Synthetic Metals 159 (2009) 2135–2140

Contents lists available at ScienceDirect

Synthetic Metals

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

Nanocomposite hydrogels—Controlled synthesis of chiral polyaniline nanofibers and their inclusion in agarose

Xuetong Zhang[a,b,*], Victor Chechik[a], David K. Smith[a], Paul H. Walton[a], Anne-Kathrin Duhme-Klair[a], Yunjun Luo[b]

[a] Department of Chemistry, University of York, Heslington, York YO10 5DD, UK
[b] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 12 April 2009
Received in revised form 14 June 2009
Accepted 3 August 2009
Available online 26 August 2009

Keywords:
Chirality
Hydrogel
Nanocomposite
Conducting polymers

ABSTRACT

Chiral polyaniline nanofibers were synthesized by using two different oxidants potassium tetrachloroaurate (PTC) and ammonium persulfate (APS) in sequence to oxidize aniline in the presence of a chiral inducing agent (1S)-(+)-10-camphorsulfonic acid ((*S*)-(+)-CSA) or (*R*)-(−)-CSA. The optical activity of the chiral polyaniline varies as a function of the mass ratio of PTC to APS, with the highest optical activity being observed in the ratio range from 1.0 to 2.5. The resulting chiral polyaniline nanofibers were then included into agarose hydrogels via 'wet process' and the chiroptical properties of the polyaniline nanofibers are retained within the composite hydrogels, although the degree of chiral organization of the polyaniline appears to be somewhat modified by the presence of the agarose matrix.

1. Introduction

Recently considerable interest has concentrated on the synthesis and properties of building blocks with potential applications in nanoscale optoelectronics [1]. These building blocks, e.g., conducting nanowires and metal nanoparticles, can mimic aspects of traditional micro-scale circuitry. There is also significant interest in the incorporation of such objects into composite materials that may have useful optoelectronic properties and applications [2].

Optically active (chiral) conducting polymers have been the focus of much recent attention due to their potential applications in chiroptical electro-luminescence devices, chiral separation, chiral recognition and surface-modified electrodes [3]. Chiral polyaniline is of great interest among the conducting polymers because it is inexpensive, relatively high stereo-selectivity, and environmentally stable [4]. In general chiral polyaniline has been synthesized *in situ* by the asymmetric oxidative polymerization of aniline in the presence of an optically active acid, which acts as a chiral inducing agent by interacting with the amines and as a doping agent as well by incorporating into the growing polyaniline chains [5]. Via controlling the polymerization conditions, chiral polyaniline nanostructures have been obtained with a great variety of morphologies: spherical [6], tubular [7], or fibrillar [8]. Although a lot of oxidizing agents [9] have been used to polymerize aniline, the influence of oxidizing agents on the chiroptical activity of the resulting chiral polyaniline has received less attention to date.

Metal nano-objects, such as gold nanoparticles, are also intriguing building blocks for application in optoelectronic devices [10]. It has been widely demonstrated that metal nanoparticles can be synthesized in a reproducible and controllable way with well-defined nanoscale dimensions [11]. Optical properties, such as the surface plasmon resonance are well-known to depend on the dimensions of the nanoparticle and as such, it is therefore possible to synthetically tune the physical behavior of these nanoscale building blocks [12].

In order to form composite materials, considerable interest has recently been focused on the use of soft materials, such as hydrogels, as supporting matrices [13]. These materials are primarily comprised of 'liquid-like' solvent (>95%), but also contain a small amount (<5%) of polymer or low molecular weight material which assembles into a nanostructured solid-like network. The presence of this solid-like network effectively immobilizes the flow of bulk solvent, creating a soft material which is ideal for the incorporation of active materials. Agarose is one of the most widely used thermo-reversible hydrogelators and has been widely used, for example, in the fields of biomedical engineering, separation science and catalysis [14]. In agarose, the hydrogel 3D network results from entangling of the nanofibers, with left-handed double helices of the co-polymer self-assembling via hydrogen bonding between axial hydroxyl groups on galactose rings [15]. Many different guest mole-

* Corresponding author at: School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China. Tel.: +86 10 68911608; fax: +86 10 68911608.
E-mail address: zhangxtchina@yahoo.com (X. Zhang).

0379-6779/$ – see front matter.
doi:10.1016/j.synthmet.2009.08.002

cules have been physically or chemically included into the agarose hydrogel [16], however none of them have previously been included with the purpose of tuning the optical activity of the agarose hydrogel.

Herein, we present a 'wet' process to incorporate different contents of chiral polyaniline nanowires into the agarose and hence tune the chiroptical properties of the hydrogel. The chiral polyaniline nanofibers were synthesized by using two different oxidants potassium tetrachloroaurate (PTC) and ammonium persulfate (APS) in sequence to oxidize aniline in the presence of a chiral inducing agent (1*S*)-(+)-10-camphorsulfonic acid ((*S*)-(+)-CSA) or (*R*)-(−)-CSA. The optical activity of the chiral polyaniline varies as a function of the mass ratio of PTC to APS, with the highest optical activity being observed in the ratio range from 1.0 to 2.5. Intriguingly, a potentially useful by-product, gold microspheres resulted from the reduction of PTC, is formed during this polymerization process. The chiroptical properties of the polyaniline nanofibers are retained within the composite hydrogel, although the degree of chiral organization of the polyaniline appears to be somewhat modified by the presence of the agarose matrix.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma–Aldrich Company Ltd. Aniline was purified by distillation before use. Other reagents were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis

One-pot synthesis of chiral polyaniline nanofibers and gold microspheres: In a typical procedure, 0.1 mL aniline (1.1 mmol) and 1.75 g (*S*)-(+)-CSA or (*R*)-(−)-CSA were dissolved in deionized water (0.75 mL). The mixture was stirred at room temperature. 0.164 g $KAuCl_4$ (0.4 mmol, dissolved into 0.2 mL deionized water) and 0.15 g $(NH_4)_2S_2O_8$ (0.6 mmol, dissolved into 0.3 mL deionized water) were added, respectively in 2 and 3 separate portions [8] in sequence into the above mixture with vigorous stirring. The intervals for the same oxidant portions were 0.5 h, however the interval for the different oxidant portions was 1.0 h. After the reaction, the resultant material was filtered and washed alternately with deionized water and methanol several times. Finally the product was easily separated into the pure polyaniline nanofibers and gold microspheres by taking advantage of a repetitive dispersion–precipitation process, with the gold microspheres sedimenting first from the aqueous mixture.

2.2.2. Inclusion

Inclusion of polyaniline nanofibers in agarose: In a typical procedure, 2% agarose (type I-B) 75 °C hot sol (1 mL) was mixed with a suspension of the polyaniline nanofibers (2 mL) (the concentration of the nanofibers was measured and adjusted by the UV absorbance). The composite hydrogel was obtained by cooling down the mixture under ambient conditions to the room temperature.

2.3. Instrumentation

The products were characterized using LEO field-emission-gun scanning electron microscope at 3 kV and FEI Tecnai G^2 transmission electron microscope at 120 kV. Samples for electron microscopy were prepared by placing a droplet of as-made product suspension or by scratching a piece of hydrogel onto a silicon wafer for the field-emission-gun SEM and carbon-coated copper grid for TEM, respectively. All samples were dried under ambient conditions.

UV spectra were obtained on a Jasco V-560 UV/Vis Spectrophotometer. CD spectra were acquired on a Jasco J810 Spectrophotometer, calibrated with a reference standard (ammonium d-10-camphor sulfonate, Jasco standard) prior to the actual experiments. All the spectra were recorded in 800–200 nm range using a 10 mm rectangular cell path length. The following parameters were used: 2 nm bandwidth, 20 nm min^{-1} scan rate, 4 s time constant and 1 nm step size. All spectra were solvent baseline subtracted and acquired at room temperature.

3. Results and discussion

The enantioselective synthesis of chiral polyaniline in their doped states has been achieved by oxidizing aniline in the presence of either (*S*)-(+)-CSA or (*R*)-(−)-CSA. Two different oxidants, PTC and APS, were employed and were added stepwise in sub-stoichiometric portions. Initially, we employed a PTC:APS molar ratio of 2:3.

The UV absorption spectra of aqueous suspensions of the products in Fig. 1a are typical of emeraldine salt of polyaniline with molecular absorption around 355 and 435 nm and a polaron band in the near IR [17]. The profile of CD spectra in Fig. 1b confirms the strong optical activity for the polyaniline synthesized in the presence of either (*S*)-(+)-CSA or (*R*)-(−)-CSA. As expected, the CD

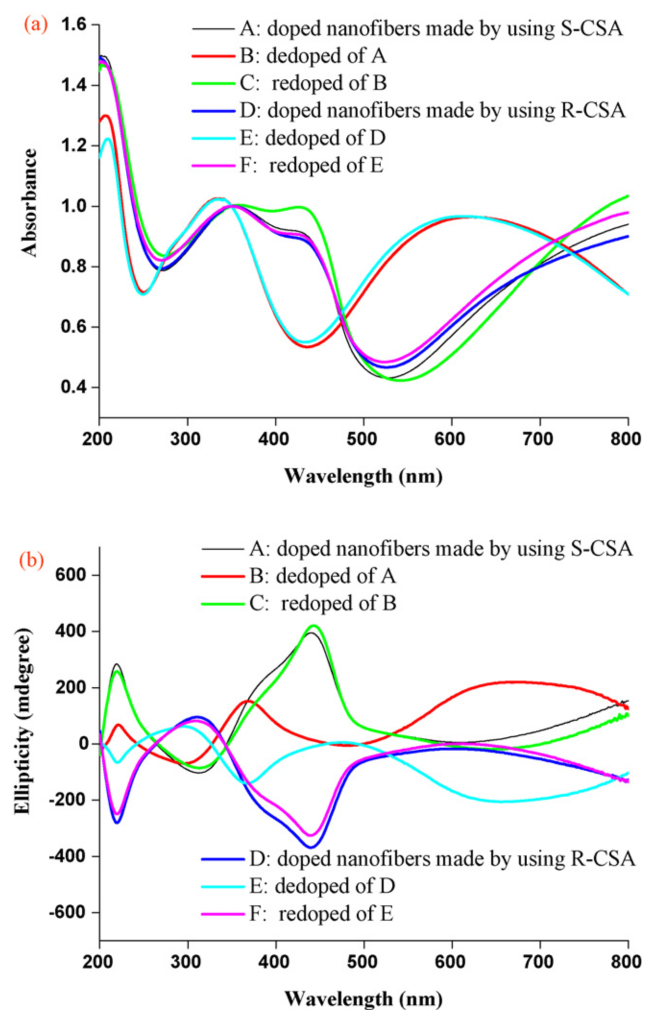

Fig. 1. UV (a) and CD (b) spectra of water-dispersed chiral polyaniline nanofibers (oxidant molar ratio of PTC to APS is 2:3).