Photoelectric Cooperative High-Density Data Storage in an Organic Bilayer Thin Film

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A bilayer materials system composed of titanylphthalocyanine−*N,N,N′,N′*-tetra(4-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TiOPc−TTB) is designed for data storage medium. The photoelectric cooperative effect on data storage is demonstrated for the first time. When the thin film is irradiated with suitable light intensity, the ON/OFF current ratio was effectively enhanced and the threshold voltage can be remarkably reduced. Accordingly, stable and reversible nanoscale data storage with lowered pulsed voltage is achieved by STM. The photoelectric cooperative performance could effectively lower the misreading rate and reduce the power consumption of storage device, and will be of great significance for designing highly efficient information storage materials and novel multifunctional photoelectric devices.

With the ever-increasing demand of expansive storage capacity and the continuous miniaturization of optoelectronic device, high-density data storage has attracted intensive attention.[1] In recent years, organic thin films have widely been employed as recording media for their versatilities in molecular design, tunable photo- or electro- responsive properties, and low cost.[2,3] To achieve nanoscale data storage on organic thin films, scanning tunneling microscopy (STM) technology has been demonstrated to be a powerful tool.[4,5] So far, stable, reliable and reversible high-density data storages have been realized using STM through the design and synthesis of novel organic functional materials with electrical bistability.[4d,5d,e] However, there are still a number of critical problems to be overcome for memory device in the future. Especially, lowering power consumption during the storage procedure is becoming one of the most important issues, since the energy consumption of electronic devices has been arousing more and more attention.[6] One effective approach to decrease the power consumption of a memory device is scaling down the threshold voltage.[7] In this work, we succeeded in lowering the threshold voltage for data storage based on photoelectric cooperative effect of an organic bilayer thin film.

The idea of photoelectric cooperation is inspired by the giant magnetoresistance (GMR) effect,[8] which indicates that very small magnetic field changes give rise to major differences in electrical resistance in a GMR system. In the same way, the photoelectric cooperative effect means a weak light may bring evident improvements on electrical performances (such as threshold voltage, ON/OFF ratio, etc.) in an electrical bistable system that also possesses optical responsive property. In fact,

it has been demonstrated that the coupling of light and electric field can effectively induce the shift of threshold voltage in organic field-effect transistor.[9] However, so far a photoelectric cooperative effect on data storage has rarely been reported. In this work, we demonstrated the first example of photoelectric cooperative effect on lowering threshold voltage in data storage based on a bilayer thin film composed of titanylphthalocyanine−*N,N,N′,N′*-tetra(4-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TiOPc−TTB), wherein, TTB served as the electron donor and hole-transporting material and TiOPc served as the electron acceptor and photoconductor.[10] Stable and reversible nanoscale data recording was achieved using STM. Furthermore, the ON/OFF current ratio of the bilayer thin film could be effectively enhanced when it was irradiated with suitable light intensity. Accordingly, reversible high-density data storage with lowered pulsed voltage was achieved on the bilayer thin film based on the photoelectric cooperative effect. The results indicate photoelectric cooperative effect will be of great significance for designing high performance data storage materials and low-power memory devices.

The chemical structures of TiOPc and TTB are shown in Scheme 1a. For macroscopic current−voltage (*I*−*V*) characteristics, the bilayer thin films of 40 nm TiOPc and 40 nm TTB were successively deposited on an indium tin oxide (ITO)-coated glass substrate. A piece of freshly cleaved highly ordered pyrolytic graphite (HOPG) was used as the upper electrode. A device with the structure of ITO/TiOPc−TTB/HOPG is illustrated in Scheme 1b. The macroscopic *I*−*V* characteristics measured in the dark are shown in Figure 1a. When a forward voltage was applied, the thin film exhibited low-conductance state (OFF state, curve I). As the voltage approached +1.8 V, a sharp increase in the current took place, indicating the thin film switched to a high-conductance state (ON state). After the transition, the thin film remained in the ON state during the

