Interfacial Effects on Resistive Switching of Polymer Films Embedded with Different Nanomaterials

Jian-Chang Li,* Wen Sui, and Yue Li

Vacuum and Fluid Engineering Research Center, Northeastern University, Shenyang 110819, P. R. China

Supporting Information

Abstract: The resistive switching of polymer films embedded with nanoparticles (NPs) has recently attracted great attention for the promising application in next-generation memory devices. In particular, the polymer/NP interface is believed to play a key role in affecting the electronic structure and charge transport of the nanocomposites films. Herein, interfacial effects on switching performance were studied by embedding different NPs so as to engineer the polymer/NP interface. An ON/OFF current ratio of >104 was observed in our device with the switching mechanism of charge trapping and detrapping. Using quantum-chemical calculations, we demonstrate that the interaction between polymer and NP can largely affect the electronic structure at the interface, resulting in different interfacial barrier. The transmission spectrum shows that the charge transport between polymer and NP may depend on the relative energetic position of the frontier molecular orbitals with respect to the Fermi level under the effects of bias. Our study may provide useful information for understanding the underlying physics of polymer memory devices.

Introduction

Organic bistable device is considered to be one of the potential candidates for next-generation nonvolatile memory applications owing to unique advantages such as low power consumption, high speed, and simple fabrication. In particular, polymer films embedded with various nanoparticles (NPs) may have a great promise as switching medium. For example, Song et al. observed electrical bistability in Al/poly(N-vinylcarbazole) (PVK)−Au/TaN device, and the switching is attributed to the electric-field-induced charge transfer between the PVK and Au NPs, while Chen indicated that the width of depletion region in Al−PVK or Au−PVK Schottky barrier plays an important role in affecting the switching behavior of Al/PVK−Au/Al device. The switching mechanism of Al/PVK−TiO2/ITO device may be governed by the filamentary conduction on account of TiO2 NPs and the defects within the PVK. The polythiophene interface was found to modify the energy level alignment due to dipole formation, which largely depends on the electronic states of both organic materials and NPs. By inserting a thin graphene layer at Al−polythiophene interface, the formation of a downward interface dipole can reduce the barrier for electron transfer from polythiophene to Al. Thermal evaporated thin Al layer (~5 nm) in Al/Alq3/Al/Alq3/Al memory device may function as the charge trapping/detrapping sites. Yang found that the thermal evaporated Al2O3 buffer layer (~4 nm) in Cu/Alq3/Al2O3/Cu device can enhance the switching performance owing to preventing the Cu diffusion and metallization. For Al/poly(methyl methacrylate)−1.25 wt % ZnO/ITO device, the switching may originate from the conduction paths formed by an aggregation of ZnO NPs, while for Al/poly(methyl methacrylate)−ZnO nanorods/ITO device, the formation and rupture of oxygen vacancies conductive filaments is assigned to the switching mechanism. Obviously, many studies on the memory effects of organic layers embedded with NPs were conducted, but few works focus on how the polymer/NP interface affects its electronic structure and charge transport.

In this article, we systematically study interfacial effects on switching behaviors of poly[(9,9-di-octylfluorenyl-2,7-diyl)−alt−(benzo[2,1,3]thiadiazol-4,8-diyl)] (PFBT) films embedded with different NPs, including NiO, ZrO2, graphene, and Au. Theoretical calculations are performed to investigate how the polymer−NP interface affects the charge transport.

Experimental Section

The chemical structure of PFBT was presented in the upper inset of Figure 1a, which was purchased from Xi’an Polymer Light Technology. The NiO NPs were synthesized using a sol−gel hydrothermal method at 200 °C for 2 h. First, the PFBT and NiO NPs were dissolved in chloroform reagent at a concentration of 0.5, 1, and 10 wt %, respectively. The blend solution was stirred for 10 min at room temperature. Then, the mixed solution was immediately spin-coated onto clean ITO substrate at 800 rpm for 5 s and 2000 rpm for 30 s. Next, the...
samples were dried on a hot plate at 80 °C for 10 min. Finally, the current−voltage (I−V) characteristics were measured using the eutectic alloy of gallium and indium (GaIn) droplet method. All processes were carried out under ambient conditions. The thickness of the composite layer in the device was obtained by examining a cross-sectional specimen with a scanning electron microscope (SEM, Zeiss ULTRA 55).

