Applied Surface Science 265 (2013) 352–357

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Fabrication of novel micro–nano carbonous composites based on self-made hollow activated carbon fibers

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ARTICLE INFO

Article history:
Received 14 October 2012
Received in revised form 31 October 2012
Accepted 3 November 2012
Available online 8 November 2012

Keywords:
Template method
Hollow carbon fibers
Chemical vapor deposition
Carbon nanotubes
Micro–nano carbonous composites

ABSTRACT

The hollow activated carbon fibers (HACF) were prepared by using commercial polypropylene hollow fiber (PPHF) as the template, and phenol-formaldehyde resin (PF) as carbon precursors. Final HACF was formed through the thermal decomposition and carbonization of PF at 700 °C under the nitrogen atmosphere, and activation at 800 °C with carbon dioxide as the activating agent, consecutively. Then, carbon nanotubes (CNTs) were grown by chemical vapor deposition (CVD) techniques using the as-grown porous HACF as substrate. The growth process was achieved by pyrolyzing ethanol steam at 700 °C using nickel as catalyst. Finally, CNTs was grown successfully on the substrate, and a novel tree-like micro–nano carbonous structure CNTs/HACF was fabricated. The as-grown HACF and micro–nano CNTs/HACF were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and thermogravimetric analysis (TG), respectively. Moreover, the formation mechanisms were also discussed.

1. Introduction

Activated carbon fibers (ACF) are characterized by high carbon contents, large specific surface areas, abundant micropores and small or narrow aperture. Hollow activated carbon fibers (HACF) are a kind of specific ACF with hollow structures. There are enrich micropores on both the internal and external surfaces of HACF, hence make it has larger specific surface areas, and possess unique advantages of fast adsorption rate, large adsorption capacity and simpler regeneration in the gas–liquid adsorption fields [1–3].

For a long time, most hollow activated carbon fibers (HACF) were prepared based on spinning technologies [2–6], which usually use various kinds of organic polymer fibers including polyacrylonitrile fiber, cellulose fiber, polyethylene fiber, and polyvinyl alcohol fiber, etc. to get hollow fiber strands, and then repass preoxidation, carbonization process to obtain expected carbon fibers with hollow structures. However, the spinning process is very complex, including the proper selection of polymer precursors, the parameters involved in electrospining process, the pre-oxidation, carbonization and activation techniques, etc. In addition, it is difficult to control the pore size distribution and pore connectivity. In recent years, alternative controllable and cost – effective HACF synthetic routes – template method has aroused intensive attention, by using the polymer or organic fibers (polypropylene hollow fiber, polyvinyl alcohol fiber, organic silica fiber, etc.) as template, carbon-rich compounds (sucrose, polystyrene, etc.) as carbon precursors. After template materials were decomposed or removed at certain temperatures, hollow structured carbon fiber with ideal regular and uniform morphologies can be obtained. Shi et al. [7] firstly reported the synthesis of hollow carbon fibers (HCFs) by using polypropylene hollow fibers templates with sucrose as carbon precursors. Cheng et al. [8] prepared circular and rectangular opening HCFs by using electrospun silica fibers as template and polystyrene as carbon source. Fatema et al. [9] reported the HCFs fabrication using PVA fibers with the aid of iodine pretreatment.

The discovery of carbon nanotubes (CNTs) by Iijima [10] has attracted great attention because of their unique structural, thermal, adsorptive, electronic, and mechanical properties, etc. [11–13]. Chemical vapor deposition (CVD) is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure with various substrates [14]. There have been many reports about CNTs growth on different carbon matrices, such as carbon fibers [15–17], carbon paper (CP) [18,19], active carbon [20,21], and ordered mesoporous carbon [22]. However, there is still no report about CNTs deposited on the hollow activated carbon fibers so far to the best of our knowledge.

In the present work, HACF has been successfully prepared by template method using polypropylene hollow fibers as template, and phenol-formaldehyde resin is firstly used as carbon precursor.

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http://dx.doi.org/10.1016/j.apsusc.2012.11.011

What more important, novel micro–nano CNTs/HACF composites are obtained using HACF as the substrate through CVD technology.

2. Experimental

2.1. Preparation process of the micro–nano carbonous composites CNTs/HACF

(i) Preparation of hollow activated carbon fibers (HACF)

A polypropylene hollow fiber (PPHF) (400 μm I.D., 30–40 μm wall thickness, 0.2 μm pore size, from Hangzhou Kaihong Membrane Technology Co., Ltd., China) was used as the template. Firstly, the pristine PPHF were cut into short fibers with about 3 cm long, and purified with alcohol for 24 h. Subsequently, purified PPHF was immersed into phenol-formaldehyde resin (PF) solution (PPHF:PF:ethanol = 0.25 g:5 g:25 mL) for 24 h, and gradually dried at 50 °C, 80 °C, 120 °C, and 160 °C for 2 h, respectively. Then, the obtained PPHF–PF was placed in the tube furnace at the heating rate of 2.5 °C/min, via carbonized at 700 °C for 60 min under nitrogen (N_2) atmosphere and activated at 800 °C for 60 min using carbon dioxide (CO_2) as activating agent, respectively, resulting in the product HACF.

