Strain Sensitivity of Carbon Nanotubes Modified Cellulose

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Abstract

Nanostructured cellulose was modified by different concentration and volume of dispersed multi-walled carbon nanotube (MWCNT) and double-walled carbon nanotube (DWCNT) solutions and its electrical properties were studied. The resulting flexible cellulose films have an electrical conductivity sensitive to changes in CNT concentration and immersion time in solution. The conductivity increases with increasing immersion time and volume and concentration of dispersed solutions; the conductivity for bacterial cellulose (BC) pellicles modified with DWCNT was increased from 0.034 S·cm\textsuperscript{-1} to 0.15 S·cm\textsuperscript{-1} and for BC pellicles modified with MWCNT it was increased from 0.12 S·cm\textsuperscript{-1} to 1.6 S·cm\textsuperscript{-1} when the immersion time was increased from 24 h to 72 h. These results are significantly higher than in previously reported work [1].

The effect of strain on the resistance during application of tensile force is shown for a simple strain gauge employing cellulose with incorporated DWCNTs. The electrical resistance of the films displays a high sensitivity to strain. It seems that this sensitivity depends on the modifying conditions, where BC pellicles which are modified in a dispersed solution with a higher concentration of CNTs show larger changes in resistance with the changes in fractional extension.

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1. Introduction

During the last decade, there has been a large interest in the development of different kinds of sensors based on nanostructured materials with high flexibility, high biocompatibility, low cost, and low weight [2-4]. Different types of carbon nanotubes (CNTs) have attracted a special interest of researchers due to their remarkable mechanical and electrical properties. It was shown that their electrical properties depend strongly on environmental changes so that for example a small mechanical deformation can significantly change the conductance of CNT-based resistors [5,6]. All these properties make CNTs a promising material to use in smart sensor systems.

Owing to its biocompatibility, being easy to modify and having a low cost, cellulose is a promising material to use as a substrate for conductive nanostructures in different applications [7,8]. Among various kinds of cellulose, bacterial cellulose (BC) can be an industrially viable material in the design of new electrical devices due to its mechanical and structural properties such as purity, high crystallinity, high mechanical stability, and low density [9].

Herein we report on a flexible electrically conductive nanocomposites based on BC modified with double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT). The conductivities of the resulting films have been compared and their behaviour has been studied as a function of induced strain.

2. Experimental

The BC was produced by Gluconacetobacter xylinum. DWCNT (+90% purity, Nanocyl) and MWCNT (+95% purity, Nanocyl) modified with carboxyl groups have been used as a conductive agents for impregnation of BC.

Dispersions with 1 mg/ml and 2 mg/ml CNT concentrations were prepared using surfactant cetyltrimethylammonium bromide (CTAB). 3×3 cm² BC pellicles were immersed in the CNT solutions for 24 h to 72 h. After treatment all samples were washed with deionized water. The pellicles were dried in a fume hood.

The total thickness of the dried BC films was 25-65 μm. A scanning electron microscope (SEM) has been used to observe the surface morphology of the samples (Zeiss Leo Ultra 55 FEG SEM). The electrical conductivity measurements were performed using a four-point probe system (CMT-SR2000N, AIT). In order to study the electromechanical properties of BC modified with DWCNT, constant tensile stress was applied using the Instron 5500 Material Testing System and the change in resistance was registered by a standard multimeter (Agilent 34401A).

3. Results and discussion

Cellulose samples modified with CNT characterized by the same flexibility as native cellulose. Films modified with MWCNT were uniformly black whereas the BC pellicles modified with DWCNT contain colorless parts. According to SEM MWCNT (diameter 10-16 nm, fig. 1a) are more homogeneously distributed on the BC surface comparing to DWCNT (diameter 5-8 nm, fig. 1b) which points to better dispersion of MWCNT.

In the case of the samples modified with the lowest concentration and volume an increase the immersion time did not give any significant effect on the electrical conductivity of the modified BC pellicles (fig. 2a). Therefore one could conclude that saturation capacity of cellulose for 1mg/ml DWCNT dispersions is not enough to form the conductive layer. However, by increasing the CNT concentration
and volume, conductivity raise significantly with the immersion time (fig. 2a) pointing to the substantial increase of the saturation capacity.

![Fig. 1. SEM image of BC modified with MWCNT (a) and DWCNT (b).](image)

The highest conductivities have been obtained for the pellicles modified in the 30 ml of 2 mg/ml solutions – 0.15 S·cm⁻¹ for DWCNT and 1.6 S·cm⁻¹ for MWCNT which is significantly higher than previously reported [1].

![Fig. 1. Conductivities of BC samples modified by DWCNT (a) and MWCNT (b) as a function of immersion time. Dependence of the fractional resistance on the fractional extension for BC sample modified with DWCNT during 72 h (c) and 24 h (d).](image)

The conductivity of the BC pellicles has been increased by one order of magnitude when the modifying agent was changed from DWCNT to MWCNT (figure 2b). Results received could be explained with formation of more homogeneous dispersions by MWCNT which is probably caused by...
higher CTAB/CNT surface ratio for MWCNT (specific surface area 115 m²/g [10]) comparing to DWCNT (specific surface area >500 m²/g).

For strain sensor applications, we need to have a material which is able to transfer strain into an electrical signal with high sensitivity. Fig. 2c shows the relatively large fractional increase in resistance with the fractional extension obtained by the application of tensile force for two samples of DWCNT modified nanocellulose. These two plots are related to the samples which are modified in different concentration of DWCNT dispersed solution. The nanocellulose pellicle which is modified with a higher concentration of DWCNT shows higher sensitivity to an increase in the strain.

In addition to the concentration of dispersed CNTs, the immersion time of the sample is another factor which appears to affect the sensitivity of the BC pellicles. Comparing fig. 2c and 2d shows that by increasing the immersion time from 24 h to 72 h, the sensitivity of the resistance to the fractional extension is increased.

4. Conclusion

Flexible DWCNT and MWCNT-incorporated films have been prepared by treatment of bacterial cellulose in CNT dispersions in the presence of CTAB. We show that the conductivity of the pellicles is related to the modification conditions such as the volume and concentration, immersion time and also to the type of modifying agent, where the MWCNT modified BC shows significantly higher electrical conductivity than the DWCNT modified pellicle under the same processing conditions.

Electromechanical measurements show that there is a strong sensitivity of the sample resistance to strain, implying a piezoresistive response of the material. This sensitivity seems to be related to the modifying conditions; samples which have been modified in higher concentration CNT solutions show a higher strain sensitivity.

References