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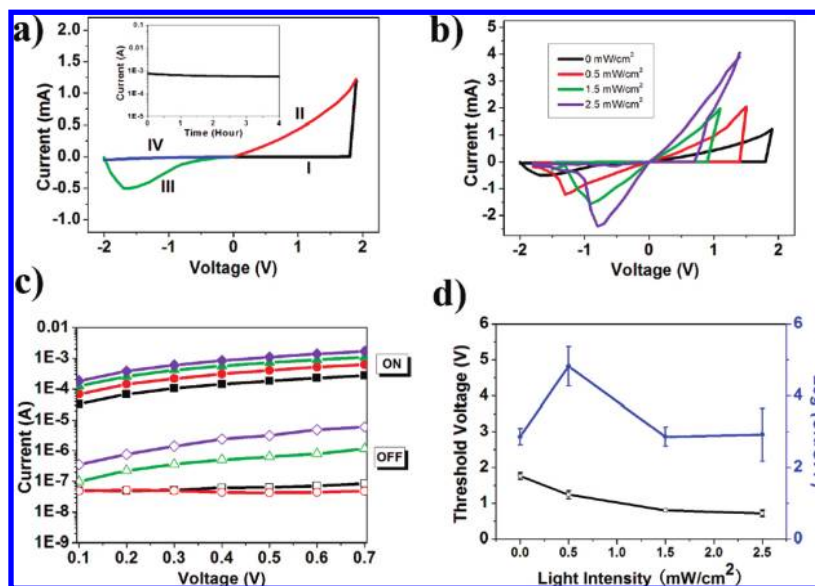
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Figure 1. (a) Macroscopic $I-V$ characteristics of the bilayer thin film in dark, exhibiting the conductance transition from the low- (OFF state) to high-conductivity state (ON state) in curve I, the memory effect of the ON state in curve II, and the recovery of the OFF state with the application of a reverse voltage scan in curves III and IV. Insert shows long-term response of the ON state under an electric field of 1.0 V. (b) The comparison of $I-V$ characteristics of the thin film under 728 nm light irradiation with different intensity. (c) The comparison of ON (filled symbols) and OFF (open symbols) state current corresponding to panel b. (d) The change in threshold voltage and ON/OFF ratio with different light intensity.

SCHEME 1: (a) Molecuar Structures of TiOPc and TTB and (b) the Device Structure Used for Macroscopic $I-V$ Measurement
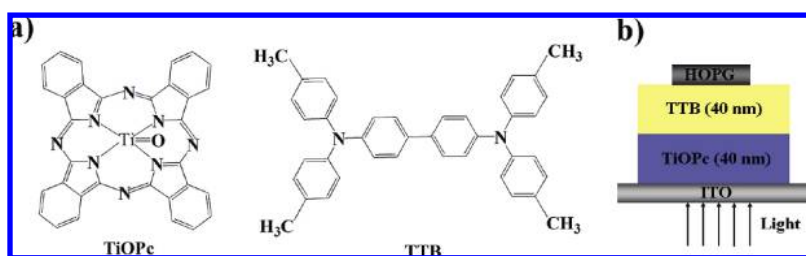
second sweep from 0 to +1.9 V (curve II). The conductivity in the ON state was about 3 orders of magnitude larger than that in the OFF state. Furthermore, the thin film was found to retain the ON state without degradation under 1.0 V bias during 4 h continuous operation (insert in Figure 1a), which indicated the ON state was very stable. The ON state returned to the OFF state as the voltage approached −1.6 V when sweeping from 0 to −1.9 V (curve III). Then it showed an OFF state, as indicated by a followed reverse scan (curve IV). The OFF state could be switched back to the high-conductivity state by applying a positive bias higher than the threshold, resulting in an OFF−ON−OFF−ON reversible trait. This stable conductance transition indicates that the bilayer thin film may be a promising material for stable and reversible data storage.

