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Microfibers from interpolymer complexation of κ-carrageenan and oligomers of polyaniline for glucose detection

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ABSTRACT

The molecular order and orientation significantly influence the physical properties of conjugated polymers and the corresponding performance in electronic devices. The precise synthesis and characterization are the challenges to obtain high quality polymer crystalline micro/nanostructures, on the basis of which, the charge transport mechanisms can be discussed and the device performance can be improved. A micro-fibrous complex of conductive polymer and natural polysaccharide has been formed during the in situ polymerization of aniline in the aqueous solution of κ-carrageenan. With the template of the polyanion, aniline is polymerized and polyaniline (PANI) chain grows in the vicinity of sulfonic acid groups. Through the comprehensive characterizations of UV–vis spectra, wide-angle X-ray diffraction, and thermal gravimetric analysis, the assembly structure of the interpolymer complex has been illuminated, i.e., oligomers of PANI with expanded conformation are formed, the electrostatic interaction between the protonated PANI oligomers and anionic κ-carrageenan makes the chains of PANI and κ-carrageenan bound together, and a micro-fibrous complex is formed with enhanced orientation of both PANI and κ-carrageenan, leading to an enhanced conductivity of the complex. The glucose biosensor made of the complex shows high detecting sensitivity and broad linear range in the recognition of the glucose due to its high conductivity and good compatibility with the enzyme.

1. Introduction

There are some electrical devices such as biosensors and biochips for the recognition and quantization for particular biological matters, made of conductive polymers and bio-macromolecules such as protein, DNA and polysaccharides. In such a device, bio-macromolecules work for the recognition of an analyte, while the conductive polymers act as mediator for electron transfer in redox reactions, as well as the matrix for immobilization of the bio-molecules [1]. In other words, conductive polymers works as an electric wire connecting the redox center of the bio-macromolecules and the electrode to perform a direct electron transfer rather than by the diffusional mediated species. The understanding of the mechanism of such devices is still a challenge because of the complexity in structure and performance due to the synthesis and fabricating unexpectations. Nowadays the research on biosensors with conductive polymers is focused on the synthesis and characterization of nano-structured conductive polymers and its performance in the device [2,3]. The blends of conductive polymers and bio-macromolecules are of complexity in their multi-level and multi-dimensional structures, including heterogeneities in composition, phase geometry and interface morphology. Even in the mono-phase of conductive polymers, it is still of complex and heterogeneous structures in dispersive dimensions, in packed or entangled polymer chains and even in single chains [3,4]. The complexity in structures leads to the difficulties to investigate the distribution and displacement of the charge carriers along or among the polymers chains, and the difficulties to illuminate the working mechanism of the bio-devices and to repeat or to enhance the device performance.

In our previous work, in order to investigate the complex structures of the polymer blends in the devices and the relation between the structure and the electrical properties, the blends of κ-carrageenan, a natural polysaccharide, and several kinds of nano-structured polyaniline (PANI), i.e., nano-granules or nano-fibers with different aspect ratios, have been prepared through sol–gel process. The multi-level structures of PANIs have been characterized. The thermal analysis and dielectric relaxation

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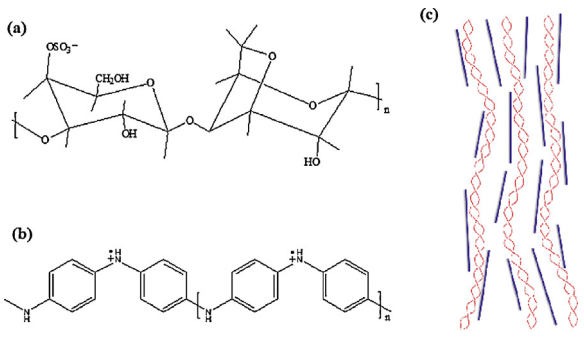
spectroscopy help to evaluate and to understand the chain relaxation and the interfacial structures of the blends. [5,6]

