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Electrical and optical properties of bacterial cellulose films modified with conductive polymer PEDOT/PSS

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ABSTRACT

Composite films based on bacterial cellulose (BC) modified with conductive polymer PEDOT/PSS are synthesized. Structural, optical and electrical properties of such composite films are investigated. It was found that the obtained BC:PEDOT/PSS films characterized by strong absorption in the red and near-infrared spectral region and by weak intensity of photoluminescence at 300 K. The temperature dependence of the resistivity of the BC:PEDOT/PSS films follows a power law in the temperature interval 300–80 K and the resistivity values vary weakly with time. The charge carrier transport in the BC:PEDOT/PSS composite films governed mainly by the charge transport in the conducting polymer. The obtained BC:PEDOT/PSS films are promising for application as biocompatible electrodes, temperature sensors and other biochips, which are compatible with technology of printable organic electronics.

1. Introduction

Development of biocompatible nanochips based on functional organic and polymeric materials and their composites is an important area of current research in the world [1]. New composites based on biopolymers modified with organic or inorganic components are perspective and inexpensive materials for organic electronics and medicine [2]. Cellulose and cellulose derivatives as abundant and renewable eco-friendly materials have drawn growing attention [3]. Cellulose-based composites are promising for use as components of flexible polymer displays [4], biocompatible and biodegradable flexible OLEDs etc. [5]. In addition in recent years there has been growing interest in bio- and nano-cellulose for use in medicine as an effective non-drying nano-cellulose membranes, artificial blood vessels, material for tissue reconstruction, coating stents [6–8]. The investigation of hybrid nanosystems, including the cellulose as a matrix, modified with conductive polymers or metal nanoparticles (nanoclusters) is topical direction in the field of modern organic nanoelectronics and medical technology. Bacterial cellulose (BC) is a straight chain polysaccharide with the same chemical structure as cellulose. Compared with plant-based conventional cellulose, BC has an ultrafine nano-sized three-dimensional fibers network structure which attractive for many above mentioned applications. The structural, electrical and optical properties of functional composites based on BC and some conducting polymers such as polyaniline, polypyrrole etc. have been thoroughly studied recently [9,10]. The state of the art of recent results on BC synthesis, structure and its modification by different conductive polymers is given in Ref. [11]. At the same time, the issues associated with the development and investigation of composites based on BC and such soluble thermochromic conductive polymer complex as poly (3,4-ethylenedioxythiophene)-poly(4-styrenesulphonate) (PEDOT/PSS) [12] are still poorly studied until recently. Moreover there is no information about temperature dependences of the dc conductivity of BC/polymer composites in the literature till now.

In this work the composite films of BC modified with conductive polymer PEDOT/PSS were obtained, and their structural, optical and electrical properties were investigated. The obtained BC:PEDOT/PSS films have strong absorption in the red and near-IR

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region and are characterized by weak photoluminescence intensity at 300 K. The temperature dependence of the resistivity of the BC: PEDOT/PSS films follows a power law and varies weakly with time. The mechanism of charge carrier transport in the investigated composites is discussed.

2. Objects and methods

Samples of the nano-gel films bacterial cellulose were obtained by cultivation Gluconaccetobacter xylinus CALU 1629 surface cultivation conditions in a nutrient substrate containing 2% glucose, 0.5% yeast extract and 2% (vol.) ethanol [13]. Modification of the BC samples was carried out in an aqueous solution of the polymer–the thermochromic conductive polymer complex poly (3,4-ethylenedioxythiophene)-poly(4-styrenesulphonate) (PEDOT/PSS) [12]. The polymer used in our experiments–PEDOT/PSS–had the following parameters: the content of PEDOT ~0.5 wt. %, PSS ~0.8 wt.%, the concentration ~1.3 wt.% solution in H_2O, the band gap, Eg ~1.6 eV, the conductivity at 300 K ~1 S/cm, pH ~2.0 at 20 °C [14]. The polymer used in our experiments for modification of BC films was purchased in Sigma–Aldrich and used without further treatment. The chemical structures of BC [15] and conductive polymer complex PEDOT/PSS [12] are shown in Fig. 1a,b. Original BC and BC:PEDOT/PSS composite films were dried at temperature ~100 C. The thickness of the dried films without substrates was 50–60 microns, with maintaining of their rather good elasticity. Fourier transform infrared (FT-IR) spectra of the BC, PEDOT/PSS, and BC:PEDOT/PSS films containing ~10 wt% PEDOT/PSS were recorded with a FT-IR spectrometer (IR Prestige 21, Shimadzu Scientific Instruments) in the range of 400–4000 cm^{-1}. Each sample was placed and dried on the special glass substrate CaF_2 and then was subjected to analysis. Analysis of the absorption spectra of the BC, PEDOT/PSS, and BC:PEDOT/PSS composite films has been done using Varian Cary-50 spectrometer (190–1100 nm, resolution 0.1 nm). The morphology and microstructure of the composite films was investigated by atomic force microscope (AFM) Solver P47-NT-MDT. Analysis of the photoluminescence spectra (PL) of the BC and BC:PEDOT/PSS films was carried out using monochromator SPM-2 operating in the range λ ~ 300–830 nm and having a spectral resolution of 0.5 to 5 nm. Pulsed ultraviolet nitrogen laser LGI- 21 with a wavelength of 337.1 nm, pulse energy density over 10^{-4} J/cm^2 and a pulse duration of ~ 10^{-8} s has been used for PL excitation. The output PL spectra were recorded in the spectral range λ ~ 300–830 nm using a photo-multiplier FEU-136 at 300 K. The resolution of the entire system was ~ 2 nm. Measurements of Current–voltage characteristics (I–Vs) of the BC:PEDOT/PSS composite films were measured on the dc using two probe method in the temperature range 300 K–77 K using an automated setup based on picoammeter Keithley 6487 and programmable power supply AKIP −1124 within voltage range −5 V to +5 V. Samples were placed on the holder of an optical cryostat with temperature stabilization–optCRYO198. Electrical contacts to the samples were made using silver wire with conductive silver (SPI) and carbon (SPI) paints.

