

The redox nature of the resistive switching in nanocomposite thin films based on graphene (graphene oxide) nanoparticles and poly(9-vinylcarbazole)



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ABSTRACT

The effects of resistive switching were investigated in composite films based on multifunctional nonconjugated polymers such as poly(9-vinylcarbazole)—PVK mixed with particles of graphene (Gr) and graphene oxide (GO). The concentration of Gr and GO particles in the PVK matrix was varied in the range of 1–3 wt%, which is close to the percolation threshold in these systems. It was found that the effect of switching in structures of the form Al/PVK:Gr(GO)/ITO/PET manifests itself in a sharp change of the electrical resistance of the composite film from a low-conducting state to a relatively high-conducting state when applying a bias to Al–ITO electrodes of ~ 0.2 – 0.4 V, which is below the threshold switching voltages for similar composites. The cyclic voltammetric measurements of PVK:Gr(GO) films were carried out. It was found that the potential of redox transition of Gr/GO belongs to the interval of redox-switching voltage of PVK:Gr(GO)/ITO/PET composite films with effect of the resistive switching. The possible mechanism of the resistive switching, which is associated with the redox processes as well as with processes of capture and accumulation of charge carriers by Gr (GO) particles introduced into the matrices of the PVK polymer due to reduction/oxidation processes is discussed.

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1. Introduction

Polymeric and hybride (organic-inorganic) materials with electrical resistive switching effect have recently attracted much attention because their high operation speed, high density data storage, low power consumption, and low cost. Therefore they exhibit significant advantages over inorganic memory materials in the fabrication of volatile and nonvolatile memory devices [1–3]. Such polymeric and hybrid materials exhibit easy processability, good flexibility, high mechanical strength, and good scalability. They require very simple solution processes such as spin coating, dip coating and inkjet printing, which can be carried out at low cost and further are applied for high density memory devices. Recently some candidate polymeric materials including fully π -conjugated polymers with memory effects and their applications have been reported [3]. It was found that such materials to exhibit dynamic random access memory (DRAM) characteristics or write-once-

read-many-times (WORM) memory behavior without polarity, depending on the film thickness. Another interesting group of polymers is nonconjugated polymers containing carbazole moieties in the main chain or side group—poly(*N*-vinylcarbazole) (PVK) [4,5]. In general, the memory characteristics of a polymer have been found to depend on its chemical structure, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), conductivity, thickness and temperature of the polymer layer as well as the employed electrodes' work function. Their memory characteristics can also be influenced by the characteristics of their interfaces with the electrodes. In recent years, of particular interest is the use of new hybrid materials based on graphene (Gr) as nonvolatile memory devices, in particular, composites based on Gr particles and particles of graphene oxide (GO) enclosed in a polymer matrix. Owing to the unique properties of Gr, such as high charge carrier mobility, high thermal conductivity, and the possibility of the effective transport of charge carriers, including the ballistic transport at room temperature [6,7], it is a promising material for optoelectronics. The introduction of Gr and GO flakes into the matrix of semiconducting polymers makes it possible to significantly increase the mobility of

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organic field-effect transistors based on such composites [8,9]. Graphene flakes, being an effective medium for the accumulation of charge carriers, are considered as a promising material for hybrid (polymer–Gr particles) nonvolatile WORM memory cells based on the effects of resistive switching. A similar role is played by GO particles with the best solubility in polymer matrices as compared to Gr particles [3]. However, the exact nature of resistive switching mechanism of polymer–Gr memory devices is still a subject of debate; therefore development of polymer–Gr (GO) based memory devices remains in the exploration stage.

In this work we investigated the effects of resistive switching in composite films based on nonconjugated polymers – poly(9-vinylcarbazole) – PVK mixed with particles of graphene (Gr) and graphene oxide (GO). The concentration of Gr and GO particles in the PVK matrix was $\sim 1\text{--}3$ wt%. It was found that the effect of resistive switching in Al/PVK:Gr(GO)/ITO/PET films manifests itself in a sharp change of the electrical resistance of the composite film from a low-conducting state to a relatively high-conducting state when applying a bias to Al–ITO electrodes of $\sim 0.1\text{--}0.4$ V, which is below the threshold switching voltages for similar composites. The cyclic voltammetric measurements of PVK:Gr(GO) films were carried out. It was found that the potential of redox transition of Gr/GO belongs to the interval of redox-switching voltage of PVK:Gr(GO)/ITO/PET composite films with the effect of resistive switching. The possible mechanism of resistive switching, which is associated with the redox processes as well as with processes of capture and accumulation of charge carriers by Gr (GO) particles introduced into the matrices of the PVK polymer due to reduction/oxidation processes is discussed.

