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Cellulose nanocrystals thin films as gate dielectric for flexible organic field-effect transistors

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ABSTRACT

We report on the fabrication of flexible field-effect transistor using poly[N-9''-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] as active channel and cellulose nanocrystals (CNC) as gate dielectric on indium tin-oxide coated polyethyleneterephthalate substrate. The use of CNC as gate dielectric material was found favorable for carrier transport at the semiconductor/dielectric interface with the device showing an on–off ratio of $\approx 10^4$. These results indicate that CNC is a promising gate dielectric layer for flexible organic field effect transistors.

1. Introduction

A transistor is a semiconductor device used to amplify and switch electronic signals and electrical power. It is composed of semiconductor material with three terminals. By applying a voltage it is possible to change the current flow. The development of new organic semiconductors for printable organic electronics has expanded over the last years for a variety of applications (i.e. RFID, sensors and memory) [1–3].

Flexible transistors are not so different with respect to traditional transistor apart from the substrate generally consisting of a plastic material, the channel made of an organic semiconductor that can be processed by solution processing and a polymeric gate dielectric.

The concept is now to develop electronic that has similar design of traditional electronic with applications for example in environmental sensors that dissolve eliminating the need for their reuse, portable devices that minimize the costs and health risks associated with recycling.

In order to develop such electronic devices, it is therefore necessary to find innovative solutions to the eco-sustainability problem of recycling materials for circuits [4].

Field-effect transistor based on polyvinyl alcohol as gate dielectric, 5,5′-bis-(7-dodecyl-9H-fl uoren-2-yl)-2,2′-bithiophene (DDFTTF) as organic semiconductor and poly(L-lactide-co-glycolide) (PLGA) as degradable substrate has been reported [5]. Deoxyribonucleic acid (DNA) has also been shown to be a potential candidate as gate dielectric in organic field-effect transistors [6].

From the environmental point of view, passive (i.e. gate dielectric) materials obtained by plant renewable sources not in competition with the food chain and integrated onto the device, should be formulated with the outcome to realize biodegradable devices.

Cellulose, one of the world's most abundant, natural and renewable biopolymer resource finds applications in many spheres of modern industry [7]. Nanocellulose (also called microfibrillated cellulose or nanofibrillated cellulose) is produced by delaminating cellulosic fibers. Cellulose molecule chains connect with each other through hydrogen bonding to form larger units known as elementary fibrils, which are packed into larger microfibrils with 5–50 nm in diameter and several micrometers in length. Nanocellulose has the appearance of a highly viscous, shear-thinning transparent gel.

Cellulose nanocrystals (CNC), extracted by an hydrolysis process uses sulfuric acid to remove the amorphous cellulose and form highly crystalline cellulose [8] that are typically rigid rod-shaped monocrystalline cellulose domains, 1–100 nm in diameter and from tens to hundreds of nanometers in length, depending on the species, cultivar and agronomical characteristics (e.g. plant maturity, characteristics of the soil) from which cellulose is obtained.

Among various conducting polymers, poly[N-90-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] (PCDTBT) along with its air stability is one excellent example for a low HOMO (-5.45 eV) as required by the 'ideal' π-conjugated polymers [9]. Thus, this promising material, as semiconducting

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material in the channel, and CNC as gate dielectric could be combined for the fabrication of organic field effect transistors with the requirements specified above.

One of the most common thin film transistor structures consists of source–drain electrodes that are on opposite sides of the semiconductor, identified as staggered. Inside these, bottom-gate structure exists, where the gate electrode is on bottom of the structure [10]. Such configuration takes into account the need to consider the process orthogonality for forming the channel, the gate dielectric and the electrode layers. The presence of C–O and O–H groups on CNCs could mimic the dielectric behavior of traditional oxide semiconductors. So it is a fair question to ask whether the use of CNC thin films acts as gate dielectrics for bottom-gate field effect transistors via solution-based deposition on plastic substrates in ambient conditions.

In this regard, in this work we report the use of cellulose nanocrystals as dielectric layer in organic field-effect transistors, fully processed at room temperature. The developed device can find application in advanced fields such as biodegradable electronic devices.

2. Experimental details

Cellulose nanocrystal (CNC) suspension was prepared from microcrystalline cellulose (MCC, supplied by Sigma Aldrich) by acid hydrolysis carried out with 64% (w/w) sulfuric acid at 45 °C for 30 min with vigorous stirring [11]. After removing the acid, dialysis, and ultrasonic treatment were performed. The resultant cellulose nanocrystal aqueous suspension was approximately 0.5% (w/w) and the yield was ca. 20%. The obtained CNC showed the typical acicular structure with the dimensions ranging from 100 to 200 nm in length and 5–10 nm in width as previously discussed [12]. FESEM analysis was performed with a Zeiss-Supra25 instrument. Fourier transform infrared spectroscopy (FTIR), in the 500–4000 cm^{-1} range, was carried out in a transmission mode on silicon substrate.

Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) (purchased from Aldrich, average molecular weight Mn 20,000) was adopted for this research. Fig. 1a shows the schematic structure employed for the fabrication of organic field effect transistor in the present work, which essentially is a bottom-gate top-contact configuration. We choose the ITO layer as bulk gate electrode to render orthogonal the electric field between the source–drain electrodes and the gate electrode and thus to the channel.

The gate dielectric layer was obtained by depositing 1 mg/mL aqueous solution of CNC onto indium tin-oxide (ITO) covered polyethyleneterephthalate (PET) foil (2 cm × 2 cm) (purchased form Sigma Aldrich, surface resistivity 20 Ω/□) by drop casting. The thickness of the CNC film was estimated to be about 140 nm by atomic force microscopy. The uniformity of the CNC film was checked recording by AFM several height profiles along the film cross section between covered and uncovered substrates. Dielectric measurements were performed on a HP4284A frequency response analyzer operable in the range from 100 Hz to 10 KHz.

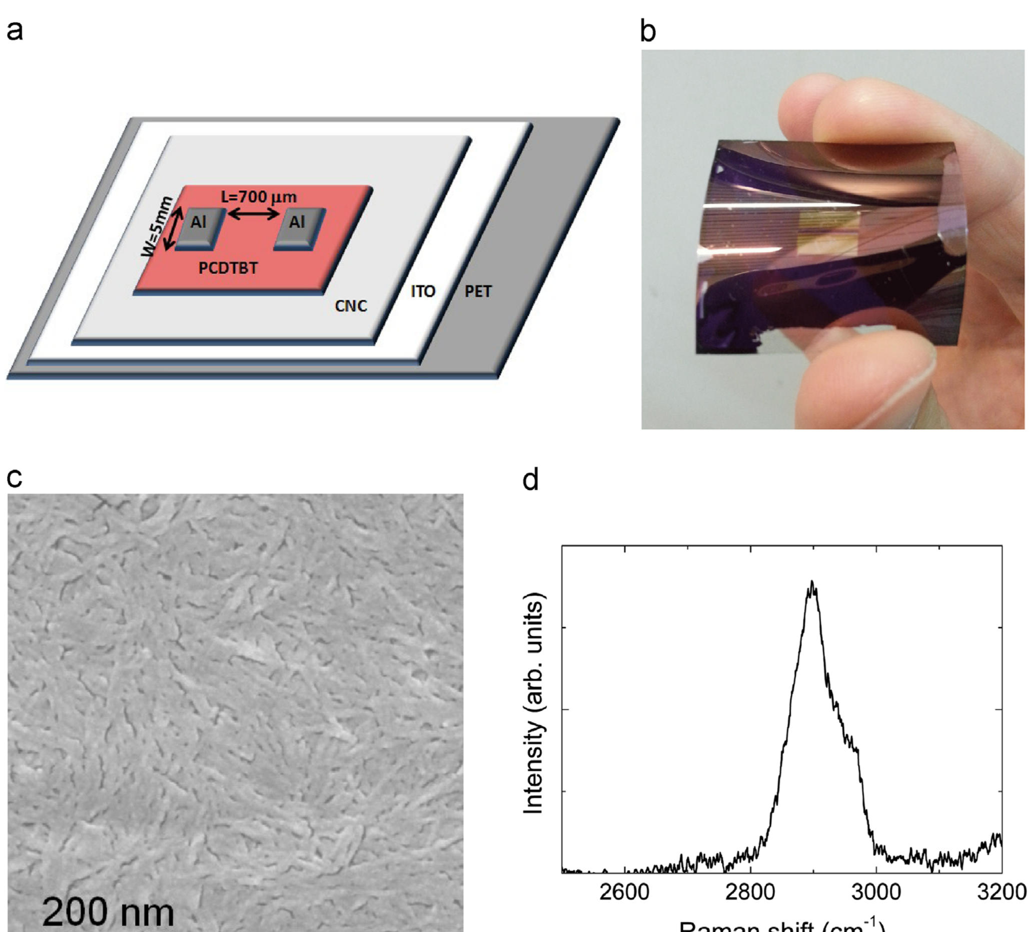

Fig. 1. (a) Schematic diagram and (b) photograph of the fabricated bottom-gate organic FET. (c) FESEM image of CNC gate dielectric layer and (d) Raman spectrum of the CNC film.