The effect of light irradiation on the macroscopic $I-V$ characteristics of the bistable system was investigated with different light intensity. The wavelength of the light is 728 nm, which corresponds to a maximum absorbance in the TiOPc moiety. Figure 1b shows a typical testing result. As can be seen, the characteristics of the curves were similar to that measured in the dark. Interestingly, the threshold voltage decreased with increasing light intensity. The low operating voltage is desirable for low-power memory devices.[7a] Figure 1c shows the comparison of the ON and OFF state currents under various light intensity. The ON state current rose along with the increasing of the irradiation intensity; while the OFF state current kept little change at relatively low light intensity, and later increased

along with the continued enhancement of irradiation intensity. The behavior resulted in a higher ON/OFF ratio under the intensity at 0.5 mW/cm². The maximum ON/OFF ratio was 2.5 × 10⁵, and that for all measured devices were typically greater than 10⁴ (Figure 1d). Such a high ON/OFF current ratio is crucial for the memory device to realize high-resolution and low error rate data storage.[11] These results suggest that the photoelectric cooperative effect is effective to lower the threshold voltage and improve the ON/OFF ratio with suitable light intensity.

The electrical bistability is the basis for high-density data storage, where the ON state and the OFF state is equivalent to the "write" and "erase" process in a digital memory device, respectively. A bilayer thin film with the thickness of about 10 nm was deposited on HOPG. To write data, suitable voltage pulses were applied between the STM tip and HOPG substrate. Studies showed that when the applied voltage pulse was above the threshold (+3.0 V) under dark conditions the recorded dots could be easily formed. Figure 2a shows a typical recording pattern on the thin film by STM, and the average size of the recording marks is about 3 nm in diameter. Furthermore, the formed marks were very stable and no obvious change could be observed during a 10 h continuous scanning process. Further studies would be done to improve the stability of the system. When a reverse polarity voltage pulse higher than an absolute value of 2.55 V was applied to the recorded region, the marks could be erased (Figure 2b,c). By applying a positive pulsed voltage on the same area of the thin film, again, a dot can be
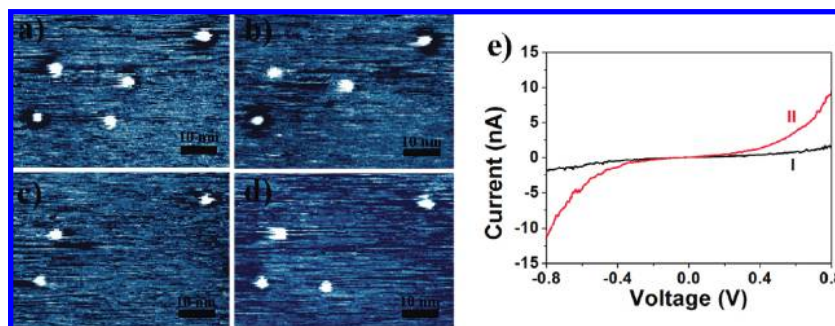
Figure 2. STM images of typical information dots pattern and the corresponding $I-V$ curves. (a) Recording pattern composed of five information dots: pulsed voltage, +3.0 V; 3.8 ms. (b, c) Erasing one and two dots, respectively: pulsed voltage, −2.55 V; 3.8 ms. (d) Rewriting one information dot: pulsed voltage, +3.0 V; 3.8 ms. (e) Typical STM $I-V$ curves in the unrecorded (curve I) and recorded region (curve II).
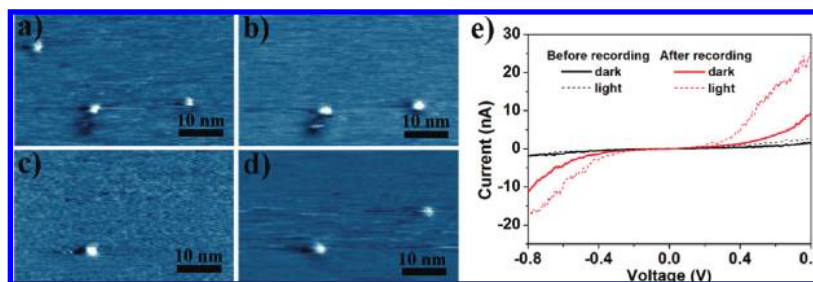

