

Structure, Morphology and Thermal Stability of Porous Carbon Nanofibers Loaded with Cobalt Nanoparticles

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ABSTRACT

Porous carbon/cobalt (C/Co) composite nanofibers with diameters of 200-300 nm were prepared by electrospinning and subsequent carbonization processes. Two polymer solutions of polyacrylonitrile (PAN), polyvinyl pyrrolidone (PVP), and Co (CH₃COOH)₂ (Co (OAc)₂) were used as C/Co composite nanofiber precursors. The study revealed that C/Co composite nanofibers were successfully prepared and cobalt particles with diameters of 20-30 nm were uniformly scattered in the carbon nanofibers. It was also observed that clear fibrous morphology with grainlike particles and good structural integrity were still maintained after calcination. The TGA analysis indicated the improved thermal stability properties of the composite nanofibers. The Brunauer-Emmett-Teller (BET) analysis indicated that C/Co composites nanofibers with meso-pores possessed larger specific surface area than that of carbon nanofibers.

INTRODUCTION

Porous carbon materials loaded with metal or metal oxide have attracted a great deal of attention because of their versatile applications in catalysis,¹ sensors,² electronic devices,³ gas and liquid separation,⁴ and memory storage.⁵ Because the composite nanofibers exhibit excellent electrochemical properties with high reversible capacity, especially the porous composite nanofibers,⁶ much research effort has been attempted to prepare the composite nanofibers with the method of electrospinning and calcination using a wide variety of polymers and inorganic materials because of its relatively simple preparation and lower cost^{7,8} such as C/Ni,⁹ C/Cu,¹⁰ C/Co,¹¹ C/Co₃O₄,¹² C/Fe₃O₄.¹³ In this study, we prepared grainlike porous C/Co composite nanofibers by electrospinning and subsequent carbonization processes, where two polymer solutions (PAN and PVP) and Co (OAc)₂ were used as C/Co composite nanofiber precursors because the PVP phase decomposed during thermal treatment, then the porous carbon nanofibers were

obtained. The grainlike cobalt particles were uniformly distributed on the fiber surface and well-dispersed in porous carbon composite nanofibers.

EXPERIMENTAL

Fibers Preparation

In the typical synthesis, the N,N-dimethylformamide (DMF) solutions of PAN/PVP (7:3, 10wt %) containing 50wt% Co(OAc)₂ were prepared at room temperature. The molecular weights of PAN and PVP were 79,100 and 40,000, respectively. Homogeneous electrospinning solutions were loaded in a 20 mL syringe with a 0.6 mm inner diameter of the metal needle. The positive voltage, working distance, and flow rate were 15 kV, 15 cm, and 0.4 mL/h, respectively. Nanofibers were collected as a fibrous web on the surface of the aluminum foil. The electrospun PAN/PVP/Co(OAc)₂ nanofibers were firstly stabilized in an air environment at 250 °C for 4 h (heating rate was 2 °C min⁻¹) and then carbonized at 800 °C for 6 h in argon atmosphere (heating rate was 5 °C min⁻¹). For comparison, pure PAN nanofibers were also prepared under the same conditions.

Characterization

X-ray diffraction patterns (XRD) of the products were recorded on an X-ray diffractometer (MAC Science Co. Ltd. MXP 18 AHF). Field-emission scanning electron microscope (FE-SEM, JSM-5600) was used to characterize the morphology of nanofibers. The nanofiber surface was analyzed using a transmission electron microscope (TEM, Philips, and CM120). The thermogravimetry experiments were carried out with a TGA/STDA 851 (Mettler/Toledo, Giessen, Germany) instrument under N₂. Surface area of CNFs was measured using Brunauer-Emmett-Teller (BET) nitrogen adsorption method (Micromeritics Gemini 2360).

