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ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 12008–12010

www.rsc.org/chemcomm

COMMUNICATION

Effect of redox proteins on the behavior of non-volatile memory†

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Received 17th August 2012, Accepted 22nd October 2012
DOI: 10.1039/c2cc35959f

Downloaded by Korea University on 27 November 2012
Published on 05 November 2012 on http://pubs.rsc.org | doi:10.1039/C2CC35959F

We demonstrated the memory effect of redox proteins in organic field-effect transistor (OFET) flash memory devices. Redox proteins include a heme structure, which has reversible redox reactions. These properties of the proteins could be successfully applied to the flash memory devices, which show a considerable memory window (~11 V) and relatively good endurance properties (~over 100 cycles).

Organic non-volatile memory devices have attracted a great deal of attention from the memory industries because they have a high potential to realize low-cost fabrication at a low-temperature and at flexible charge storage sites. Among the diverse types of memory devices, many studies have focused on organic flash memory devices owing to their higher chip density and compatibility with the complementary metal-oxide-semiconductor (CMOS) process.[1–3] The memory effect of flash memory devices based on organic field-effect transistors (OFETs) is originated from the changes in the threshold voltage (V_{th}) by trapping/releasing the charge carriers of the semiconducting channel under external gate bias.[4] In general, charge trap sites can be produced on metal nanoparticles, inorganic–organic hybrid materials, or redox molecules.[5–7]

Redox proteins are beginning to gain significant attention in the bioelectric field such as bio-sensors[8] and bio-fuel cells[9] because they can control a variety of biochemical reactions. Recently, some remarkable attempts have been made to utilize the proteins in memory devices. For example, a flash memory device with cobalt oxide (Co_3O_4) nanodots (CoNDs) assembled by a protein template was reported by Fuyuki *et al.*[10] However, the protein was only used as the template for ordering CoNDs, which are the direct memory elements in the fabricated memory devices. Also, the resistive switching memory (ReRAM) device including with poly-electrolyte/enzyme multilayer fabricated by a layer-by-layer (LbL) method as the memory active elements was reported. However, in spite of good feasibility, complicated and cumbersome processes are required to organize the memory storage sites in the LBL assembly method using the polyelectrolyte/enzyme.[11]

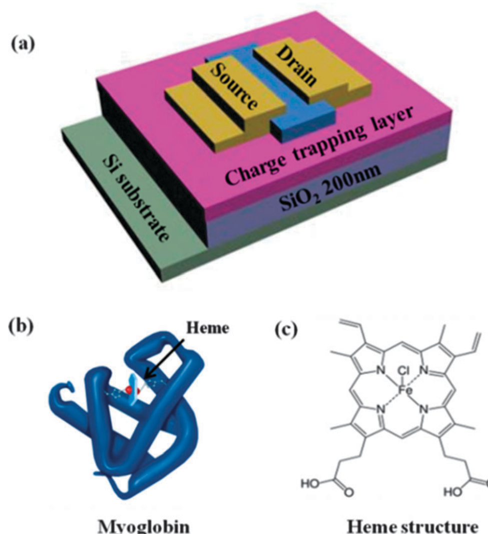

Fig. 1 (a) Schematic illustration of the OFET-based flash memory device including myoglobin as the charge trapping layer. The structure of (b) myoglobin and (c) heme in the charge trapping layer.

In this communication, we first demonstrate a simple approach to fabricating an OFET-based flash memory device that solely uses various redox proteins as the charge trapping layer. The redox proteins include organic ligands and transition metal ions such as Fe(II) and Cu(I). In general, repeatable oxidation and reduction reactions are generated due to transition metal ions in diverse environments.[12,13] The proteins, which exhibit a charge trapping effect mainly caused by the presence of redox active sites, can be applied as charge storage elements for OFET-based flash memory devices. In addition, we expect that the large cyclic organic rings surrounding the transition metal ions can act as a tunneling insulator layer.

