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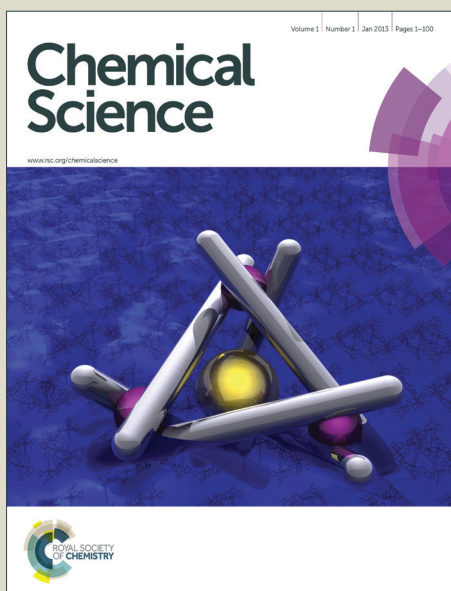
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EDGE ARTICLE

Inorganic-Organic Hybrid Polymer with Multiple Redox for High-Density Data Storage

Benlin Hu,[a] Chengyuan Wang,[a] Jiangxin Wang,[a] Junkuo Gao,[a] Kai Wang,[b] Jiansheng Wu,[a] Guodong Zhang,[a] Wangqiao Cheng,[a] Bhavanasi Venkateswarlu,[a] Mingfeng Wang,[b] Pooi See Lee,[a] Qichun Zhang*[a]

Although organic multilevel resistance memories have attracted numerous attentions for potential realization of the exponentially-increasing density of data storage, the ambiguous structure-property relationship and the unclear switching mechanism impeded further development of multilevel resistance memory devices. Therefore, it is very urgent to ingeniously design multilevel memory materials with a certain switching mechanism. In this contribution, we have employed a multi-redox (multiple barriers) polyoxometalate-based inorganic-organic hybrid polymer (whose effective carriers are electrically controllable) to realize a ternary resistance switching memory (multilevel memories). We do believe that the as-designed inorganic-organic polymer can integrate multi-redox states of POM and the processability of flexible polymers together. The as-fabricated multilevel memory devices exhibit rewriteable switching properties among three redox states by applying different RESET voltages, good endurance with distinct operation windows, and long retention. Our results could provide a new strategy to design controllable multilevel resistance memories with excellent performance.

Introduction

As the increasing requirements for the large capacity of data storage in the past decades, organic resistive nonvolatile memories have attracted numerous attentions due to their charming advantages such as high density data storage, simple structure, and good solution processability.[1] Among these merits, the high-density data storage of organic resistive memories is one of the most important potentials, which can reach 10^6 times or higher than that of traditional magnetic memories.[2] Generally, there are three ways to increase the density of memories: (1) scaling down the device size,[2,3] (2) employing multilayer device structure,[4] and (3) applying multilevel memory materials.[5] Whereas, compared to the first two methods, applying multilevel memory materials could be more practical because this type of compounds does not need to (i) change the structure of traditional memory devices, (ii) highly depend on micro-fabric technology, and (iii) require the materials tough enough to etch and further solvent treatment in photolithography process.[4a,6] Furthermore, the density for data storage of multilevel memories can be increased exponentially with the increase of device cell numbers, while the density change through scaling down device size or employing multilayer structures can only be linear with the number of layers and/or square to the sizes of devices.[5a,5c,7] Thus, a multilevel memory could be a more effective and more simple way to realize high density data storage. Indeed, there have emerged some inspiring results relevant to multilevel memories, including controlling the density of the high conductance molecules, using different compliance currents, and employing multiple donor-acceptor molecules and multiple tunnelling sites.[4b,5,7b,8] Nevertheless, the exploration of structure-property relationship is rare. Obviously, well-understanding this relationship is very helpful to develop new

