Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 62 (2008) 1155–1158
materials letters
www.elsevier.com/locate/matlet

Fabrication of Polyacrylonitrile/polypyrrole (PAN/Ppy) composite nanofibres and nanospheres with core–shell structures by electrospinning

Xianfeng Li [1], Xiufeng Hao, Hubei Yu, Hui Na*

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun, 130012 PR, China

Received 31 May 2007; accepted 1 August 2007
Available online 7 August 2007

Abstract

One simple method was introduced to prepare core–shell nanostructured conductive Ppy composite. Core Ppy particles were first introduced in the flexible shell solutions and then different core–shell structures can be prepared by electrospinning method. The results showed that: this method is very powerful to form core–shell nanostructures with electroconductive Ppy.

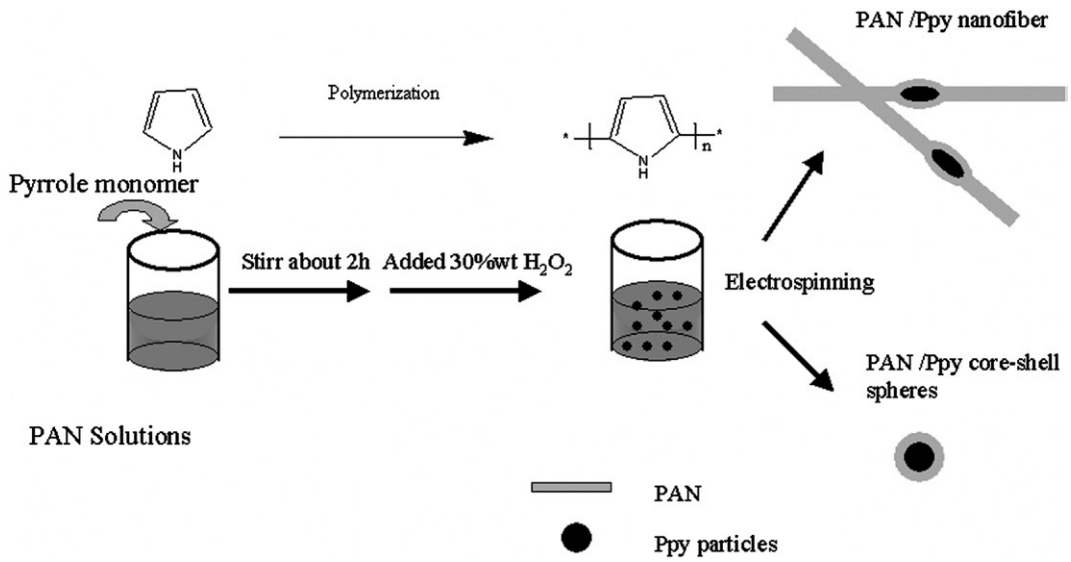
Keywords: Core–shell structures; Electrospinning; Ppy

1. Introduction

Nanostructured materials with defined size, shape and geometry in the nano- to micro-scale possess unique properties that are different from bulk materials. They have found tremendous interest in diversified technological applications including, catalysis, optics, electronics, biosensing, as well as in medicine [1–3]. It has been well known that performing reactions in a confined micrometer and nanometer-sized environment (nanoreactor) may yield new nanomaterials of interesting properties. A wide range of nanomaterials including metals, semiconductors, inorganic oxides, and polymers have been produced by using various nanoreactor systems, such as micelles or reverse micelles [4], liquid crystals [5], microemulsions [6], microgels [7], amphiphilic polymers or block copolymers [8], liposomes [9] and dendrimers [10]. Different nonreactor systems are able to create nanomaterials with intriguing properties having both the guest (nanomaterials) and host (nanoreactors) material characteristics. Among the nanostructures, multifunctionalized micro/nanostructures of conducting polymers have received great attention because of their unique properties and technological applications in electrical, optical, and magnetic materials and devices. Among those multifunctionalized micro/nanostructures, electromagnetic functionalized micro/nanostructures of conducting polymers are of special interesting due to their potential applications in electromagnetic interference (EMI) shielding and microwave absorbing materials [14]. Core–shell structures based on latex particles have gained an interesting importance in many industrial applications; typical examples are paints, coatings diagnostics drug delivery, or support for catalysts. They principally consist of a stiff core and a flexible shell. Typically they are obtained by a two step emulsion polymerization, whereas the core is prepared first and then surrounded with a flexible polymer shell by emulsion polymerization. Electrospinning as a very simple method can form various nanostructures, which include nanofibers, nanospheres etc. During electrospinning, when the voltage applied overcomes the surface tension of polymer solutions, the jets of polymers are ejected from the tip of the nozzle and fly towards the collectors [11–13]. This process depends on a number of parameters, including the type of polymers, conformation of polymer chains, viscosity of solutions, polarity and surface tension of the solvents, electric field strength and the distance between spinnerets and collectors etc. In this paper, the electrospinning method was first introduced to form different core–shell electro conductive Ppy nanostructures. The Ppy core particles were first introduced in flexible shell solutions by in-situ polymerization, and then different core–shell structures

* Corresponding author.
E-mail addresses: lxf_chem@yahoo.com (X. Li), huina@jlu.edu.cn (H. Na).
[1] Current address: Centre for Surface Chemistry and Catalysis, Faculty of Bioengineering Sciences, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, 3001 Leuven, Belgium.

