Organic Electronics 14 (2013) 1419–1423

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Anomalous charge transport in multiple interconnected polyaniline nanofibers

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ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form 1 March 2013
Accepted 1 March 2013
Available online 19 March 2013

Keywords:
Polyaniline
Interconnected nanofibers
Magneto-transport
Magnetic and electric field dependence
Temperature dependence
Morphology dependence

ABSTRACT

We report the unusual charge transport phenomena in polyaniline nanofiber networks and its dependencies on temperature, applied magnetic and electric field, and on the type of fiber morphology. The conductivity of nanofiber networks follows quasi 1-D variable range hopping (VRH) and demonstrates a peak at ~240 K in samples with high density of interfiber intersections. This anomalous peak of conductivity is attributed to change in the interfiber contact resistance with temperature. In all polyaniline nanofiber networks, positive and negative magnetoresistances (MRs) are observed and accounted for by shrinkage of localized electron wavefunctions and suppression of quantum interference among possible tunneling paths by magnetic field. We found that the magnitude of both positive and negative MR gets smaller with decreasing density of interfiber intersections and can be explained by decreasing of hopping barriers as well as decreasing of number of current pathways within VRH network. We also detected that the magnitude of MR in polyaniline nanofiber networks is affected by the applied electric field which we propose is due to field-induced suppression of the hopping activation energies.

1. Introduction

Conducting polymers have attracted attention for the last decades due to their unique and tunable electrical, optical and structural properties [1]. These features come from the chain structure of polymers. The chains interact in very complicated ways and form irregular network for charge transport (for description of such conducting networks see, e.g. models [2,3]). Recently, various synthesizing methods [4–7] have been developed for preparing polymer nanofibers.

The conducting polymer nanofibers are interesting due to possible nanotechnology applications [8–11] and differ from conducting polymer films with complex morphology, higher disorder and nano-scale confinement [12,13,8,14]. Electrical transport properties of single polymer nanofibers and nanofiber pellets have been reported previously, particularly for polyacetylene, polypyrrole and polyaniline [12,15–19]. Long et al. [20,14] reported that junction resistance of crossed nanowires is much larger than the intrinsic resistance of a single nanowire. An anomalous peak in the temperature dependence of conductivity for nanofiber films was reported by Adetunji et al. [21] and attributed to nature of the interfiber contacts based on optical and transport studies in polyaniline nanofiber films and pellets. Although these studies provide insight into the anomalous transport behavior of polymer nanofibers [1,9,16,17,21], the mechanisms governing the anomalous charge transport in multiple interconnected nanofibers have not been fully identified. Better understanding of the transport in polymer nanofibers is required for integrating them into

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http://dx.doi.org/10.1016/j.orgel.2013.03.001

future applications such as efficient solar cells, displays, nano-diodes and transistors.

In this Letter, we report the transport phenomena in multiple interconnected polyaniline nanofibers and determine the effects of nanofiber morphology, temperature, magnetic field and electric field on charge conduction. Experimental results for polyaniline nanofiber network samples which have different density of interfiber intersections have been compared and analyzed. We report the evanescence of the conductivity peak as the number of nanofiber intersections through which the electrical charges transport decreases. This morphology sensitive transport phenomena in nanofiber networks can be explained by high conduction barriers at the nanofiber intersections and their temperature dependent mechanical nature. We also determine that both positive and negative magnetoresistances (MRs) observed in polyaniline nanofiber networks scales with the density of nanofiber intersections. Long et al. previously reported positive MR at low temperatures for isolated nanofibers and compared with MR of nanofiber pellets in which the morphology is destroyed under high pressure. However no negative MR has been reported for single nanofibers [22,23]. In addition to morphology, temperature and magnetic field dependencies of magneto-transport, we demonstrate that MR depends on the applied electric field [24]. Here, detailed DC electrical transport results of various polyaniline nanofiber samples and possible mechanisms responsible for the magneto-transport behavior are discussed.