3. Results and discussion

The FT-IR reflectance spectra of BC, PEDOT/PSS, and BC:PEDOT/PSS films are shown in Fig. 2a and b. The bands at 3360, 2895, 1641, 1429 and 1042 cm^{-1} in Fig. 2a are associated with native BC [9,16]. A strong band at 3360 cm^{-1} arises from the stretching of hydroxyl groups. The bands at 2895 and 1641 cm^{-1} arise from C—H stretching and the H—O—H bending of the absorbed water respectively. The band at 1429 cm^{-1} relates to H—C—H in-plane bending vibration. A strong band at 1042 is due to the C—O—C ring skeletal vibration. Fig. 2b (curve 1) illustrates the FTIR reflectance spectrum of the commercially available PEDOT/PSS film (thickness ~150 nm). Bands at 1574 cm^{-1} (C=C), 1265 cm^{-1} (C—C) and 948 cm^{-1} (S—O) originate from the thiophene rings in PEDOT.

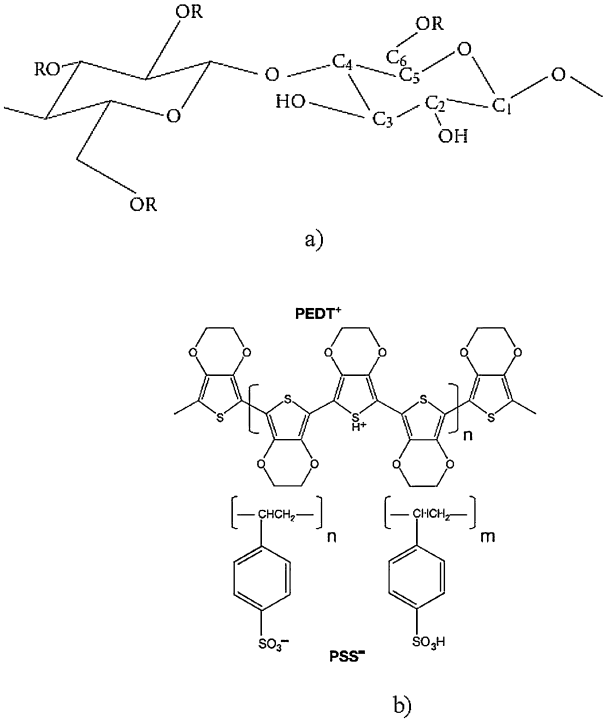

Fig. 1. Chemical structure of bacterial cellulose (a) and a conductive polymer complex PEDOT/PSS (b).

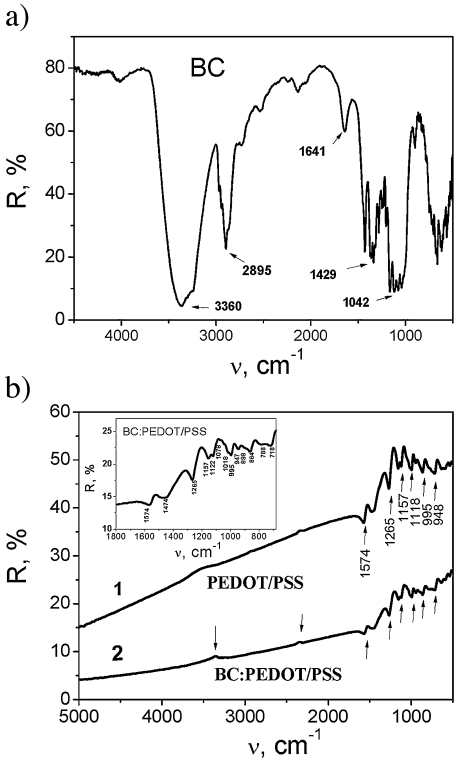

Fig. 2. (a) Reflectance FTIR spectra of the BC; (b) PEDOT/PSS (1) and BC:PEDOT/PSS (2) (and inset) films.