0167-577X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2007.08.003



Scheme 1. Schematic illustration of the mechanism of core–shell structures.

will be obtained by electrospinning method. The morphology of the resulted nanostructures can be controlled by changing the concentration of the solutions. Polyacrylonitrile (PAN) as one of important polymers can be easily made into fibers and spheres by electrospinning. In this paper Ppy was selected as as-dispersed phase (cores) and PAN as continuous phase (shell). We first introduce the Ppy nanoparticles into PAN solutions. Then we will electrospin the solutions with different concentrations to make the core–shell structures with Ppy as cores and PAN as shells.

2. Experimental

2.1. Preparation of PAN solutions with uniformly distributed Ppy particles

5% weight ratio of pyrrole monomer to PAN polymers were first solubilized in DMF to form solutions with different weight concentrations (the weight concentration PAN in DMF is selected as 5% and 10%, which is named PAN/Ppy-1 and PAN/Ppy-2 respectively), stirred about 1 h, then equal mol 30 wt.% H_2O_2 (to amount of the pyrrole monomer) was slowly added to it, stirred for about 4 h to make pyrrole polymerization (Scheme 1).

2.2. Electrospinning of the PAN solutions

The core–shell nanostructures were prepared by electrospinning PAN solutions with uniformly distributed Ppy particles. The electrospinning set-up used in this paper was similar with our former report [15]. The silver-coated needle of a syringe was connected to a high voltage power supply and a glass plate as a collector was grounded. In this experiment the voltage was kept at 12 kV, the distance between the collector and electrode was kept at 15 cm.

2.3. SEM and TEM

The scanning electron microscope (SEM) measurements were performed on a Shimadzu SSX-550 microscope. The transmission electron microscope (TEM) experiments were performed on a JEM-2000EX microscope with an acceleration voltage of 200 kV.

3. Results and discussion

Ppy as one type of polymers, cannot solubilize in any solvents, which makes it very difficult to be dispersed in PAN solutions uniformly. In-situ polymerization method was adapted to make the Ppy dispersed in PAN solutions uniformly (Scheme 1). Pyrrole monomer was first added into the PAN solutions then make the Ppy uniformly distributed PAN solutions polymerization of pyrrole in the PAN solutions. And this method was proved to be a powerful way to form Ppy particles in solutions by our former publication [16]. Then the PAN solutions with Ppy particles will be electrospinned to make the core–shell structures. FTIR was used to confirm the existence of Ppy in PAN solutions. Fig. 1 shows the FTIR results of PAN, PAN/Ppy-1 and PAN/Ppy-2 respectively. The peaks at 1270 cm^{-1} and 1654 cm^{-1} are induced by the C–N and C═N stretching respectively. As shown in PAN there is no related stretching with C–N. The stretchings at 1454 cm^{-1} and 2237 cm^{-1} were the characteristics vibrations of PAN. From the FTIR, Ppy particles were successfully introduced into PAN solutions. Moreover the dynamic light scattering (DLS) experiment was carried out on the PAN/Ppy-1 and PAN/Ppy-2 solutions to determine the size of the resulted Ppy particles. The size of Ppy in the two solutions is 116 nm and 226 nm respectively.

The electrospinning results of the PAN/Ppy-1 and PAN/Ppy-2 solutions were shown in Fig. 2. Fig. 2a and b respectively shows the typical scanning electron microscopes (SEM) and transmission electron microscopes (TEM) micrographs of electrospinning results of PAN/Ppy-1 solutions. The morphology of the electrospinning products are nanospheres when the concentration of PAN is kept at 5%. Moreover the spheres are shown obviously as core–shell structures from the TEM result, which confirms to our suggestions. In this system Ppy particles cannot solubilize in DMF, the particles were brought out by PAN during electrospinning, which leads to the formation of core–shell structures with Ppy particles as cores and PAN as shells. Fig. 2c and d shows the SEM and TEM micrographs of the electrospinning results of PAN/Ppy-2 solutions. The morphology of the products are shown as nanofibers. The result changes from PAN/Ppy-1 to PAN/Ppy-2 may be induced by solutions properties of PAN. The increasing of the