RESULTS AND DISCUSSION

The XRD pattern of the C/Co composite nanofibers annealed at 800 °C is presented in *Figure 1*. The broad peaks near 25° corresponded to the (002) diffraction peaks of graphite (JCPDS 75-1621), suggesting that the PAN fiber was completely converted into disordered carbon. The other three peaks near 44°, 52° and 76°, which corresponding to (111), (222) and (220) crystal planes, well indexed to cobalt metal (JCPDS File No. 15-0806). Because cobalt acetate decomposes at a temperature of around 200 °C,^{10,14} cobalt oxide should be obtained in the composite when the preoxidation is carried out at 230 °C. As the temperature further increased in the annealing process, PAN decomposed gradually into carbon, which could also reduce the cobalt oxide into metal at the high temperature. Thus, the final product was a carbon–cobalt composite. Assuming the complete conversion of cobalt oxide into metallic cobalt and a fully dense morphology of the fibers, the composition of the C/Co composite is about C (50 wt.%)–Co (50 wt.%). By applying the Debye–Scherrer formula on the (111) diffraction peaks, the average crystallite size of the cobalt were found to be 8 nm. It was much smaller than the diameter of carbon fibers, indicating that the cobalt particles could be easily dispersed in the fibers.

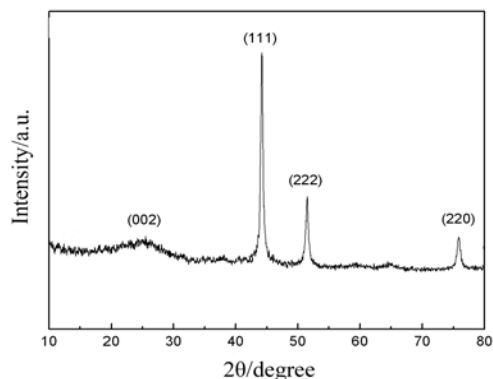


FIGURE 1. XRD pattern of the C/Co composite nanofibers annealed at 800 °C.

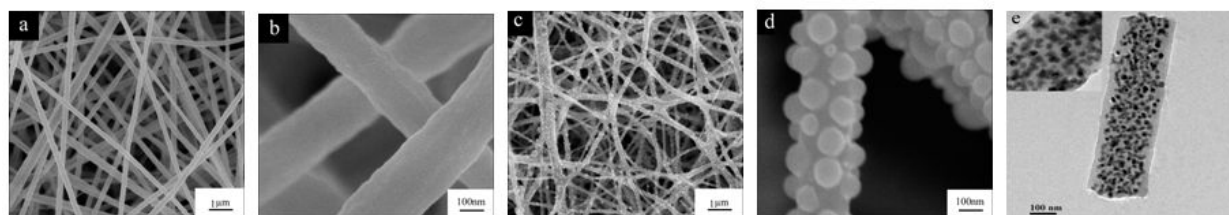


FIGURE 2. SEM images of PAN/PVP/Co(OAc)₂ precursor (a and b), carbonized composite nanofibers (c and d), and TEM image of carbonized composite nanofibers (e) with the same bar-size of 100 nm as (d).

The SEM images of PAN/PVP/Co(OAc)₂ precursor and carbonized composite nanofibers are shown in *Figure 2*. It was obviously observed that the PAN/PVP/Co(OAc)₂ precursor nanofibers exhibited relatively smooth surface morphology, uniform diameter, and straight fiber structure (*Figures 2a and b*). The diameter of precursor nanofibers was about 300 nm. The SEM images of carbonized composite nanofibers show that grainlike structures were formed on the fiber surface (*Figures 2c and d*), indicating that Co was formed during the high-temperature carbonization process. The formation of metallic Co was caused by the reducing environment created by the carbonization reactions. It could also be clearly seen that the surface of composite nanofibers was changed to rough after carbonization process, and the diameters decreased from about 300 to 200 nm. The presence of Co nanoparticles could also be further observed from the transmission electron microscope (TEM) images (*Figure 2e*), which had the same magnification with *Figure 2d* (100 k). Cobalt particles with diameters of 20–30 nm were well-dispersed along porous carbon nanofibers. Such a result suggested that the physical size of particle was larger than the size calculated by Debye–Scherrer formula, because 8 nm was the average diameter of individual grains for crystal growth direction parallel of (111) plane.

