Effects of buffer layer and thermal annealing on the performance of hybrid Cu₂S/PVK electrically bistable devices

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Abstract: Hybrid organic/inorganic electrically bistable devices (EBDs) based on Cu₂S/PVK nanocomposites have been fabricated by using a simple spin-coating method. An obvious electrical bistability is observed in the current-voltage (*I-V*) characteristics of the devices, and the presence of the buffer layer and the annealing process have an important effect on the enhancement of the ON/OFF current ratios. Different electrical conduction mechanisms are responsible for the charge switching of the devices in the presence and absence of the buffer layer.

Keywords: Electrically bistable devices; Organic/inorganic; Cu₂S

1. Introduction

With the development of nanotechnology, EBDs based on organic/inorganic nanocomposites have been attracted much attention due to their simple fabrication techniques, low-cost and high-mechanical flexibility, which hold a bright prospect in the next generation nonvolatile memory devices^[1, 2]. In general, a typical hybrid organic/inorganic EBD is made up of a layer of organic/inorganic nanocomposites sandwiched between the two electrodes^[3]. To date, different types of colloidal inorganic nanocrystals have been used in the fabrication of the EBDs, and the inorganic nanocrystals are often dispersed in a polymer matrix^[4, 5]. Very recently, our groups reported the hybrid organic/inorganic EBDs based on the nanocomposites consisting of dodecanethiol-capped Cu₂S or

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Ag₂S nanocrystals and the conjugated polymers, which exhibited an obvious electrical bistability.^[6]

In the previous reports on the organic photovoltaic cells, poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was widely used as buffer layer to improve the film smoothness and the potential barrier ^[7-9]. In 2003, S. Möller observed a write-once-read-times (WORM) memory effect in the organic devices, which could be attributed to the redox reaction between the PEDOT and the metal electrode ^[10]. In 2011, J. Y. Kim et al demonstrated that the top metal electrode played a critical role in the electrical bistability of the sandwiched device metal/PEDOT:PSS/Al^[11]. To date, there is few report on the role of the buffer layer PEDOT:PSS in the hybrid organic/inorganic EBDs. Herein, the hybrid EBDs based on Cu₂S/PVK nanocomposites have been fabricated in the presence and absence of buffer layer PEDOT:PSS, and the charge switching mechanism has been discussed based on the organic electronic model. Moreover, the effects of the thermal annealing on the electrical bistable are also studied in this report. This study may offer some technical ways to enhance the ON/OFF current ratios of hybrid EBDs.

2. Experimental

Materials

Cu₂S nanocrystal capped by 1-dodecanethiol was prepared using one pot method as mentioned in our previous report ^[12]. Poly-N- vinylcarbazole (PVK) and PEDOT:PSS were purchased from Aladdin Chemical Reagent Co., Ltd., China. Other solvents such as ethanol and acetone were commercially available products in analytical grade, which were purchased from Beijing Chemical Reagent, China. All the materials were used as purchased without further purification.

Fabrication of Devices

The $\text{Cu}_2\text{S}/\text{PVK}$ nanocomposites were formed by dissolving Cu_2S nanocrystals and PVK into a certain volume of chloroform with a mass ratio of 1:1 and the concentration of solution is 20mg/mL. A typical fabrication process of EBDs is given as follows: the ITO-coated glass substrates were treated by ultrasonic in deionized water, acetone and anhydrous ethanol orderly and then were treated in ultraviolet ozone. Afterwards, a 80 nm PEDOT:PSS solution was spin-coated onto the ITO substrates. Subsequently, a 100 nm thick nanocomposite layer was formed by spin-coating the mixture onto the top of PEDOT:PSS film. The thickness can be controlled by adjusting the rotating speed of rotating coating machine and measured by surface profilers (Dektak X T). Subsequently, a 100 nm thick top Al electrode was coated by thermal evaporation under vacuum at a pressure of 1×10^{-5} Torr and its thickness was controlled and measured by a thickness controller (Protek, U2000A). Finally, The as-devices were annealed in a vacuum drying oven at 120 °C for 20 min. In comparison, the device without PEDOT:PSS was fabricated based on the same process mentioned above. For the sake of convenience, device I and device II represent the EBDs in the presence and absence of PEDOT:PSS. The schematic illustration of the device structure and the molecular is shown in Fig.1.