■ RESULTS AND DISCUSSION

Figure 1a shows the typical I−V curve of a GaIn/PFBT−NiO NPs/ITO device measured with bias sweeping from −4.5 to +4.5 V (see more nature I−V curves in Figure S1 in the Supporting Information). Initially, the film is in a high resistance state (HRS). With the bias sweeping to about −2 V, the device suddenly switches to a low resistance state (LRS). The LRS remains stable in subsequent sweeping until the device switches back to HRS at about +2.3 V. The device shows clear nonvolatile bipolar resistance switching, and the maximum ON/OFF ratio at −1 V is ~10^3. Figure 1b presents the XRD pattern of NiO NPs grown on glass substrate, in which a clear (200) peak of NiO is observed. As calculated by the Scherrer equation, the NP size is ~27 nm, which is consistent with the SEM observation (see the inset of Figure 1b). According to the cross-sectional SEM image of the device, the thickness of the active polymer layer is ~100 nm. The effect of NP concentration on the switching behaviors is studied (see Figure 1c). The values of threshold voltage and ON/OFF ratio for each NP’s weight percent are averaged from more than 25 measurements taken on the same sample and at various positions. As shown in Figure 1c, the ON/OFF ratio shows obvious enhancement with increasing NiO concentration from 0 to 0.5 wt %, while the switching performance deteriorates with further increase in NiO concentration. Such observation may be ascribed to the easier charge transport across the dense neighboring NPs.

To explore how the NPs affect the switching performance, the devices embedded with NPs of NiO, ZrO_2, graphene, and Au are systematically studied. As shown in Table 1, the largest ON/OFF ratio and V_{ON} are observed in the PFBT−graphene sample, while the lowest ones exist in device with Au NPs. However, the introduction of ZrO_2 and NiO has a slight impact. The V_{ON} distribution of PFBT−Au samples is relatively unstable compared with the others (see Figure S2 in the Supporting Information). Ouyang reported that the switching behavior of a polystyrene film containing 2-naphthalenethiol (2NT)-capped Au NPs was attributed to an electric-field-induced charge transfer between the Au NPs and the 2NT. When replacing 2NT with 1-dodecanethiol and introducing 0.4 wt % 8-hydroxyquinoline, the V_{ON} reduced from 5 to 2.7 V and the ON/OFF ratio was enhanced by one order of magnitude. In our case, the different switching behavior may be attributed to interfacial effects between the NPs and PFBT as well as the relative energy band alignment of PFBT with that of NPs.

Table 1. Threshold Voltage, ON/OFF Ratio and Slopes of log(I)−log(V) curves for PFBT and PFBT Embedded with 0.5 wt % NPs of Graphene, ZrO_2, NiO, and Au, Respectively

<table>
<thead>
<tr>
<th>device structure</th>
<th>V_{ON}/V</th>
<th>ON/OFF ratio</th>
<th>slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PFBT/GaIn</td>
<td>2.33</td>
<td>5773</td>
<td>2.07</td>
</tr>
<tr>
<td>ITO/PFBT−graphene/GaIn</td>
<td>2.94</td>
<td>17517</td>
<td>3.31</td>
</tr>
<tr>
<td>ITO/PFBT−ZrO_2/GaIn</td>
<td>2.24</td>
<td>5928</td>
<td>1.89</td>
</tr>
<tr>
<td>ITO/PFBT−NiO/GaIn</td>
<td>2.53</td>
<td>8227</td>
<td>2.17</td>
</tr>
<tr>
<td>ITO/PFBT−Au/GaIn</td>
<td>2.22</td>
<td>2551</td>
<td>3.18</td>
</tr>
</tbody>
</table>
which can largely modify the charge transport and switching properties of the devices.7

To understand the charge transport, the $I$–$V$ curves are analyzed in terms of available theoretical models.20 Table 1 summarizes the slopes of log($I$)–log($V$) plots in HRS. For PFBT, PFBT–NiO, and PFBT–ZrO$_2$ samples, the slopes are ~2 between $V_{T1}$ and $V_{TD}$, which corresponds to the space-charge-limited conduction (SCLC).21,22 However, for PFBT–graphene and PFBT–Au ones, the slopes are ~3 and the trapped-charge-limited conduction (TCLC) is the dominant mechanism.23,24 All of the samples follow the Ohmic conduction in LRS (data not shown).21 When graphene, ZrO$_2$, and NiO NPs are introduced, the slopes and the transition voltage have a similar trend as that of ON/OFF ratio. To obtain further information, we examined the $I_{HRS}$ at ~1 V. The $I_{HRS}$ of PFBT, PFBT–graphene, PFBT–ZrO$_2$, and PFBT–NiO samples are ~1.3, 0.4, 1.86, and 1.18 μA, respectively. The magnitude of $I_{HRS}$ reflects the different degrees of charge transport inside the composite films, which may result from the different polymer/NP interface, that is, the relative energy band alignment of PFBT with that of NPs. The larger ON/OFF ratio of PFBT–graphene sample may be ascribed to the deeper interfacial traps, and charges will be captured by the traps, reducing the $I_{HRS}$ to some extent. For PFBT–Au one, the $I_{HRS}$ reaches the highest value of ~2.09 μA, which is evidence of the lowest ON/OFF ratio. This observation, on the one hand, may be related to the charge leakage caused by the nonuniform dispersion of the Au NPs. Son et al.25 indicated that increase in concentration of Au NPs to 0.48 wt % will lead to the formation of Au NPs agglomeration in Al/PVK–Au/ITO/device. On the contrary, it may be determined by the electric-field-induced charge transfer between Au NPs and PFBT. Beebe et al.26 found that $V_{ON}$ scales linearly with the offset in energy between the Au Fermi level and the highest occupied molecular orbital, which may correspond to the tunneling barrier height. In our case, it may be associated with the interfacial trap depth or trap density of the composites.23,24