(ii) Fabrication of the micro–nano carbonous composites CNTs/HACF based on HACF (i)

The above prepared HACF was placed into nickel nitrate solution (0.1 mol/L) for 5 h at ambient temperature to ensure nickel ions were adsorbed onto surface sites. A thermal reduction process was carried out at 400 °C for 60 min under the atmosphere of reductive hydrogen (H_2) and shielding gas N_2 with the chemical composition of vol. N_2:H_2 = 3:1, thus nickel ions was reduced to elements. Then, a CVD technique was used to grow CNTs on the nickel (Ni) coated HACF with ethanol (C_2H_5OH) vapor as the carbon source, and N_2 as the carrier gas. The vapor deposition process was carried out in the quartz tube of tube furnace at 700 °C for a growth period of 50 min, in order to form the resultant CNTs/HACF hybrid micro–nano carbonous composites. Finally, the as-grown samples were immersed into nitric acid (5 mol/L) at 80 °C for 6 h in order to remove the catalyst particles.

2.2. Microstructure characterization of the micro–nano carbonous composites CNTs/HACF

The morphological features of the as grown HACF and CNTs/HACF micro–nano carbonous composites were analyzed on scanning electron microscope (Quanta 200F, FEG, USA) and transmission electron microscope (JEM-2100F, JEOL, Japan). The structure of HACF and CNTs/HACF were investigated by X-ray diffraction using a high power X-ray diffractometer (D8 Advance, Bruker, German) with Cu Ka radiation (λ = 0.15418 nm). The pyrolysis characteristics of HACF and CNTs/HACF were performed by thermal gravimetric analysis with a thermal analyzer (STA449C, Netzsch, Germany) under nitrogen atmosphere at the heating rate of 10 °C/min.

3. Results and discussion

3.1. Morphologies and structures of the HACF and CNTs/HACF

The morphologies, surface structures, and dimension of HACF and CNTs/HACF hybrids were characterized by SEM at different magnifications and view angles. Fig. 1(a) and (b) displays the cross-sectional images of the obtained HACF at different magnifications. The hollow structure indicates that thermal decomposition of PPHF does not result in the collapse of the fibers. The external and internal diameters of the HACF are about 420 and 330 μm, respectively, and the wall thickness of HCF is about 90 μm. Fig. 1(b) fully demonstrates that the HACF consists of compact structures and high porosity on the surfaces and cross-sections. Compared with the HCF synthesized in Ref. [7], at first, the carbon source used here is phenolic resin, which can form high crosslinked structure after thermal decomposition than sucrose precursor. Then, we adds an physical activated process in preparing the HACF, to open the inherent pores or etch out new micropores in the surface of hollow carbon fibers through carbon dioxide reacted with carbon atoms at high temperature 800 °C. Therefore, the obtained HACF in this work has higher structure stability and porosity.

Fig. 1(c) and (d) presents the cross-sectional SEM images of the CNTs/HACF through CVD process, which apparently shown that plenty of CNTs are grown on the external, internal and fracture surfaces of the substrate HACF, and a novel micro–nano carbon composite structure is successfully fabricated. The magnified longitudinal SEM images of CNTs grown on the external surface of HACF are displayed in Fig. 1(e) and (f), showing a large number of dense CNTs grows on the substrate. In addition, Fig. 1(f) clearly shows that most CNTs grown toward the same direction which perpendicular to the external surface of HACF, which results in the formation of tree-like structures, that is, the self-made HACF acquired by template method acts as the “trunk”, and the grown CNTs obtained by CVD technique as the “branch”.

After acid treatment, most of the catalysts have been removed, as shown in Fig. 1(g) and (h). It can be clearly seen that some gaps appeared on the tops of carbon nanotubes, which means that nitric acid had washed the nickel catalyst at the tip of the carbon nanotubes, but did not bring obvious damage to the morphology and structure of the as-grown CNTs and their distribution on the substrate HACF.

The contrasted bright field image of as synthesized CNTs is shown in TEM images of Fig. 2. Fig. 2(a) shows the presence of some undesired carbon impurities and uncompleted grown tubes along with CNTs. But it still clearly presents the Ni catalyst position and morphology and structure of as-grown nanotubes, which is beneficial to know the carbon nanotubes formation process and principle. In addition, from Fig. 2(a) and (b) photos, we can drawn that the outer diameter and wall thickness of obtained CNTs are uniformly in the range of 70–90 nm, and 20–30 nm, respectively.

XRD was applied to investigate the crystal structure of as-grown samples. Fig. 3 shows the X-ray diffraction patterns of the (a) as-grown HACF, (b) CNTs/HACF, and (c) acid treatment CNTs/HACF. The diffraction pattern of the HACF shows a high narrow diffraction peak at $2\theta = 22.5°$, corresponding to the C(002) reflection of a turbostratic carbon structure [23] of HACF. After the growth of CNTs on the HACF, C(002) reflection become stronger, demonstrated that the structure order degree of the as-grown micro–nano CNTs/HACF composite has increased significantly than HACF substrate. In addition to the peaks of carbons, the diffraction peaks induced by the existence of catalyst particles Ni(111) were also observed at $2\theta = 44.4°$. However, after the cleaning of 5 mol/L nitric acid, both the intensity and the FWHM (full width at half maximum) of the Ni peaks decreased obviously, indicating the removing of catalyst particles Ni. Moreover, the C(002) diffraction is getting further stronger, which also proved the removing of Ni in the interior of CNTs or on the surface of HACF enhanced the order degree of whole carbon structure.

TGA analysis was used to study the thermal stability of the as-grown HACF (Fig. 4(a)) and CNTs/HACF (Fig. 4(b)) structures. Fig. 4(a) shows that there is a small weight loss about 5% occurred at 50–120 °C due to the volatile of water and air, etc. impurities, after which a slowly weight loss is observed in the temperature range from 120 to 350 °C, which maybe caused by the pyrolysis of residual phenolic resin that did not completely carbonization in