Fig.1 Schematic illustration of the device structure and molecular structure of PVK (Bottom right) as well as the TEM image of Cu_2S nanocrystals (Upper right).

The TEM images shown in Fig.1 were employed to study the size and morphology of dodecanethiol-capped Cu_2S nanocrystals, and the as-obtained Cu_2S nanocrystals exhibit a spherical

shape with a uniform size distribution. The average diameter is estimated to be 8.2 ± 0.7 nm.

3. Results and discussions

3.1 Influence of PEDOT:PSS on the properties of devices

Fig.2 AFM height images of the surface of the active layer consisting of $\text{Cu}_2\text{S}:\text{PVK}$ solvents

(a)with PEDOT:PSS (b) without PEDOT:PSS

In order to investigate the influence of PEDOT:PSS on the morphology of device I and device II, we measure the AFM patterns of two devices. It can be seen from Fig.2 that the film become smoother after PEDOT:PSS is spin on the ITO.

Fig.3 depicts the I - V curve of the hybrid EBDs of device I and II under the sweeping voltages from -10 to 0, 0 to 10, 10 to 0 and 0 to -10V with sweeping speed 1 V/s. The arrows represent the operation of device through their different states. A high-conducting state (ON state) and a low-conducting state (OFF state) are observed at the same sweeping voltage, which indicates that both the devices have memory characteristics. Such an obvious electrical hysteresis behavior is an essential

feature for the EBDs. Herein, we take the I - V curve of the device I with PEDOT:PSS as an example to describe the electrical hysteresis.

Fig.3 I - V curves of the hybrid EBDs in the presence and absence of the buffer layer PEDOT:PSS, and the arrows represent the directions of the sweeping voltage.

Fig.4 Experimental (open scatter) and the theoretical linear fitting (solid line) results of I - V characteristics in the positive voltage region: (A) linear fitting in double logarithmic plot in the

region of 0-10 V (Off state); (B) linear relationship between $\log I$ versus $V^{1/2}$ in the voltage region of 10-0 V (On state).

In the positive region, the current increases with the sweeping voltage increasing from 0 to 10 V and reaches the maximum current at 10 V, which indicates that the conducting states transform from OFF to ON state. The current can stay in the ON state during the sweeping voltage from 10 to 0 V. When the sweeping voltage scans from 0 to -10V, the current reaches its maximum at -5V and then decreases rapidly when the sweeping voltage exceeds -5 V, which is a typical NDR effect ^[13, 14]. And then the conducting states transform from ON to OFF states. According to the aforementioned results, the buffer layer PEDOT:PSS is not the decisive for the electrical bistability of the Cu₂S/PVK devices, which is just helpful to enhance the ON/OFF current ratios, and the dodecanethiol-capped Cu₂S nanocrystals are crucial for the electrical bistability effects.

To investigate the charge switching and carrier transport of the hybrid based EBDs with and without the buffer layer PEDOT:PSS, the I - V curves have been fitted based on the different theoretical models of the charge conduction^[15]. Herein, the carrier transport belongs to the space-charge-limited-current (SCLC) when the I - V curve coincides with the Eq.1

$$I \propto V^\alpha, \alpha \geq 2 \quad 1)$$

While the carrier transport belongs to Ohmic law when the I - V curve coincides with the Eq.2:

$$I \propto V \quad 2)$$

If the ration between I and V is accord to Eq.3, the carrier transport attribute to thermionic emission (TE) model.