Figure 3. STM images of typical information dots pattern formed under illumination (a) Recording pattern composed of three information dots: pulsed voltage, +2.0 V; 3.8 ms. (b, c) Erasing one and two dots, respectively: pulsed voltage, −1.65 V; 3.8 ms. (d) Rewriting one dot in adjacent area: pulsed voltage, +2.0 V; 3.8 ms. (e) Local $I-V$ characteristics of the bilayer thin film under dark and illumination (728 nm, 0.5 mW/cm^2) conditions before and after recording.

rewritten (Figure 2d). With alternating exposure of the thin film to positive and negative voltages beyond the threshold value, write−read−erase cycles were demonstrated in the same region. The local electrical properties of the TiOPc−TTB thin film were characterized by examining the $I-V$ characteristics using STM. As shown in Figure 2e, the thin film exhibits a different conductance before and after formation of the recorded marks. Curve I shows that the conductivity of unrecorded regions on the thin film is in a high resistance state, while it is on a low resistance state at the recorded region during the same voltage conditions (curve II). The comparison indicated that the applied voltage pulse has induced a conversion of the conductance of the thin film from a high resistance to a low one.

While the bilayer thin film was exposed to light (728 nm, 0.5 mW/cm^2), a much lower voltage pulse (+2.0 V) could facilitate the formation of recorded dots (Figure 3a). Furthermore, the reverse polar voltage pulse (−1.65 V) for erasing information dots was also minished. The images in Figure 3b and c indicated, respectively, the situation after one and two information dots were erased. By applying a positive pulsed voltage (+2.0 V) on the adjacent area of the thin film, another dot could be rewritten on it (Figure 3d). The local $I-V$ characteristics under dark and illumination conditions of the bilayer thin film before and after recording were compared (Figure 3e). It can be seen clearly that the current of the recording area exhibited obviously higher conductivity under illumination condition compared with that of dark condition. The results are in accordance well with the macroscopic electrical property.

The conductance transitions based on organic materials have been explained by different mechanisms.[12] A field induced reversible charge-transfer is generally regarded as the main reason for the switching behavior in a donor−acceptor system.[5,13] The switching mechanism in this bilayer system is more complicated. In order to investigate the recording mechanism

of the bilayer thin film, quantum chemical calculations were performed by using the hybrid Hartree−Fock/density functional theory (HF/DFT) method of B3LYP[14] with the 6-31G* basis set.[15] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of TTB are −4.54 and −0.68 eV, respectively, and those of TiOPc are −5.09 and −2.97 eV, respectively (Figure 4a,b). The relatively high HOMO energy level of TTB indicates that TTB is a *p*-type material with holes as the dominant charge carriers.[16] For the first positively sweep, HOPG (Φ (work function) = 4.65 eV) was used as the anode,[17] and ITO ((Φ (work function) = 4.8 eV)) was used as the cathode.[18] The energy band diagram of the ITO/TiOPc−TTB/HOPG system is shown in Figure 4c. Under a low bias voltage (0−1.8 V), hole mobility is blocked by the TiOPc with a low HOMO energy level (−5.09 eV). The thin film is at the low conductivity state (OFF state). When the electric field exceeds the barrier, holes are injected into the HOMO of TTB, and electrons are injected into the LUMO of TTB. The charged HOMO of TTB and LUMO of TiOPc form a conductive channel for charge carriers through charge transfer interactions (illustrated in Figure 4d). This phenomenon can be further supported by the change of UV−vis spectrum (Figure S1). Thus the thin film switches to high conductivity state (ON state). Because of the strong electron-withdrawing ability of TiOPc with a high LUMO, electrons trapped in TiOPc can be retained and coexisted with the positively charged TTB. Moreover, the interface between the two layers also play an important role in collecting the charges.[19] Therefore, the high conductivity can be retained. Under a reversed bias, TiOPc loses the charge state to neutralize the positively charged TTB moiety, and the thin film returns to the OFF state.