To further explore the charge transport, quantum-chemical calculations of simplified PFBT–NPs models are performed by density functional theory (DFT) at the B3LYP/6-31G(d) level with the Gaussian09 package.27 In the calculation, the NPs physically contact with the molecule at a distance of ~2.25 Å. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of PFBT are centered at the binding energies of about ~5.57 and ~2.32 eV, respectively (see Figure S3 in the Supporting Information). Because of its high electron mobility, PFBT is one of the electron-transporting materials and the change of LUMO may largely affect the carrier transport.28 When introducing NiO NPs, the HOMO–LUMO gap decreases by 2.02 eV with the new LUMO of ~3.72 eV, and the flat PFBT molecule becomes slightly bent with atoms at the ends of the benzothiadiazole chain (see Figure 2). A similar phenomenon is also observed in PFBT–ZrO$_2$ sample with the new LUMO of ~3.46 eV. This indicates that the new gap states are mainly originated from the interaction between NP and PFBT, which may change the interfacial electronic structure and result in deeper traps. The positive electrostatic potential regions may serve as traps to block the charge transport and lead to switching behavior. Compared with that of PFBT–ZrO$_2$ sample, the larger $V_{ON}$ and ON/OFF ratio for PFBT–NiO ones may be related to the deeper interfacial traps, while for PFBT–graphene sample, the HOMO–LUMO gap decreases by 0.48 eV with the new LUMO of ~2.92 eV. Different results are observed in PFBT–Au sample; chemical bonds are formed between benzothiadiazole group and Au NPs. The HOMO is mainly located at the Au side, while the LUMO is partly located at the benzothiadiazole group. The switching mechanism of GaIn/PFBT–Au/ITO device can be explained from electric-field-induced charge transfer between Au NPs and benzothiadiazole chain.29 Traps in PFBT are more likely to be filled up, showing the lowest $V_{ON}$ in PFBT–Au device. As will be discussed later, the narrow gap and lower LUMO caused by the interfacial interaction of PFBT and NPs may be responsible for the charge transport.

To acquire insight into the interfacial effects of charge transport, the zero-bias transmission coefficients for all the investigated systems are calculated using the NEGF-DFT method (see more details in the Supporting Information). To reduce the computation time, a simplified PFBT model without alkane chain was first optimized in the Gaussian 09 package at the B3LYP/6-31G(d) level.27 The device models were then built using ATK,29 with the optimized molecule sandwiched between two NPs electrodes. As shown in Figure 3a, the highest conductance is observed for the PFBT–ZrO$_2$ geometry,
which mainly arises from the broad peak structure below the Fermi level, while for PFBT−NiO, only a few unconspicuous transmission peaks can be observed within the energy range (see the peaks marked by arrow in Figure 3a). This is evidence of the lower \( I_{\text{HRS}} \) and larger \( V_{\text{ON}} \) in PFBT−NiO sample.

Comparison of PFBT−graphene and PFBT−Au shows that introduction of the graphene sheet can enhance the conductance due to the broad transmission peak around the Fermi level. Indeed, the width of the transmission states is a measure of the molecule−NP coupling strength. Thus the transport differences may originate from the different PFBT−NP interfacial coupling degree, which will subsequently affect the current conduction in the memory devices. Figure 3b plots the transmission spectra of PFBT−graphene from +0.3 to +1.5 V with a step of 0.3 V. The transmission peak shifts into bias window with respect to the increasing bias, indicating that the charge transport may depend on the molecule/NP interface changing with the applied voltage. The above results further confirm that the polymer−NP interface plays a key role in determining the charge-transport process.