Fig. 1(a) shows a schematic illustration of the device structure. A heavily p-doped silicon (Si) wafer was used as the gate electrode, with 200 nm of thermally grown silicon dioxide (SiO_2) acting as a blocking insulator. SiO_2 has a high band gap, which induces a very low leakage current that results in charge accumulation. A charge trapping layer, myoglobin from equine heart (Sigma-Aldrich), was spin coated to fabricate the thin film on the surface of the SiO_2/Si substrate. The myoglobin solution was prepared from 1% sodium buffer solution at a pH of 7.2 and stirred overnight under ambient

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc35959f

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Published on 05 November 2012 on http://pubs.rsc.org | doi:10.1039/C2CC35959F
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conditions at room temperature. This solution was spin coated at 2000 rpm for 30 s and then the myoglobin film was annealed at 80 °C for 1 h. Prior to spin coating, the substrate was exposed to ultraviolet ozone (UVO) for 30 min to uniformly coat the overall surface.

Cross-sectional scanning electron microscopy (SEM) images and atomic force microscopy (AFM) images in Fig. S1 (ESI†) were acquired to investigate the thickness and the morphology of the myoglobin layer prepared using 0.5 mM myoglobin solution. The values of the thickness and the RMS roughness were about 36 nm and 0.673 nm, respectively, as measured. A 50 nm thick layer of pentacene, a semiconducting p-type polymer, was evaporated under 3×10^{-6} Torr through a shadow mask. Finally, 100 nm thick Au electrodes were used as a source–drain electrode and deposited by the thermal evaporation with a deposition rate of 4 Å s^{-1}. The channel length (L) and width (W) were 100 μm and 1000 μm, respectively. The memory characteristics of our fabricated OFET-based flash memory devices were measured using an Agilent 4155B semiconductor parameter analyzer under dark conditions at room temperature. Fig. 1(b) presents the structure of myoglobin which is the monomeric heme protein and is mainly found in muscle tissue. The physiological importance of myoglobin is principally related to its ability to bind molecular oxygen.

As shown in Fig. 1(c), the heme structure is a prosthetic group that is made up of an iron atom surrounded by large heterocyclic organic ring called a porphyrin. Heme contains one central bound iron atom that is normally Fe^{2+}, or ferrous. The oxygen carried by heme proteins is bound directly to the ferrous iron atom. Oxidation of iron to the Fe^{3+}, ferric, oxidation state renders the molecule incapable of normal oxygen binding. During the process of binding oxygen, Fe^{2+} is temporally oxidized to Fe^{3+}, Fe^{3+} is reduced to the Fe^{2+} state when the oxygen is released. These reversible redox reactions of the iron ion in myoglobin induce the reasonable memory effect of OFET-based flash memory devices because heme proteins seem to be sufficient for trapping and releasing the proper amount of charge carriers. As shown in Fig. 2, the memory transistor that includes myoglobin presents the memory windows as a function of the concentration of myoglobin 0.05 mM (a), 0.1 mM (b) and 0.5 mM (c). At a gate voltage sweep range of 20 V to −40 V, the programming/erasing biases were −70 V/+70 V for 2 s. In OFET-based flash memory devices, the memory window is defined as a variation of V_{th} with the respect to the applied programming/erasing bias.

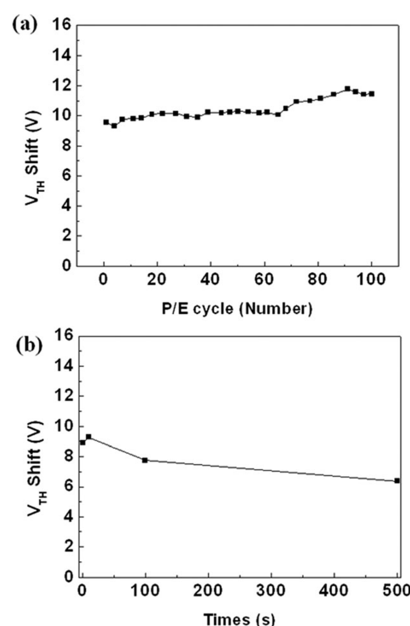

Fig. 3 (a) Endurance properties and (b) charge retention characteristics of the OFET memory device with a myoglobin layer. Both endurance and retention tests were conducted under ambient conditions at room temperature.