2. Objects and methods

We investigated the electrical and optical properties of composite films based on soluble in organic solvents multifunctional polymer – poly(9-vinylcarbazole) – PVK – $(C_{14}H_{11}N)_n$, average molecular weight $M_w \sim 1.1 \times 10^6$, band gap $E_g \sim 3.6$ eV and its composites with Gr particles from 200 to 300 nm in diameter (high temperature reduced graphene–HTRG) and GO particles from 400 to 500 nm in diameter. The concentration of Gr and GO particles in the polymer matrix of PVK was varied in the range of 1–3 wt%, therefore the samples of the composite films were at the boundary or below the percolation threshold in these systems. The molecular structures of the PVK polymer and GO [10] are shown in Fig. 1. The PVK polymer

and ITO/PET substrates used in our study were purchased from Sigma–Aldrich and then used without further treatment. The Gr and GO flakes were purchased from AkKoLab (Moscow, Russia) and were used without further modification. During the preparation of the samples, the PVK polymer was dissolved in chloroform, which was also used for the preparation of a colloidal solution of Gr and GO particles. The solutions were mixed and sonicated (Bandelin Sonopuls HD 2070, $f \sim 20$ kHz) for 3–5 min. The obtained 20% solution of the PVK with Gr (or GO) particles in chloroform (with a concentration of Gr or GO particles ranging within 1–3 wt.%) was applied to flexible PET substrates with ITO (In_2O_3/SnO_2) conducting layer, ITO/PET, (the surface resistivity of the ITO layer was $\sim 60 \Omega/cm^2$) by spin coating at 2500–3000 rpm, followed by drying at $\sim 80^\circ C$ for 20 min under nitrogen atmosphere. The thickness and morphology of the obtained PVK:Gr(GO) films on ITO/PET substrates were evaluated using a P47 Solver atomic force microscope (AFM) and amounted to $\sim 100\text{--}120$ nm. The absorption spectra of the composite films were measured on a Varian Cary-50 spectrophotometer. The photoluminescence (PL) spectra of the PVK, PVK:Gr and PVK:GO composite films were measured on a high sensitivity fiber optic spectrometer with ultralow light scattering AVANTES-AvaSpec-ULSi2048L-USB2 OEM operating in the spectral range of 322–1100 nm with a spectral resolution of 2 nm. PL was excited using an LGI-21 pulsed ultraviolet nitrogen laser with a wavelength of 337.1 nm, an energy density per pulse of more than $10^{-4} J/cm^2$ and a pulse duration of $\sim 10^{-8}$ s. The resolution of the entire system was ~ 2 nm. The current–voltage (I-Vs) characteristics of the PVK:Gr, PVK:GO composite films were measured under direct current at 300 K in a sandwich geometry after thermal evaporation of Al electrode on top of the PVK:Gr(GO)/ITO/PET structure using an automated measurement setup based on a Keithley6487 picoammeter in the voltage range from -5 to $+5$ V. The typical structure of a Al/PVK:Gr(GO)/ITO/PET samples for I–V measurements is shown in Fig. 2a. The electrochemical cyclic voltammetric (CV) measurements were performed in a three electrode glass cell. The experimental potentials were measured and given relative to a Ag/Ag(+) reference electrode in 0.1 M $AgNO_3$ acetonitrile solution (0.1 M electrolyte $TBAClO_4$ in acetonitrile (AN)). Its potential was 0.6 V relative to the standard hydrogen electrode. Argon or Nitrogen were passed through the solution to remove molecular oxygen. The CV measurements were carried out on an AUTOLAB PGSTAT 12 instrument (ECO CHEMIE, Netherlands) at

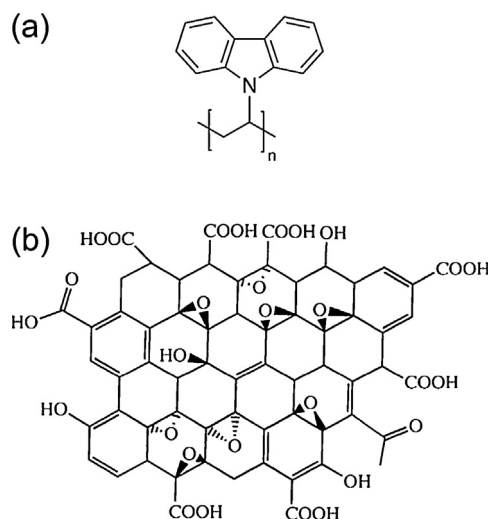


Fig. 1. Molecular structure of the polymers (a) PVK ($E_g \sim 3.6$ eV) and (b) graphene oxide [10].

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