multilevel memories. On the other hand, the ambiguous mechanism has hindered the further development and the commercialization of multilevel memories. Therefore, developing novel multilevel-memory materials through ingenious structure-property design is very important to realize high density data storage. As known, the resistive switching is driven by energy (voltage or current); correspondingly, materials with such memory function should have one barrier (two-state memories) or more barriers (multilevel memories). Furthermore, the switching elements should have effective carriers, whose amount can be controlled by applying a bias voltage (energy). Inspired by previous multilevel memory devices based on proton-doping poly(Schiff base),[7b] we will develop a new nonvolatile multilevel memory material based on a multi-redox polyoxometalate-based inorganic-organic hybrid polymer, in which the amount of effective carriers can be controlled by the redox of polyoxometalate under electric field. Furthermore, the retention of multilevel memory is enhanced by the larger energy barrier compared to that of proton-doping poly(Schiff base).[7b]

Polyoxometalate (POM) is a kind of polyanionic nano-clusters, which can be envisioned as soluble molecular semiconducting oxides.[9] POMs have been widely investigated in the fields such as catalysis and medicine in the past decades.[10] Recently, POMs have been explored as zero dimensional (0D) semiconductors with n-type conducting character (electron mobility as high as 4×10^{-3} cm^2/V·s), which suggests that they have potential applications in electronics.[11] More importantly, they can reversely gain/lose one or more electrons without any structure change. The generated charges can be delocalized to several metal centers even at room temperature under the help of light or an electric field.[11b,12] Many POMs exhibit several discrete redox states in a narrow potential range, suggesting the

existence of the barriers among these states, which may be employed for multilevel memories.[13] When the redox occurs, the charges of polyanionic and the amount of the counter cations (the effective carriers) will change accordingly and the conductivity will follow this change. Both the ability that POMs can maintain the stable skeleton even after one or more electrons are added or subtracted, and the multi-redox states in a narrow potential range, could contribute to a rewriteable multilevel resistive memory with excellent performance.[13a,14]

In this contribution, we report a ternary memory from a ternary redox POM-based inorganic-organic hybrid polymer. Our success could provide a new strategy to approach multilevel memories from multiple redox POM-based hybrid polymers. To the best of our knowledge, this is the first report about an inorganic-organic hybrid polymer, which integrates the multi-redox states of POM and the processability of polymers together for the application in multilevel resistive switching memory devices.
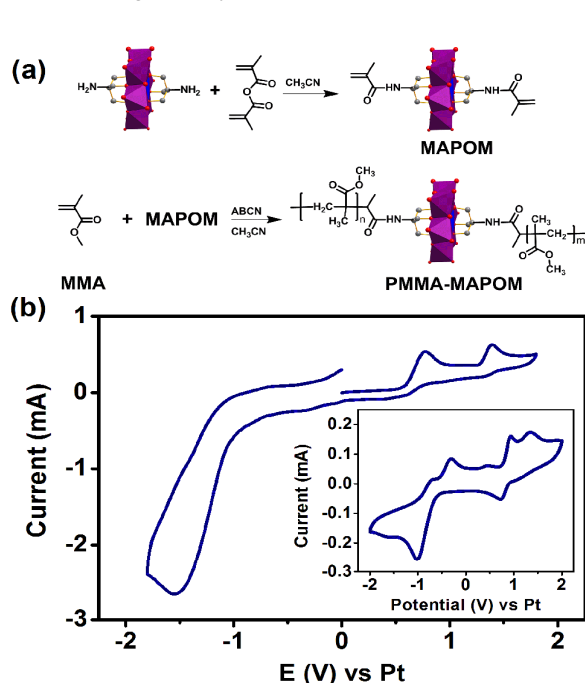
molecular weight of the as-synthesized PA is 33.2 kDa, with a polydispersity index of 1.63 as measured by GPC analysis. The glass transition temperature (T_g) of PMMA-MAPOM is higher than of PMMA, which suggests the existence of some degree of crosslinking in this POM–based inorganic-organic hybrid polymer (TGA in Figure S1 and DSC in Figure S2). To avoid the gelation, the content of MAPOM in the polymer is limited (the molar ration of MAPOM to MMA is 1:400 in PMMA-MAPOM), which leads to weak or even no signal in traditional characterized spectra (e.g. ^{1}H-NMR, UV-Vis, FT-IR, Figure S3 to S6). Thus, the Mo content of PMMA-MAPOM was only obtained from EDX (Figure S7) to verify the incorporation of MAPOM into the PMMA-MAPOM polymer. The cyclic voltammogram (Figure 1b) of PMMA-MAPOM exhibits two oxidation peaks (Mn (II) to Mn (III), Mn (III) and Mn (IV), respectively) and one reducing peak (Mn (III) and Mn (IV) to Mn (II)),[17] which suggests that different states may be obtained in the corresponding memory device.
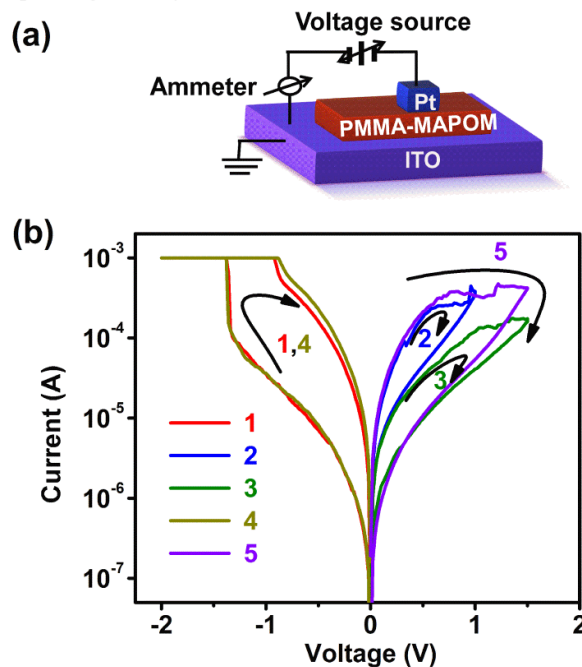