In this article, an interpolymer complex made of protonated PANI and κ-carrageenan, has been prepared by the oxidative polymerization of the aniline in the aqueous solution of κ-carrageenan and D-(+)-Camphor sulfonic acid (CSA). PANI protonated with CSA demonstrate the morphology of fiber or fiber network either in the aqueous solutions [7,8] or at the interface of an immiscible organic/aqueous system [9]. Li and Wang [10] have reported a novel approach to synthesize the chiral PANI nano-fibers in an aqueous solution of the chiral acid as CSA. κ-Carrageenan is a natural polysaccharide extracted from red algae, linearly composed of an alternating disaccharide repeating units of 1,3-linked β-D-galactopyranose residues, which are sulfated on position 4, and 1,4-linked 3,6-anhydro-α-D-galactopyranose. The repeating structure of κ-carrageenan is shown in Scheme 1(a). The molecules of κ-carrageenan exhibit the conformation of random coils at high temperature and in low ionic strength, while show another favored conformation of single helix at low temperature and in high ionic strength [11]. κ-Carrageenan is a strongly anionic molecule, at the presence of cationic ions such as K^+, Cs^+,Ca^{2+}, Mg^{2+}, the gel will be formed with the formation of some selective salt bridge [12,13]. Some polymer complexes or blends of polysaccharide and conductive polymers have been reported, such as κ-carrageenan with carbon nanotube (CNT) [14], β-1,3-glucan with PANI or CNT [15,16]. In those complexes, conductive polymers are considered in the hydrophobic cavity formed by the polysaccharide helix. In another complex of PEGylated curdlan and cationic polythiophene, the supramolecular complexation occurs between the strand of polysaccharide and the chiral conductive polymers [17]. In our work, the PANI is template polymerized in the presence of polyanion, growing in the vicinity of sulfonic acid groups, resulting in a product of non-stoichiometric interpolyelectrolyte complex or interpolymer complex [18]. So in this article the term of complex or complexation is used to describe the in situ polymerized product of PANI and carrageenan (noted as complex of PANI-Carr). Scheme 1 shows the chemical structures of the disaccharide repeating units of κ-carrageenan, PANI in protonated emeraldine salt, and the schematic of the complex prepared, interpolymer complexation of the helical κ-carrageenan with cationic PANI oligomers. We have observed that the complex of PANI-Carr is in morphology of microfibers, and proved those complex structures described in Scheme 1. The glucose biosensor made of the complex demonstrates high detecting sensitivity and broad linear range in the recognition of the glucose due to its high conductivity in charge transportation and large capacity to embed the enzyme.



Scheme 1. Chemical structures of (a) κ-carrageenan, (b) emeraldine salt of PANI, and (c) schematic of the complex of PANI-Carr, in which the short blue rod is PANI oligomers, and the red helix is κ-carrageenan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials

Aniline (99%), hydrochloric acid (HCl, 35 ~ 37 wt.%), and κ-carrageenan were purchased from Wako Pure Chemical Industries, Ltd. The molecular weight of κ-carrageenan was Mn = 9.3 × 10^4 g/mol, Mw = 1.4 × 10^5 g/mol, tested with gel permeation chromatography (GPC) by using pure water as fluent and calibrated by PEG standard samples. D-(+)-Camphor sulfonic acid (CSA) and ammonium peroxodisulfate (APS, 98%) were purchased from Nacalai Tesque Inc., Kyoto Japan. Aniline was purified by distillation under reduced pressure, APS was purified by re-crystallization. Glucose oxidase (GOx from *Aspergillus niger*, 100–250 U/mg) and D-(+)-glucose were purchase from Sigma–Aldrich.

2.2. Preparation

The polymerization of aniline was performed in the aqueous solution of polysaccharide with the weight concentration of 1%. APS was used as the oxidant and CSA as the doping acid. The concentration of the CSA was 0.1 mol/l, and the molar ratio between the aniline and APS was fixed at 4. In a beaker with 40 ml distilled water, 0.5 g κ-carrageenan (1 wt.%), 0.5 g aniline and 1.2 g CSA (0.1 mol/l) were fed, after the solutes were full dispersed and cooled to 8–10 °C, 0.3 g APS dissolved in 10 ml water was dropped into the solution slowly. The polymerization was allowed to continue 18 h, and the temperature was controlled between 8 and10 °C, the color of the solution turned to dark green and the viscosity increased gradually. After the reaction was completed, the whole solution was poured into 200 ml ethanol, the precipitation was filtered, then washed with ethanol and acetone for several times. The obtained solid product was termed as Complex PANI-Carr. The elemental analysis showed that molar ratio of C and N is 13, S:N is 0.6, here the origin of S was both from CSA and carrageenan. Since C:N in PANI is 6 and C:S is 12 in carrageenan and 10 in CSA, so in the complex the molar ratio between PANI and carrageenan monomers was about 2:3, and mass ratio was about 1:1. In comparison, PANI was prepared in the aqueous solution of APS and CSA without κ-carrageenan, following the same polymerization conditions. The difference between the synthesis of PANI-Carr and PANI is that at the end of the polymerization of complex PANI-Carr, the viscosity of the solution became high, which was not observed in the PANI preparation. The product of PANI was in powder-form, and that of PANI-Carr was in pieces.

The blend of PANIs and κ-carrageenan (blend PANI-Carr), as well as the κ-carrageenan film solely, was prepared for comparison. The aqueous solution of κ-carrageenan with the concentration of 1.5 wt.% was made at 50 °C, the powder of PANI prepared was grounded, ultra-sonically treated and mixed in the polysaccharide solution, the mass ratio of PANI and κ-carrageenan was 1:1. The solution was allowed to be cooled down at room temperature, the gel was soon formed, dried at room temperature and further dried in vacuum to remove the residual solvent.

The complex and blend were used to prepare an enzyme biosensor for glucose detecting. In the preparation of the electrode, firstly the glassy carbon electrode (GCE) was polished with 0.3 and 0.05 μm Al_2O_3 powder slurries, and sonically cleaned in distilled water for 5 min. The electrode was then treated with 1:1 (v/v) nitric acid solution for 5 min, ultrasonically cleaned in ethanol and water for 5 min, respectively, and dried at ambient temperature. The glucose oxidase (GOx) solution was prepared in PBS (pH 6.2) with the concentration of 5 mg/mL. The PANI-Carr complex or blend was dispersed in distilled water by sonication for 1 h, and mixed with