$$I \propto V^{1/2} \quad 3)$$

Fig.4 gives the experimental results and the corresponding fitting results of the two devices for the ON and OFF states in the entire sweeping voltage region. As shown in Fig.4 (A), the I - V characteristics

on the double logarithmic plot for the OFF state in the voltage region of 0-10 V show two distinct linear fitting regions with different slope values. In the sweeping voltage region of 0-1.8 V, the slope of 0.91 is obtained for the device I, which is well fitted with Ohmic law ($I \propto V$). For the device II, the slope is 1.92, which is close to SCLC model, indicating that the electrical conduction is governed by TCLC conduction. In the region of 1.8-10 V, a large linear slope of 7.49 and 4.57 is obtained in the I - V characteristics of device I and II, respectively. This indicates that the conduction is dominated by the trap-controlled space-charge-limited (TCLC) model ($I \propto V^\alpha$, $\alpha \geq 2$) at higher voltages, which may result from the charge traps of dodecanethiol capped Cu₂S nanocrystals with an exponential distribution in the forbidden gap^[16]. As shown in Fig.4 (B), after the conduction state transition from OFF state to ON state, the I - V curve on $\log I$ and $V^{1/2}$ can be fitted to a straight line in the voltage region of 10-0 V and the slopes of device I and II are 0.80 and 1.22., respectively. The results indicate that the current of ON states may be dominated by TE model, in which the charge injection is derived from the Al electrode^[17]. This result indicates that the conduction mechanism of the EBDs is different in the presence and absence of the buffer layer PEDOT:PSS, which may result from the different interfacial characteristics or potential barrier between the cathode and active layer.

3.2 Influence of thermal annealing technology on the properties of devices

Thermal annealing is an important process to enhance the photovoltaic performance of the organic bulk-heterojunction solar cells. Herein, the effects of thermal annealing on the EBDs have been studied, and Fig.5 gives the I - V characteristics of the EBDs based on the sandwiched structure of ITO/PEDOT:PSS/ Cu₂S:PVK/Al with and without thermal annealing. As shown in Fig.5, an obvious electrical bistability is observed in the EBDs without (device III) or with thermal annealing (device IV), and the magnitude of the I - V hysteresis is larger for the device III than device IV. The maximum

ON/OFF current ratio of the device III is three times as large as that of the device IV, which indicates that the thermal annealing contributes to the enhancement of the ON/OFF current ratio of the EBDs. As stated in D. G. Ma's work, the thermal annealing changed the morphology of PVK film and the interface dipole was destroyed, thus the interfacial barrier could be increased, which contributes to the electrical bistability^[18]. The synergistic effects of the dodecanethiol-capped Cu₂S nanocrystals and PVK film by thermal annealing can increase the ON/OFF current ratios of the hybrid EBDs.

Fig.5 *I-V* curves of the device III and device IV, and the arrows represent the directions of the sweeping voltage.

Fig.6 AFM patterns of device III(a) and device IV (b).

In order to investigate the film morphology of device III and device IV, we measure the AFM patterns of two devices. It can be seen from Fig.6 that the film become smoother after the device are annealed. Thus, annealing can improve the character of device.

3.3 The charge memory process of the EBDs device

Fig.7 Schematic diagram of the energy level of ITO/ PEDOT:PSS/Cu₂S&PVK/Al device.

The electrical bistability in the ITO/ PEDOT:PSS/Cu₂S&PVK/Al device can be explained in terms of electric-field-induced charge transfer between Cu₂S and PVK as mentioned in the reference ^[19]. The LUMO (energy levels of the lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) of each layer are given in Fig. 7, respectively. If a positive voltage is applied on this device, the electrons will inject from Al electrode into LUMO level and then the electrons existing at LUMO level of PVK are transported along the direction of applied voltage. The Cu₂S & PVK layer is charged positively and negatively, respectively, which results in an internal electric field along the same direction as the applied voltage. The devices perform the transition from OFF state to ON state and keep this state after removing the external electric field. This may be because the 1-dodecanethiol layer out of Cu₂S nano crystals can prevents the charge recombination, which make the negative charge on the nanoparticles are stable. The charge recombination will occur after applying a negative voltage to

the device and the device will transform from ON state to OFF state^[20].

