Photo-electrical response of nanocomposites from single-walled carbon nanotubes incorporated in tris(keto-hydrozone) discotic mesogen

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Abstract. We report an experimental study on photo-electrical response of new nanocomposites produced from discotic mesogen LTTH-6 (possessing columnar liquid-crystalline phase) and single-walled carbon nanotubes (SWCNTs) with diameter ~ 1.5 nm. The SWCNTs were incorporated in LTTH-6 at concentration of 1 wt.%. Thin layers of SWCNTs/LTTH-6 nanocomposites were formed with a thickness of 3 μm. The light-induced change in electrical conductivity of these layers was ascertained at room temperature by current-voltage measurements, upon illumination with a low-intensity (~ 1 mW/cm²) continuous visible light. The effect of photoresponsivity of the glassy-like columnar phase of SWCNTs/LTTH-6 manifests the potential of such nanocomposites to be functional materials for applications in molecular electronics, sensorics and mechatronics.

1. Introduction

Discotic liquid crystals (DLCs) have disk-like molecules, consisting of a mesogenic core and flexible tails. The flat-shape molecules provide extensive π-orbitals above and below the main plane. This way, the multiple π-π interactions between the neighboring molecules promote the formation of long columns in phase-to-phase manner [1,2]. The most common liquid-crystalline (LC) states of DLCs are nematic (N) and columnar phases (Col) [3,4]. Depending on the specificity of the DLCs, the columns might be either simply arranged parallel to each other (N) or self-assembled in highly-ordered fashion, with hexagonal (Colh), rectangular (Colr) or oblique (Colob) styles [5].

As a new field of scientific and commercial interest, DLCs are used in nanocomposite design. Since the DLCs are known as 1D semiconductors, the alternation or new functional properties might be gained by combination of DLCs with different nano-sized species such as quantum dots, gold nanoparticles and rods, wires, nano-planes (such as graphene), carbon nanotubes (CNTs), fullerenes and others [3,4,6,7]. Such novel nanocomposite LC materials have found diverse applications in organic electronics, biosensing, energy storage, highly conducting flexible electrodes, large flexible wet-spin fibers, supercapacitors, etc. [6,8–10].

Here we study a new photoresponsive nanocomposite based on star-shaped tris-hydrazone discotic mesogen (henceforth called LTTH-6). In this LC material were incorporated single-walled carbon nanotubes (SWCNTs) with diameter ~ 1.5 nm, at concentration of 1 wt.%. Mesophase characteristics and the presence of columnar LC phase of these nanocomposites were established elsewhere [11]. The
aim of the present work is the estimation of the photo-electrical response of such LC nanocomposite materials that have $Col$ phase at room temperature, being of interest for organic electronics, sensorics and mechatronics.

2. Experimental

Details on the materials and preparation of samples, as well as characterization of structural homogeneity of SWCNTs/LTTH-6 nanocomposites, are given elsewhere [11]. LTTH-6 is a star-shaped discotic mesogen (figure 1). Single-walled carbon nanotubes (SWCNTs) (Meijo Nano Carbon Co., Ltd. Advanced Carbon Technology) of diameter ~ 1.5 nm were incorporated into LTTH-6 at concentration 1 wt.%. For preparation of SWCNTs/LTTH-6 nanocomposites, the organic solvent $N$-Methyl-2-pyrrolidone (NMP) was used as a good solvent for both LTTH-6 and SWCNTs. Important in our case is that the solvent evaporation was ultrasonically assisted. For this purpose, a Petri dish with the nanocomposite suspension was placed onto the surface of an ultrasound transducer. The ultrasound energy efficiency was ensured by water-based contact gel, placed between the Petri dish and the transducer. The area of the transducer and that of the dish was the same. The power of the ultrasound device was adjusted so that a slight solvent “fog” was invoked above the surface of the suspension.

![Figure 1. Molecular structure of LTTH-6.](image)

The homogeneity of the nanocomposite suspension was achieved by an innovative ultrasound (u.s.) drying process. It is important in our case, that the solvent evaporation was ultrasonically assisted. For the purpose, the suspension consisting of the solution from SWCNTs and the liquid crystal was placed in a Petri dish of about 3 cm diameter. The dish was fixed onto the surface of the head of the u.s. transducer operating at 1 MHz, whose area was the same as that of the dish. The u.s. energy efficiency was ensured by water-based contact gel, placed between the Petri dish and the transducer. The power of the u.s. device was adjusted so that a slight solvent “fog” was invoked above the surface of the suspension. The continuous u.s. power prevented the typical CNTs aggregate formation when the concentration of the solute increases during the drying process.