In our case, we employed GaIn liquid droplet as the top electrode, and the superficial layer of Ga\(_2\)O\(_3\) can prevent the metallic ions from injecting into the organic layer. The possibility of metal filament formation can thus be excluded. The work done by Lee et al. indicated that the switching mechanism of Al/PVK−TiO\(_2\)/ITO device may be governed by the filamentary conduction due to the oxygen-deficient TiO\(_2\) NPs and the defects within the PVK. Chu et al. demonstrated the ionized oxygen vacancies in Al/PMMA−ZnO nanorods/ITO device charge and discharge electrons to achieve cycles of the formation and rupture of conductive filaments. However, the concentrations of ZrO\(_2\) and NiO NPs are both 0.5 wt % in our experiment, which is not enough to form oxygen-deficient conductive paths. On the basis of the experimental and calculated results, we suggest that the switching behavior may be most probably caused by a charge trapping/detrapping process owing to the defects within PFBT and the strong interaction between PFBT and NPs. Figure 4 presents the schematic structure and energy level diagrams corresponding to the switching process for the investigated devices. Taking the GaIn/PFBT−graphene/ITO device as an example, the carrier transport can be described as follows (see Figure 4a). Initially, the energy levels of the PFBT−graphene

Figure 3. (a) Zero-bias transmission coefficients for all the investigated systems. (b) Calculated transmission spectra for PFBT−graphene from 0.3 to 1.5 V with a step of 0.3 V. The Fermi energy is set to zero and the two dashed lines represent the bias window.

Figure 4. As-proposed energy level alignment and charge-transport processes for (a) PFBT−graphene, (b) PFBT−Au, (c) PFBT−ZrO\(_2\), and (d) PFBT−NiO, respectively, with the negative bias on the GaIn electrode.
bend downward and the square barrier gradually becomes a triangular-shaped one under the negative bias. Then, the electrons are injected into the composites by the Fowler–Nordheim tunneling and trapped by $T_1$, $T_2$, and $T_3$. DFT calculation suggests that the nonuniform electrostatic potential surfaces of PFBT can serve as traps $T_1$. The interaction between graphene and benzothiadiazole chain lowers the LUMO of PFBT, resulting in deeper traps $T_2$ at the PFBT/Graphene interface. Moreover, the as-fabricated graphene may have a small band gap, and thus $T_3$ may form between the conduction band of graphene and the LUMO of PFBT. The trapped electrons will induce a countering space charge layer, which, in turn, resists the injection of electrons. As the bias voltage is further increased to the threshold point where the traps are completely filled with electrons, the injected electrons can traverse the films, resulting in a transition from OFF to ON state. PFBT–graphene sample shows a larger tendency to block the charge carrier than PFBT-only ones, causing the charge transport of TCLC. As shown in Figure 4b, the charge transport of Galn/PFBT–Au/ITO device also corresponds to TCLC, while SCLC dominates the charge transport of PFBT–ZrO$_2$ and PFBT–NiO samples due to the shallow traps (see Figure 4c,d).

## CONCLUSIONS

We investigate the interfacial effects on switching performance by embedding different NPs so as to engineer the polymer/NP interface. An ON/OFF current ratio of $>10^4$ was observed in Galn/PFBT–graphene/ITO device with the switching mechanism of charge trapping and detrapping. The HRS current conduction is dominated by SCLC in PFBT, PFBT–ZrO$_2$, and PFBT–NiO films, while TCLC acts as the main mechanism in PFBT–graphene and PFBT–Au samples. Using quantum-chemical calculations, we show that the interaction between polymer and NP can largely affect the electronic structure at the interface, resulting in different interfacial barrier. DFT calculation and transmission spectrum show that the charge transport between polymer and NP may depend on the relative energetic position of the frontier molecular orbitals with respect to the Fermi level under the effects of bias.

## ASSOCIATED CONTENT

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b03116.

   Nature $I$–$V$ curves and threshold voltage distribution for the investigated devices. DFT result for PFBT and calculation details of transmission. (PDF)

## AUTHOR INFORMATION

### Corresponding Author
E-mail: jcli@mail.neu.edu.cn.

### ORCID
Jian-Chang Li: 0000-0001-9463-9208

### Notes
The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Financial support comes from the Fundamental Research Funds for Central Universities of China (N110403001).

## REFERENCES


18. Onlaor, K.; Thiwawong, T.; Tunhoo, B. Electrical Switching and Conduction Mechanisms of Nonvolatile Write-Once-Read-Many-


(29) ATK, version 11.8.2; QuantumWise: Copenhagen, Denmark.