4 Conclusions

In conclusion, we have shown the effects of presence of buffer layer and thermal annealing on the hybrid organic/inorganic EBDs based on Cu₂S/PVK nanocomposites. The dodecanethiol-capped Cu₂S nanocrystals play a decisive role in the electrical bistability, and the presence of PEDOT:PSS layer and thermal annealing treatment contribute to the increase magnitude of the I-V hysteresis. The different theoretical models of the charge transport have been employed to discuss the conduction mechanism of the EBDs for different states. The electric-field-induced charge transfer between Cu₂S and PVK is used to explain the electrical bistability properties of the EBDs device.

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Reference

- [1] Baeg K J, Noh Y Y, Ghim J, Kang S J, Lee H, and Kim D Y. Adv. Mater. 2006; 18(23):3179-3183.
- [2] Li B, Yoo J W, Kao C Y, Jang H W, Eom C B, Epstein A J. Org. Electron. 2010; 11(6):1149-1153.
- [3] Sun Y M, Li L, Wen D Z, Bai X D. Org. Electron. 2015, 25: 283-288.
- [4] Li S Y, Zheng Y L, Jakoby R, Klein A. 2012, 22: 4827-4832.
- [5] Ribierre J, Aoyama T, Muto T, André P. 2011, 12: 1800-1805.
- [6] Tang A W, Qu S C, Hou Y B, Wang Y S, Wang Z G. J. Solid. State. Chem. 2011;184(8):1956-1962.
- [7] Khatei J, Rao K S R. Mater. Chem. Phys. 2011, 130: 159-164.

- [8] Huang J S, Miller P F, Wilson J S, de Mello A J, de Mello J C, Bradley D D C. *Adv. Funct. Mater.* 2005, 15(2): 290-296.
- [9] Nawrocki R A, Galiger E M, Ostrowski D P, Bailey B A, Jiang X, Voyles R M, Kopidakis N, Olson D C, Shaheen S E. *Org. Electron.* 2014, 15: 1791-1798.
- [10] Moller S, Perlov C, Jackson W, et al. *Nat.* 2003; 426: 166-169.
- [11] Kim J K, Jeong H Y, Kim J W, Yoon T H, Choi S Y. *Curr. Appl. Phys.* 2011; 11(2): e35-e39.
- [12] Tang A W, Teng F, Hou Y B, Wang Y S, Tan F R, Qu S C and Wang Z G. *Appl. Phys. Lett.* 2010; 96:163112-1-3.
- [13] Tu C H, Kwong D L, Lai Y S. *Appl. Phys. Lett.* 2006, 89:252107-1-3.
- [14] Lau C N, Stewart D R, Williams R S, and Bockrath M. *Nano Lett.* 2004, 4:569-572.
- [15] Tang A W, Teng F, Liu J, Wang Y C, Peng H S, Hou Y B, Wang Y S. *J. Nanopart. Res.* 2011; 13(12): 7263-7269;
- [16] Li J T, Tang A W, Li X, Cao Y P, Wang M, Ning Y, Lv L F, Lu Q P, Lu Y Z, Hu Y F, Hou Y B, Teng F. *Nanoscale. Res. Lett.* 2014, 9: 128.
- [17] Islam S M, Banerji P, Banerjee S. *Organ. Electron.* 2014; 15(1): 144-149.
- [18] Lin J, Ma D G. *Appl. Phys. Lett.* 2008; 93: 093505.
- [19] Tang A W, Teng F, Qian L, Hou Y B, and Wang Y S. *Appl Phys Lett* 2009; 95:143115-1-3.
- [20] Son D I, You C H, Jung J H and Kim T W. *Appl Phys Lett* 2010; 97: 013304.

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