Short communication

Preparation and catalytic behavior of hollow Ag/carbon nanofibers

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ABSTRACT

A novel carbon nanofiber containing silver nanoparticles (NPs) with hollow structure was fabricated via co-electrospinning and in situ reduction. The hollow structure avoided the waste of silver NPs embedded in the nanofibers while ensuring high specific surface area. The formation of silver NPs was confirmed by Field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The catalytic behavior of the nanofibers obtained to the reduction of methylene blue with $NaBH_4$ was tracked by UV–visible spectroscopy. The results showed that carbon nanofibers containing silver NPs with hollow structure possessed significant catalytic properties.

1. Introduction

Dyes and their decomposition products contained in textile industrial effluent are harmful to human health and should be urgently treated [1]. Carbon materials have been applied in various fields due to their high specific surface area, excellent electric conductivity, thermal conductivity, and good environmental stability. Some carbon materials show intrinsic catalysis [2,3] and some carbon materials are used as catalyst carrier or reinforced materials in various catalytic reactions [4–9]. Especially, carbon nanofibers (CNFs) are used as catalytic support materials owing to their high specific surface area and their ability to disperse catalytically active particles [10–12]. The dyes' sorption on the carrier materials favors the contact between dyes and active sites on catalysts [13]. Recently, carbonizing electrospun PAN nanofibers is widely used to prepare CNFs. Hollow nanofibers with independently functionalized inner and outer surfaces could be fabricated by co-electrospinning [14]. Hollow structure ensures the high specific surface area and the catalytic active species on both surfaces enhancing the chances of contact between active sites and reactants. Moreover, the solid structure converts into hollow structure avoiding the waste of catalytic active species to some extent. Silver is a group IB transition metal with a $4d^{10}5s^1$ electronic layer structure. Silver-based materials have been a popular functional material applied in catalysis, sensing and antibacterial materials due to its specific physical and chemical structures [15–22].

In this study, silver doped PAN-based hollow carbon nanofibers were prepared combining co-electrospinning technique with in situ reduction and their catalytic behavior were studied preliminarily.

Morphology and structure were characterized by Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), and the catalytic behavior was examined by UV–visible spectroscopy.

2. Experimental

Polyacrylonitrile (PAN) woolen yarn, a commercial product, was purchased from Shanghai Sanli Wool Textile Co., Ltd. Polyvinyl pyrrolidone (PVP), pharmaceutical grade, was purchased from Boai NKY Pharmaceuticals Ltd. N,N-dimethylformamide (DMF) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Silver nitrate was purchased from Tianjin Yingda Rare Chemical Reagents Factory. Methylene blue (MB) was purchased from Tianjin Tensing Fine Chemical Research Develop Centre. Sodium borohydride ($NaBH_4$) and sodium hydrate (NaOH) were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. Except for PAN and PVP all reagents were analytical grade and used as received.

2.1. Fabrication of nanofibers by electrospinning and co-electrospinning

In order to prepared the nanofibers, PAN/DMF solution with a concentration of 13 wt.% and containing a certain amount of silver nitrate (0 and 1 wt.%) were prepared under dark; PVP/DMF solution with a concentration of 12 wt.% was prepared. The PAN solutions were electrospun at a positive voltage of 15 kV, a working distance of 15 cm, and a flow rate of 0.3 mL/h. Under same condition the core-shell nanofibers with and without silver nitrate were co-electrospun with the PAN solutions as outer spinning solution and the PVP solution

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as inner spinning solution. All the as-spun nanofibers were dry at 60 °C to remove the residual solvents.

2.2. Heat treatment of nanofibers

The as-spun core-shell nanofibers were stabilized under atmosphere with a heat rate of 5 °C/min and kept for 1 h at 300 °C. A constant tension was imposed to the two opposite edges of the nanofibers to protect it from shrinking. After cool to room temperature the nanofibers were carbonized under a nitrogen atmosphere with a heat rate of 5 °C/min to 300 °C, subsequently up to 750 °C with a heat rate of 3 °C/min and kept for 1 h. Finally the samples were cooled down to room temperature naturally.

2.3. Catalytic tests

Firstly, 50 mL MB aqueous solution with a concentrate of 4.0×10^{-5} mol/L was prepared. Then 1.0 g NaBH$_4$ was added and 0.1 g NaOH was added for the stabilization of NaBH$_4$. 0.4 g carbon nanofibers were immersed into the aqueous solution under nitrogen atmosphere. The absorbance of the solutions was determined at different intervals.

2.4. Characterization

The structural information of PAN was characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (Bruker TENSOR 37, Germany). The formation of silver NPs was characterized using X-ray diffraction (XRD) (Rigaku D/MAX-2500, Japan) and X-ray photoelectron spectroscopy (XPS) (ThermoFisher K-alpha, England). The morphologies of the nanofibers were obtained using Field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan) and transmission electron microscopy (TEM) (Hitachi H-7650, Japan). The catalytic behavior of the nanofibers was recorded by UV–visible spectroscopy (UV-1800).