When the thin film is exposed to light, the TiOPc will absorb photons and result in the formation of excitons (electron−hole pairs).[10a−c] As known, the generation of photocurrent depends primarily on the density of photogenerated excitions, the fraction

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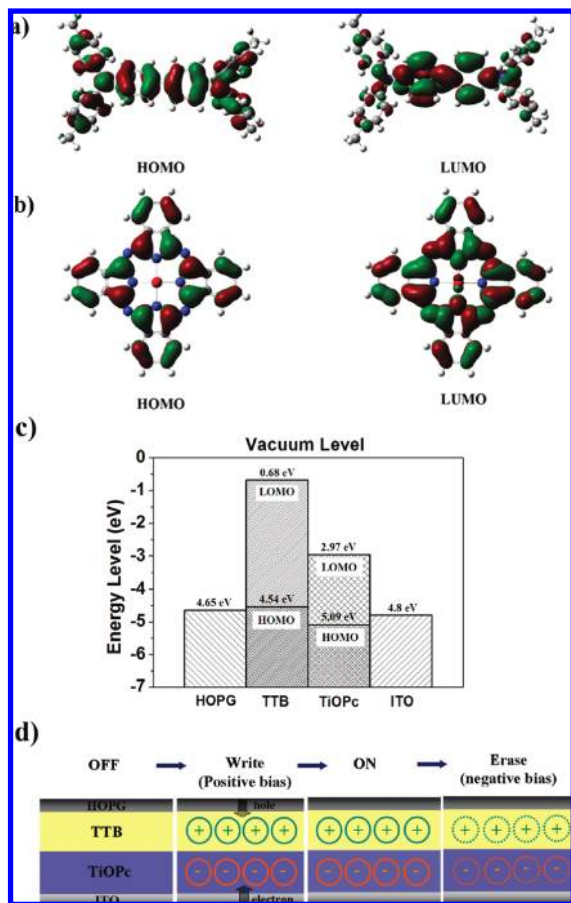*J. Phys. Chem. C, Vol. 113, No. 20, 2009* **8551**

Figure 4. HOMO and LUMO molecular orbitals of (a) TTB and (b) TiOPc calculated by the HF/DFT method of B3LYP with the 6-31G* basis set. (c) Energy band diagram of TiOPc−TTB (from calculation results). (d) Plausible electronic processes to produce the storage effects in the bilayer thin film.

of excitons that are dissociated, and the internal resistance of the device.[20] When the thin film under OFF state (high-resistance), photogenerated excitions (holes in this case) can not move or move very slowly, so the OFF state current shows no obvious change under a relatively low intensity light. Under higher intensity light illumination, more photogenerate excitons were obtained and consequently more dissociated holes result in the increasing of the OFF state current. While the device switched to high-conductivity, photogenerated holes can easily transport in the thin film under the action of an electric field. Thus ON state current was increased with higher illumination intensity. So the ON/OFF current ratio can be effectively improved with suitable light intensity. On the other hand, photogenerated electrons were accumulated and trapped in the interface of the bilayer. These accumulated electrons could effectively lower the threshold voltage.[9] Further researches to understand the switching mechanism are under progress.

In conclusion, a bilayer thin film composed of TiOPc−TTB was designed for data storage medium. The photoelectric cooperative effect on data storage was demonstrated for the first time. When the thin film was irradiated with suitable light intensity, the ON/OFF current ratio was effectively enhanced, and the threshold voltage could be remarkably reduced. Accordingly, stable and reversible nanoscale data storage with lowered pulsed voltage was achieved by STM. The photoelectric cooperative performance could effectively lower the misreading rate and reduce the power consumption of storage device, and will be of great significance for designing highly efficient

information storage materials and novel multifunctional photoelectric devices.

Supporting Information Available: Experimental details and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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