continuously pushed out the syringe at a constant rate of 0.8 mL h⁻¹. The deformed drops

converted to ultrathin fibers when they touched the high voltage. The fibers were collected on the counter electrode covered with an aluminum foil. After dried under vacuum at 60 °C for 24 h, the PFA/PVAc/silica nanofibers were obtained.

Preparation of mesoporous carbon nanofibers

The as-prepared PFA/PVAc/silica nanofibers were carbonized under N₂ atmosphere through the following procedures. First, the temperature was raised from 20 °C to 750 °C (or 650 °C) at a ramping rate of 2 °C min⁻¹. Then, the temperature was held at 750 °C (or 650 °C) for 2 h. After it was fully cooled to room temperature, the product was poured into a 10% HF solution. The silica template was removed during 12 h of the etching procedure. Mesoporous carbon was obtained by washing the etched product with water and then drying it at 80 °C under vacuum for 12 h.

Preparation of PVAc nanofibers (for comparison)

1.0 g of PVAc was dissolved in 10 mL of acetone at room temperature. The solution was moved to a plastic syringe, which was equipped with a metallic nozzle. During electrospinning, a high voltage of 18 kV was applied to the nozzle. The solution was continuously pushed out the syringe at a constant rate of 0.8 mL h⁻¹. The deformed drops converted to ultrathin fibers when they touched the high voltage. The fibers were collected on the counter electrode covered with an aluminum foil. After dried under vacuum at 60 °C for 24 h, pure PVAc nanofibers were obtained.

Preparation of PFA membrane (for comparison)

11.76 g of sulfuric acid and 0.0015 g of CTAB were dissolved in 20 mL of water first. Then, 20 mL of toluene solution containing 2.0 g of FA was slowly dropped into the above solution. A two-phase system was thus formed and FA molecules were polymerized at the toluene-water interface. The reaction was performed for 1 h. Insoluble product with dark red color was obtained. The raw product was washed using water first, then ethanol. The product was dried at 80 °C under vacuum for 12 h. Thus, pure PFA membrane was obtained.

Pyrolysis of PVAc nanofibers and PFA membrane

The PVAc nanofibers and PFA membrane were carbonized under N₂ atmosphere through the

following procedures. First, the temperature was raised from 20 °C to 750 °C at a ramping rate of 2 °C min⁻¹. Then, the temperature was held at 750 °C for 2 h. After complete cooling, the carbonized products were obtained.

Characterization

Fourier transform infrared spectroscopic (FT-IR) measurements were performed on a Nicolet 5700 FT-IR spectrometer. Scanning electron microscopic (SEM) images were taken on a Philips XL-30 scanning electron microscope. The SEM was equipped with an Oxford INCA energy dispersive X-ray spectroscopic (EDX) system to detect the elements containing in the mesoporous carbon nanofibers and measure their concentration. Transmission electron microscopy (TEM) experiments were performed on a Jeol JEM-2011 electron microscope. X-ray diffraction (XRD) pattern of the mesoporous carbon nanofibers was recorded using an X-ray diffractometer (Bruker D8 Advance) at 40 kV and at a current of 40 mA with Cu K α radiation. The nitrogen adsorption and desorption isotherms were measured using a Micromeritics ASAP 2020 analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface areas. The pore volume and pore size distribution were derived by using the Barrett-Joyner-Halenda (BJH) model.

Physicochemical parameters of the products are defined as follows: mesopore surface area (S_{meso} , m² g⁻¹) was calculated using BJH method from the desorption branches; total pore volume (V_{total} , cm³ g⁻¹) was measured at $P/P_0 = 0.995$; mesopore volume (V_{meso} , cm³ g⁻¹) was derived from the difference between the total pore volume (V_{total}) and the micropore volume determined by t -Plot method; pore diameter (D_{pore} , nm) was calculated using BJH method from the adsorption branches.