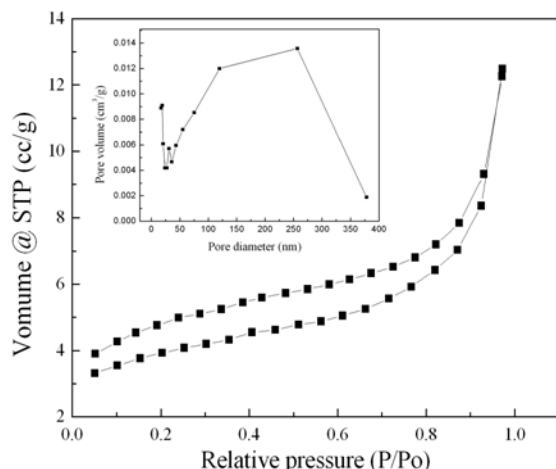


FIGURE 3. Nitrogen adsorption-desorption isotherms and pore size distribution curves of C/Co composite nanofibers

The nitrogen adsorption-desorption isotherms and pore size distribution curves of C/Co composite nanofibers are shown in Figure 3. It exhibits type IV isotherms with type H4 hysteresis loops according to IUPAC classification,¹⁵ which are typical characteristics of mesoporous materials. The average pore size was about 16.5 nm. The mesopores were produced by decomposition of PVP during carbonization at higher temperature. The BET surface area of C/Co composite nanofibers was 10.8 m²/g, which was much larger than that of pure PAN carbon nanofibers (2.7 m²/g).

Thermal stability of the electrospun nanofibers was evaluated using TGA in nitrogen atmosphere. The TGA curves of the pure PAN and PAN/PVP/Co(OAc)₂ composite nanofibers are shown in Figure 4. The onset thermal stability of PAN/PVP/Co(OAc)₂ composite nanofibers was enhanced relative to that of pure PAN nanofibers. These results indicated the cations of some transition metals (e.g., Co²⁺) might decrease the thermal stability of PAN/PVP nanofibers. The effect was attributed to the ability of the cation to form complexes in which the metal atoms were coordinately bonded to nitrile group.¹⁷

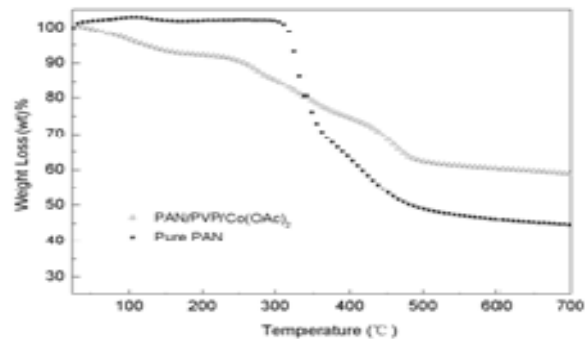


FIGURE 4. TGA curves of the pure PAN and PAN/PVP/Co(OAc)₂ composite nanofibers

When the temperature was over about 350 °C, the composite nanofibers had better thermal stability with high charred residue. It could be found that the residues of the PAN and composite nanofibers at 700 °C were about 40.9 and 55.3%, respectively. That was attributed to the porous structure (so called protective barrier) formed by the decomposition of PVP and Co(OAc)₂, which retarded the volatilization of the pyrolysis products.

CONCLUSIONS

In the present study, grainlike porous C/Co composite nanofibers with enhanced thermal stability and large specific surface area were prepared by electrospinning and subsequent carbonization processes. The results of this work suggested a new way to explore carbon-metal composite nanofibers, such as C/Fe, C/Ni, C/Cu or C/Sn composite nanofibers.

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