2. Experimental

The camphorsulfonic acid (CSA) doped polyaniline (PANI) nanofibers used in this study were synthesized via dilute chemical oxidative polymerization as previously reported in [24,25]. In order to understand the effect of the fiber morphology on transport properties, we prepared three types of PANI–CSA nanofiber network samples: dense (Fig. 1a), dilute (Fig. 1c) nanofiber networks and nanofiber micro-clusters (Fig. 1e) in which the charge transport is through different number of nanofibers and nanofiber intersections. For dense and dilute nanofiber network samples, PANI–CSA dispersion of different dilutions were dropped cast on gold electrodes (30–100 μm separation) that were prepared by photolithography on glass substrates. For PANI nanofiber micro-cluster samples, first the dilute dispersion was placed between gold electrodes (separation of 30 μm). Then using a scanning electron microscopy (SEM) a nanofiber cluster was selected and two platinum wires were deposited between the cluster and the gold electrodes by focused ion beam (FIB) deposition (FEI Helios Nanolab 600). A Keithley 2400 SourceMeter was employed to apply constant current and measure voltage. Four-probe techniques were used for transport measurements in dense/dilute nanofiber networks. In PANI nanofiber micro-clusters two probe measurement is used (four-probe measurement could not be configured due to restricted connection area). Applied current was limited to 100 nA in order to prevent damaging of the fibers in micro-clusters. All the magneto-transport measurements were conducted in a controlled environment (Quantum Design physical property measurement system chamber) for temperatures 2–250 K and magnetic fields up to 8 T which were applied perpendicular to the nanofiber network plane. Magnetoresistance is defined as $MR = [R(H) - R(0)]/R(0)$ where $R(0)$ and $R(H)$ are the resistances of the system within zero and non-zero magnetic fields. The conductivity of dense nanofiber network is calculated using the width of the electrodes and the gap between them. To determine the thickness of the network, a profilometer was used. The absolute conductivity of the dilute nanofiber network could not be determined due to random width and thickness of the conduction path. The dimensions of the nanofiber micro-clusters are estimated from SEM and used for conductivity calculations.

3. Results and discussion

Fig. 1 shows the SEM images and temperature dependences of the conductivity for nanofiber network samples in which the charge transport is through differing number of nanofiber intersections. We determined that as the number of interfiber contacts through which the charge carriers are traveled increases, the temperature dependent part of conductivity (e.g. $\rho_{300K}/\rho_{25K} \sim 10^3$ for dense nanofiber networks, ~6 for nanofiber micro-clusters) becomes more dominant. The strong temperature dependence of conductivity for dense nanofiber networks is proposed to originate due to large energy barriers at the nanofiber crossings. Despite the difference in ρ_{300K}/ρ_{25K}, for all of our polyaniline nanofiber network samples the conductivity follows quasi-1D variable range hopping (VRH) described by,

$$\rho(T) = \rho_0 exp(T_0/T)^{1/2} \quad (1)$$

Similar quasi-1D VRH behavior was previously reported for doped PANI [26] and poly (o-tuoluidine) films [27]. From the linear fit of $\ln\rho$ vs $T^{-1/2}$, T_0 that reflects the effective energy barrier between the localized states, is determined to be 2850 K and 45 K for the dense nanofiber networks and nanofiber micro-clusters, respectively. The typical calculated room temperature conductivity in nanofiber micro-clusters ($\rho_{RT} \sim 3.0\ \Omega^{-1}\ cm^{-1}$) is by an order of higher than the one of dense nanofiber networks (ρ_{RT} - $\sim 0.35\ \Omega^{-1}\ cm^{-1}$). The lower conductivity in dense networks can be explained by lower density of nanofiber contacts within the random conduction path.

An anomalous peak is observed at 240 K in the temperature dependent conductivity for dense nanofiber networks. The conductivity peak diminishes as the number of interfiber contact decreases and entirely vanishes in nanofiber micro-clusters that have only a few nanofiber intersections (Fig. 1e). The conductivity peak in nanofiber networks can be attributed to interplay between two competing transport mechanisms. The first one is the phonon-assisted hopping within the nanofiber system that follows quasi-1D VRH. The former is the transport at interfiber intersections which changes with temperature dependent mechanical contacts. As the temperature is lowered from room-temperature to 240 K, interfiber contacts become more robust and the