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Enhanced actuation of PPy/CNT hybrid fibers using porous structured DNA hydrogel

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ABSTRACT

A high-surface-area material has recently attracted interest in actuator systems. We report on improved performance of the simultaneous electrochemical linear actuation of conducting polymer (CP)/carbon nanotube (CNT) hybrid fibers using porous structured deoxyribonucleic acid (DNA) hydrogels. It was deduced that individual DNA-wrapped CNTs had efficiently doped the PPy on its inner and outer surface through the association of PPy with the DNA via a supramolecular interaction. To assess the potential of the PPy/DNA/CNT hybrid fibers for use in electrochemical capacitors and actuators, we showed that the redox response of the hybrid fibers was improved by the addition of DNA to the PPy/CNT film. The values of the measured electrochemical capacitance (∼371 F/g in a lithium bis(trifluoromethylsulfonyl)imide aqueous solution, where the joint mass of PPy, DNA, and CNT was considered) were higher than those of previous CNT/PPy composite films with a controlled pore size (∼250 F/g). The fibers showed actuation stability with an expansion and contraction of ∼4.41% under a low potential (±1 V). DNA/PPy/CNT hybrid fibers will form the basis for new intelligent materials for applications such as bio-artificial muscles.

1. Introduction

Conducting polymer (CP)/carbon nanotube (CNT) hybrid materials are attractive for some applications, such as actuators and sensors [1,2], and several studies have demonstrated that they enhance electrochemical properties, such as actuation performance. Spinks et al. first discussed the actuation of polypyrrole (PPy)/CNT hybrid materials [2]. However, the PPy component did not have an influence on the composite, and actuation performance of the hybrid was similar to that of actuators composed of CNT alone because of the insufficient space to induce movement in the nanotubes themselves [3]. Subsequently, Kim and co-workers developed PPy/CNT composite films with controlled pore sizes using silica substrates that allowed control of their capacitance [4]. However, the actuation performance of these materials has not been reported on. The porous material must be flexible enough to allow improvement of the actuator. A CNT-based matrix is attractive for applications but is not flexible enough because of the lack of a suitable binder [5]. A high-surface-area material has recently attracted interest in actuator systems [6]. Highly porous structures provide a relatively high active surface area and render the facile electrolyte diffusion into bulk materials [7]. It is conceivable that, using these porous materials, higher strains could be attained in the future [8].

Using deoxyribonucleic acid (DNA) as a dopant can enhance the quality and electrochemical and mechanical stability of CPs because of the hydrogen bonding interaction between DNA and PPy [9,10]. DNA induces an increased active CP mass, and the CP can mitigate the weakness arising from the binding between the CNTs. In our previous work [11,12], DNA hydrogels with an entangled network were chosen as an attractive template. DNA hydrogels are good candidates for improved actuation with PPy/CNTs, as DNA is negatively charged in an aqueous solution [13], making it possible to use DNA as a counteranion for PPy formation incorporated in a DNA hydrogel with a high number of pores. Here, electrical stimulation will result in the reduction of the PPy backbone, achieving a hybrid fiber with high surface area.

Consequently, PPy/CNT hybrid fibers may improve electrochemical actuation and capacitance, as PPy/CNT hybrid fibers with a high surface area can assist electrolyte diffusion into the PPy/CNT hybrid fibers and provide transport channels for the conductive ions. Here, we report on improved performance of the simultaneous electrochemical linear actuation of PPy/CNT hybrid fibers using porous structured DNA hydrogels.

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2. Experimental

2.1. Materials and preparation

The DNA (double strand, salmon sperm, 20,000 base pair (bp)) used was purchased from Sigma–Aldrich Chemicals (St Louis, MO, USA). The room temperature ionic liquid used, 1-ethyl-3-methyl imidazolium bromide ([emim]Br), was purchased from the Solvent-Innovation Co. (Koln, Germany). All other chemicals were used without further purification. The SWNTs (HiPCO, CNI) were used as purchased and contained a 5 wt% iron residue, as determined by elemental analysis. The pyrrole, LiTFSI, bytron, and ethanol used were purchased from Sigma–Aldrich Chemicals (St Louis, MO, USA).

To fabricate the fibers, DNA/CNT fibers were prepared according to the modified procedure of Lee et al. [14]. Chemical oxidative polymerization of DNA/CNT-doped PPy was carried out in an aqueous solution containing LiTFSI as the dopant and bytron as an oxidant. The pyrrole monomer was purified by distillation under reduced pressure and stored in a deep-freezer at −5 °C before use. The molar ratio of monomer to dopant was 1:1. The weight percentages of bytron (oxidant) used were 50%, 100%, and 200% to prepare polymers with various doping concentrations. The DNA/CNT hydrogel fibers were swollen for a period of 15 min until the equilibrium state was reached. In the case of swollen DNA/CNT hydrogel fibers, the entire mixture containing the monomer, dopant, and oxidant was allowed to react for a period of 17 h at 4 °C. The samples obtained after 17 h were washed with a 50 wt% ethanol solution and then dried at room temperature for a period of 30 min.

2.2. Characterization

The structure of the DNA/CNT/PPy hybrid fibers was examined using an SEM (Hitachi Model S4700, Japan). A TEM (Tecnai-12, FEI, USA) was also used to confirm the structure of the fibers, and the images were acquired using a CCD camera (Multiscan 600W, Gatan, USA).