3. Results and discussion

3.1. FT-IR

The chemical structures of the core-shell nanofiber before and after heat treatment were studied by FT-IR spectroscopy. The FT-IR absorbance spectra of all the nanofibers are shown in Fig. 1. The peaks for the core-shell nanofibers before heat treatment can be assigned as follows: 2920 cm^{-1} corresponding to the CH stretching in CH and CH$_2$ groups, 2245 cm^{-1} corresponding to the C≡N stretching, and 1730 cm^{-1} corresponding to the C=O stretching. After stabilization
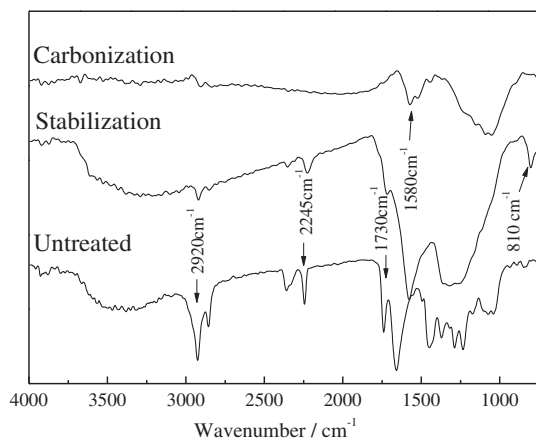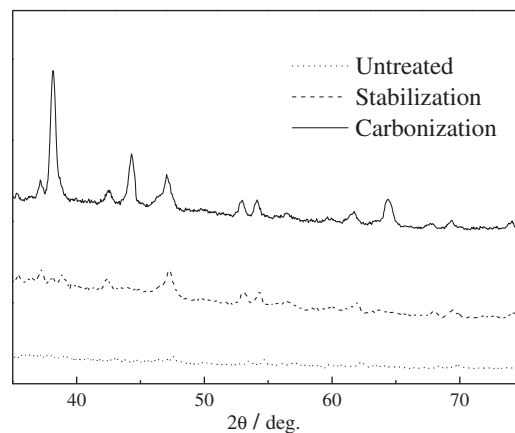

Fig. 2. XRD spectra of the nanofibers.

the spectrum of core-shell nanofiber shows significant changes. The intensities of all the above absorption peaks are weakened. New overlapping peaks between 1700 and 1000 cm^{-1}, corresponding to C=C, C=N, C=O, C—O, –OH and NH stretching, and absorption peak at 810 cm^{-1} corresponding to the aromatic ring out-of-plane bending of C–H appear. These changes are due to the cyclization of the molecular chain of PAN and the thermolysis of PVP. After carbonization these weakened absorption peaks disappear. The absorption peak at 1580 cm^{-1} corresponding to C=N stretching and between 1250–850 cm^{-1} corresponding to the aromatic ring in-plane bending of C–H illustrate the formation of the graphite structure. The spectra indicate that carbon nanofibers are obtained after carbonization.

3.2. XRD

The XRD spectra of the silver NPs in the nanofibers before and after heat treatment are shown in Fig. 2, respectively. The diffraction peaks with 2θ values of 38.2°, 47.1°, 61.6° and 74.2° are corresponded to the (111), (200), (220) and (311) crystal faces of the fcc crystalline silver. Compared with the three spectra it can be found that the intensities of the diffraction peaks are weak due to the incompletely reduction of AgNO$_3$ with DMF. After carbonization the intensities are enhanced with the increase in the amount of the silver NPs.
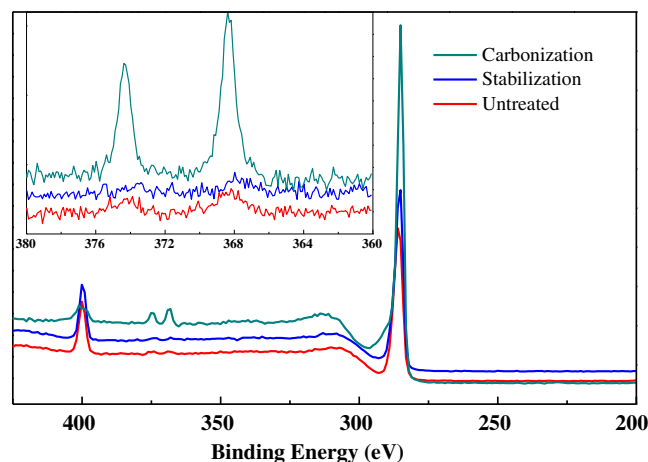

Fig. 1. FT-IR spectra of the nanofibers.

Fig. 3. XPS spectra of the nanofibers.