Figure 1. (a) The synthesis of the POM hybrid polymer. (b) Cyclic voltammogram of the POM polymer (PMMA-MAPOM) film; the inset is the cyclic voltammogram of MAPOM in acetonitrile.

Figure 2. (a) Schematic illustration and (b) the *I–V* characteristics of the memory device based on the POM hybrid polymer.

Results and discussion

The synthetic route of POM-based hybrid polymer (PMMA-MAPOM) was shown in Figure 1a (see Supporting Information (SI) for the detailed experiments and characterization). The starting polyoxometalate ([N(C$_4$H$_9$)$_4$]$_3$[MnMo$_6$O$_{18}$\{(OCH$_2$)$_3$-CNH$_2$\}$_2$]) is an organic-inorganic hybrid Anderson-type heteropolymolybdate with two amino groups.[15] The rod-like crystal of monomer MAPOM was obtained by the condensation of methacrylic anhydride and polyoxometalate diamine in acetonitrile, and then recrystallization with the diffusion of ether vapour into the solution of MAPOM in acetonitrile. The hybrid polymer, **PMMA-MAPOM**, was synthesized by the copolymerization of methyl methacrylate (MMA) and MAPOM with 1,1'-Azobis(cyclohexanecarbonitrile) (ABCN) as the initiator.[16] PMMA-MAPOM shows an excellent solubility in organic solvents, such as tetrahydrofuran, cyclohexanone, acetonitrile, and *N,N*-dimethylformamide. The number-average