The dried nanocomposite was not self-supported. Some amount of the composite was placed between the walls of a cell with a gap of 3 $\mu$m, heated up to the isotropization point of the
nanocomposite and then cooled to room temperature. On this way were prepared thin layers with a thickness of 3 µm. Layers of SWCNTs/LTTH-6 nanocomposite with area ~ 50 mm² were sandwiched between two clean (untreated) glass plates with indium tin oxide (ITO) coatings that serve as electrodes. Layers with the same thickness between identical glass plates were also prepared from a neat LTTH-6, for comparative measurements. The neat LTTH-6 and SWCNTs/LTTH-6 nanocomposites were characterised by differential scanning calorimetry (DSC) using DSC 204 F1 Phoenix (Netzsch). According to a preliminary heating of the neat LTTH-6 and SWCNTs/LTTH-6 nanocomposite, the isotropisation point of both was established to be at about 190°C. Hence, the samples were heated up to 200 °C, kept at that temperature about 10 minutes and then cooled down. The DSC thermograms were analyzed in terms of the specific heat capacity $C_p = HF/v$, where $HF$ is the heat flow in mW/(g.K), and $v$ is the cooling rate in °C/s. The quantity $C_p$ experiences the change at second-order phase transitions. At constant $v$, $C_p$ is directly proportional to $HF$ (and $\Delta C_p \propto \Delta HF$, respectively).

To obtain the current-voltage characteristics, the current through the layers (perpendicular to the layer plane) was measured as a function of the voltage of the electric field applied transversally to the layer. Direct-current (DC) Volt-Ampere (V-A) characteristics were measured by computer-controlled potentiostat BioLogic SP–200. The DC voltage was linearly swept in the range 0 – 5 V by steps of 50 mV, at a scan rate 50 mV/s. Alternating-current (AC) V-A characteristics were measured by lock-in amplifier UHFLI (Zurich Instruments), interfaced to computer. Sinusoidal voltage sourced from the built-in generator of the lock-in instrument was linearly swept in the range 0 – 1 V by steps of 40 mV, at a scan rate 8 mV/s. The accuracy of the values of the measured current was ± 1 %, the voltage accuracy was ± 1 nV. The examined layers were illuminated with unpolarized beam from a He-Ne laser (Model HNL050RB from Thorlabs) (wavelength $\lambda = 632.8$ nm, power ~ 5 mW). Unfocused laser beam was directed normally to the sample. The laser beam has a low divergence (less than 1 mrad), TEM₀₀ spatial profile, Gaussian intensity distribution and a beam diameter (full width at 1/e² intensity level) of about 0.8 mm. In order to avoid any possible beam-induced effects of degradation of organic material caused by light absorption from the samples, the light intensity on the samples was attenuated to 1 mW/cm². During the measurements, identical experimental conditions were kept, only the exposure dose of the continuous light illumination was varied at a fixed temperature. The temperature of the layers was maintained by hot stage Mettler FP82 with thermo-stabilization automatics. The temperature accuracy was ± 0.1°C. V-A characteristics were obtained one after another in sequence within the temperature range from 20°C to 40°C.

3. Results and discussion

Figure 2 reports DSC scans of as-prepared SWCNTs/LTTH-6 nanocomposite, as well as the neat LTTH-6 in the range 20 °C to 200 °C. At room temperature, LTTH-6 exhibits a stable thermodynamic state in which below ca. 30 °C the $C_p$ line steeply drops (figure 2a) that suggests a change in the molecular motions – below 30 °C they are strongly hindered. The $C_p$ behavior of SWCNTs/LTTH-6 nanocomposite in the low-temperature range is similar (figure 2b), but the abrupt drop of the $C_p$ line takes place at about 25 °C, i.e., at slightly lower temperature than for the neat LTTH-6.
Figure 2. DSC thermograms recorded on heating of: (a) neat LTTH-6; (b) LTTH-6 with 1 wt.% SWCNTs. The heating rates were 10 °C/min in both cases.

By elevating temperature, two peaks in the DSC thermograms of the neat LTTH-6 were observed at ca. 70°C and 108°C, that can be attributed to crystal phase transition $Cr_1$–$Cr_2$ and crystal-to-columnar (Col) LC phase transition, respectively. Significantly, the thermograms in figure 2 demonstrate that the nanodopants substantially modify the LTTH-6 host, in particular the transition to Col state. This suggests a considerable disorder introduced from SWCNTs. Most probably, there is also a formation of SWCNT network in the bulk of SWCNTs/LTTH-6 nanocomposites.