A three-electrode electrochemical cell coupled to a CHI 600B potentiostat (USA) was used for the cyclic voltammetry and actuator tests. A hybrid fiber was used as the working electrode with an Ag/AgCl reference electrode and a Pt mesh counter electrode. In the actuator tests, the sample was held vertically in the electrochemical cell with the bottom end of the fiber firmly clamped and the top end of the fiber connected to the lever arm of a dual mode force sensor/controller (Aurora Scientific) with an AD Instruments MacLab interface. The fibers were allowed to equilibrate over a period of several hours under a desired tensile load in a 0.1 M LiTFSI electrolyte. The specific capacitance, Cmass, was derived from the current plateau (at ±1 V), I, for a given scan rate, v, and the weight of the DNA/PPy/CNT hybrid fiber, m, (where $\text{Cmass} = I/(v \times m)$).. The mechanical tests were performed with the fibers submerged in a 0.1 M LiTFSI electrolyte using a dual mode force sensor/controller.

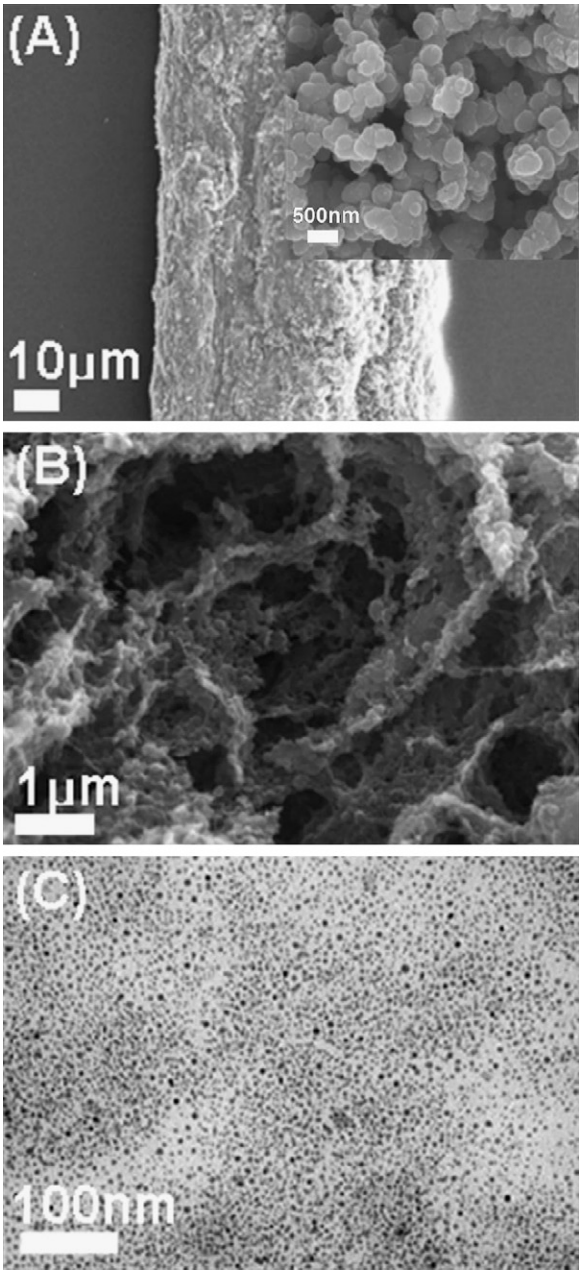

Fig. 1. (A) SEM images of DNA/PPy/CNT hybrid fibers showing that chemical polymerization occurred to form the hybrid fibers, which were then dried. The inset image shows the surface morphology of a uniformly deposited PPy layer on a CNT/DNA hydrogel fiber. (B) An image of the round cross-section of DNA/PPy/CNT hybrid fibers showing uniformly deposited PPy on the porous structure of the CNT/DNA hydrogel fibers. (C) A TEM image of the cross-section of a DNA/PPy/CNT hybrid fiber.

3. Results and discussion

DNA/PPy/CNT hybrid fibers were easily obtained by chemical polymerization. Scanning electron microscopy (SEM) images indicated that the PPy was uniformly deposited on the nanoscale on the outer surface of DNA/CNT hydrogel fibers (Fig. 1A, inset). A closer examination of the fiber cross-section (Fig. 1B) showed that the PPy had deposited on the porous structure to form a network of individual DNA-wrapped CNTs with an entangled structure. Fig. 1C shows a cross-section of a DNA/PPy/CNT hybrid fiber obtained using a transmission electron microscope (TEM). The size of PPy dot was ∼10 nm, and they were uniformly deposited on the entire surface of the hybrid fiber. It was deduced that individual DNA-wrapped CNTs had efficiently doped the PPy on its inner and outer surface through the association of PPy with the DNA via a supramolecular interaction [15].

To assess the potential of the PPy/DNA/CNT hybrid fibers for use in electrochemical capacitors and actuators, we measured their electroactivity in liquid electrolytes using cyclic voltammetry (CV). Fig. 2 shows that the redox response of the hybrid fibers was improved by the addition of DNA to the PPy/CNT film, as observed in a previous paper [15]. Our composite fibers were formed using relatively immobile DNA/CNT hydrogel fibers as the charge-balancing anionic dopant during the polymerization of PPy. In the reduced state, the PPy chains are neutral, and the negative charge on the physically entrapped and anionic DNA/CNT must be