The memory devices were prepared by spin-coating a PMMA-MAPOM solution on ITO glass substrate, then the film of PMMA-MAPOM was dried and a layer of Pt was deposited on the film as top electrodes, where Pt was used to avoid metal filament from the electrode diffusion.[18] The thickness of the hybrid polymer is 70 nm with a roughness of ~ 3.5 nm (Figure S8). The schematic structure of the sandwiched devices is depicted in Figure 2a. The multilevel memory effect of PMMA-MAPOM film was explored by *I–V* characteristics of ITO/PMMA-MAPOM/Pt memory devices. As shown in Figure 2b, the as-fabricated ITO/PMMA-MAPOM/Pt memory devices are in OFF state or high resistance state (HRS, Level **0**) with a current in the range of 10^{-7}-10^{-4} A (see sweep 1& sweep 4 in Figure 2b). By applying a voltage around -1.35 V, an abrupt current augment can be observed (with a current compliance of 1 mA), indicating that the device has been set to ON state or a low resistance state (LRS, Level **2**). This OFF-to-ON transition is defined as the "Write" or "SET" process, and the responding switching voltage is defined as "SET Voltage". The device will retain this ON state even after the power is turned off or during the

subsequent negative backward sweeping. As the positive sweeping voltage increases to ~ 0.8 V, the device current will reach its maximum value. The device current will reach to two different resistance states according to the applied positive sweeping voltage. If the sweeping voltage arrives to 1 V and then backward to 0 V, a current decrease can be observed (sweep 2 in Figure 2b), indicating that the device is switched from ON state to an intermediate state (Level 1). If the sweeping voltage enlarges to 1.5 V (sweep 3 in Figure 2b), the device current will further decrease (the maximum current of the responding voltage is about 1.36 V), in which process the device current returns to OFF state. These ON-to-OFF transitions can function in a memory device as an "Erase" or "RESET" process and the responding switching voltages are defined as "RESET Voltages". The resistance ratios (the ratios of R_{HRS}/R_M and R_M/R_{LRS}, where R_{HRS}, R_M and R_{LRS} are the resistance values at Level 0, Level 1 and Level 2, respectively) are ~5 and ~4, respectively. The devices also can be directly reset from ON state to OFF state with a positive sweeping voltage from 0 V to 1.5 V and backward to 0 V (sweep 5 in Figure 2b). These results demonstrate that our multilevel memory device is rewriteable and the resistive states can be well modulated by applying the RESET voltage amplitudes.

In order to investigate the endurance of ITO/PMMA-MAPOM/Pt devices, cyclic switching operations have been conducted (Figure 3a). After setting a memory device to LRS with a sweeping voltage to -2 V, the device is reset to two different HRS by applying two positive voltage sweeping, of which the maximum voltage are 1.0 and 1.5 V, respectively. The evolution of the resistance of these three well-resolved states over more than 50 cycles exhibits the good endurance of ITO/PMMA-MAPOM/Pt devices. The resistance values were read out at 0.3 V in each voltage sweep. Although there is a slight fluctuation of the resistances, the resistance ratios show distinct operation windows during RS cycles. In addition, the switching voltages to all three states during the cyclic testing also exhibit good operation windows with a little fluctuation (Figure S9). The retention performance of ITO/PMMA-MAPOM/Pt devices is shown in Figure 3b. The measurement was carried out in ambient atmosphere at room temperature with a reading voltage of 0.3 V. The fluctuation of the resistances of all three states, after 1×10^4 s without durable stress, is very small, which confirms the nonvolatile nature of the as-fabricated memory device.