After producing, the 3 µm-thin layers of SWCNTs/LTTH-6 nanocomposites studied in this work, they were heated up to temperature of the melting and then cooled. After cooling they remain in columnar LC ‘glassy’ state, as evidenced by DSC [11]. Thus, the Col phase takes place also at lower temperatures. The Col phase is not destroyed, but there is a local change in the mobility of the molecules – their motions are strongly hindered. This applies to both neat LTTH-6 and SWCNTs/LTTH-6 at temperatures below their melting points, including the room-temperature range from 20 °C to 40 °C which is of special interest in the present study.

Figure 3. DC Volt-Ampere characteristics measured for 3-µm thin layers of SWCNTs/LTTH-6 (a) and neat LTTH-6 (b), exposed on light ($\lambda = 632.8$ nm). Data obtained under identical experimental conditions, at temperature 26 °C, only varying the dose of the light exposure (0 means no light). (c) AC Volt-Ampere characteristics measured for the same LTTH-6 layer at frequency of the AC field $f = 1$ kHz.

Figures 3(a,b) present DC current-voltage dependencies measured for the studied thin layers of both SWCNTs/LTTH-6 and LTTH-6, being exposed to light, in our case – illumination with He-Ne
laser beam. It can be seen that at a given value of the voltage, the electrical current through the SWCNTs/LTTH-6 layer is gradually reduced by gradually increasing dose of the lightening (figure 3a). Comparison with figure 3(b) shows that such light-induced effect was absent by reference layer of LTTH-6 measured under identical experimental conditions. A supplementary measurement of V-A characteristics for the same LTTH-6 layer under AC electric field gave the same result (figure 3c). Reasonably, the large difference in the currents through LTTH-6 and SWCNTs/LTTH-6 is due to the well known high electrical conductive properties of SWCNTs, and especially of SWCNT networks [12–14]. Note that in our case the highly-conductive nanodopants were incorporated in the host LTTH-6 at relatively high concentration of 1 wt.%.

Figure 4(a) reports V-A characteristics of the same layer of SWCNTs/LTTH-6 (not illuminated), measured at various temperatures of the layer. As seen, the electrical current at a given value of the voltage is a decreasing function of temperature. The similarity between the light-induced and thermally-induced changes shown in figure 3(a) and figure 4(a), respectively, strongly suggests that the observed light-induced decrease in electrical conductivity occurs due to a local heating of SWCNTs/LTTH-6 nanocomposite. This results through absorption of the light by SWCNTs/LTTH-6 nanocomposite layer owing to the incorporated SWCNTs. Due to the large thermal conductivity of SWCNTs and their networks [15], the absorbed light energy is quickly transferred to a heat that does change the resistance of the SWCNTs/LTTH-6 nanocomposite. As reported for networks of SWCNTs, their resistance is increased as the temperature increases [16,17]. Most likely, such network is formed in the studied SWCNTs/LTTH-6 nanocomposite. For the sake of comparison, figure 4(b,c) shows V-A characteristics of reference layer with neat LTTH-6 measured identically, for which no thermo-induced change in electrical conductivity were present. The observed light-induced and thermally-induced changes in electrical conductivity will be further thoroughly investigated by means of complex electrical impedance spectroscopy (work in progress).

Figure 4. DC Volt-Ampere characteristics of the examined layer SWCNTs/LTTH-6 (a) and neat LTTH-6 (b), measured at various temperatures. (c) AC Volt-Ampere characteristics measured for the same LTTH-6 layer by varying the temperature. The frequency of the AC field was $f=1$ kHz.

4. Conclusion

New photoresponsive nanocomposite produced from discotic mesogen LTTH-6 and SWCNTs at concentration 1 wt.% was studied. The effect of SWCNTs embedded in the discotic liquid-crystalline material was established by DSC and electrical studies. It was found that at room temperature micrometer-thin layers of these nanocomposites exhibit photo-induced change in electrical conductivity, that can be activated by relatively low-intensity continuous light in the visible. The current-voltage characteristics of the SWCNTs/LTTH-6 layers clearly demonstrated that their electrical conductivity can be controlled by light, utilizing the controllable intrinsic thermal behaviour of the electrical conductivity of SWCNTs and SWCNT network formed in the SWCNTs/LTTH-6
nanocomposite. Certainly, this property would be of practical interest for optoelectronic applications, and the studied (eventually optimized) SWCNTs/LTTH-6 nanocomposites will be capable of serving as active layers for sensors, mechatronic and organo-electronic devices at ambient temperature.

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