The mechanism of the multilevel resistive switching of this POM-based hybrid polymer can be attributed to the multi-redox states of manganese centres in polyoxoanion, which can change the effective carrier density in the hybrid-polymer-switching layer under an electric field. Under electric stimuli, the gain or loss of the electrons of central Mn atoms will change the charge state of the polyoxoanion, and then the amounts of counter cations will alter correspondingly. In consequence, the effective carriers will adapt to this change, which leads to the switching of the conductivity in the bulk heterojunction film. In OFF state, the switching-layer film possesses the minimum effective charges and the conductivity of the film is lowest. Since Mn atoms are almost in the highest valence state (Mn (IV)) and the charge of polyoxoanion is the minimum, hence the amount of the corresponding counter cations is also the minimum. During the SET process (sweep 1 & sweep 4 in Figure 2b), Mn (IV) ions will be directly reduced to Mn (II) by applying a negative voltage of -2 V, and the charge of the polyoxoanion will increase to the maximum. As a result, the amount of counter cations will reach the maximum, and the conductivity of the film switches to the highest conducting state (sweep 1 & 4 in Figure 2b). On the contrast, Mn (II) ions in the RESET process will be oxidized to higher valence states with applying different positive voltage to the POM hybrid film. If the applying voltage is 1 V (sweep 2 in
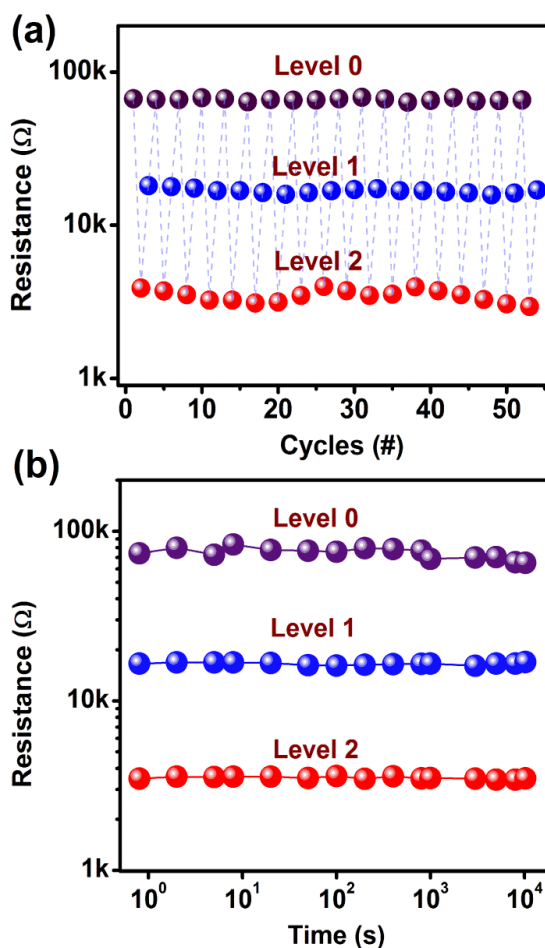
Figure 2b), Mn (II) ions will be oxidized to Mn (III) ions, and the charge of polyoxoanion, the amount of counter cations, and the conductivity will be reset to an intermediate value. If the applying voltage reaches 1.5 V (sweep 3 in Figure 2b), Mn (III) ions will be further oxidized to Mn (IV) ions, the conductivity will be in OFF state. The valence state of Mn centres can also be directly switched from II to IV with a sweep voltage of 0-1.5 V (sweep 5 in Figure 2b), and the device will be reset directly from ON state to OFF state. Since the amount of the effective carriers in previous research can be changed continuously,[7b] the energy barrier among different states is very little or even can be ignored. Therefore, the corresponding resistive switching shows volatile and needs a constant stress to maintain the LRS states. However, the barrier among these three states in this POM-based device is much larger, so these states can be maintained without constant stress and the devices show nonvolatile and excellent retention.

Conclusions

Multilevel memory devices based on a POM-based inorganic-organic hybrid polymer have been developed and these devices exhibit good endurance and good retention. This controllable multilevel resistive switching property of the inorganic-organic hybrid polymer-based devices is attributed to the multi-redox properties of POM clusters under electrical fields. Our success in employing a multi-redox inorganic-organic hybrid polymer

Figure 3. Endurance (a) and retention (b) of the multilevel memory based on the POM hybrid polymer.

as active layers to realize multilevel memories could offer a good opportunity to design and develop novel multi-redox materials for high-performance data storage devices.

Acknowledgements

Notes and references

[a]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798,Singapore. Email: _qczhang@ntu.edu.sg_
[b]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459,Singapore

Electronic Supplementary Information (ESI) available: Details of experimental procedure, TGA, DSC, UV-Vis and 1H NMR of the monomer and polymer, AFM image; switching voltages during cyclic testing. See DOI: 10.1039/b000000x/

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