The memory properties were proportionally expanded with increased concentration of myoglobin solutions with the highest concentration at 0.5 mM. A maximum memory window of ~11 V was obtained at a myoglobin solution concentration of 0.5 mM. This result was generated from a shift in the electrical properties of myoglobin by reversible redox reaction because the charge distribution in the transistor was altered. A comparison of the transfer characteristics between the myoglobin chargeable layer included and excluded OFET-based flash memory devices is shown in Fig. S3 (ESI†). The initial on–off ratio and carrier mobility were measured to be 10^4–10^5 and 0.0574 $cm^2 V^{-1} s^{-1}$, respectively. The myoglobin chargeable layer included OFET memory device showed fairly good transfer characteristics compared with the myoglobin chargeable layer excluded OFET memory device at a gate voltage sweep range of 20 V to −40 V and a drain voltage of −40 V.

To gain an understanding of the influence of the pH of buffer solution on the OFET memory device performance,

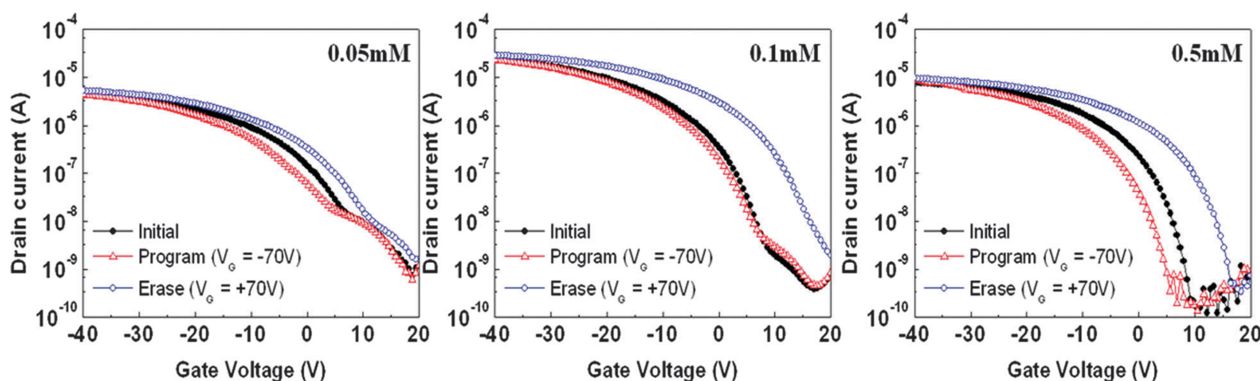

Fig. 2 Transfer characteristics of the organic transistor memory device according to the concentration of myoglobin solutions: (a) 0.05 mM, (b) 0.1 mM and (c) 0.5 mM. The memory window was obtained after programming with −70 V for 2 s and erasing with +70 V for 2 s.

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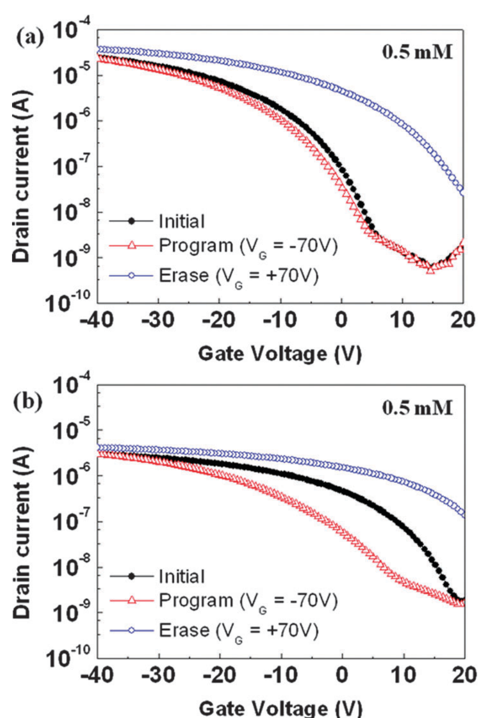

Fig. 4 Transfer curve for determining considerable changes in threshold voltage after applying P/E bias to the gate. The OFET memory device with (a) hemoglobin and (b) cytochrome *c* as the charge trapping layer.

transfer characteristics of the flash memory device in accordance with the pH of the buffer solution are shown in Fig. S4 (ESI†). The transistor properties and reliable memory window were observed at a pH of 7. In their acidic and basic state, the heme structure and organic rings are building blocks of redox proteins, which are more prone to denaturing in these states than at neutral pH.[14]

Good data retention capability and endurance performance are necessary requirements for memory devices to maintain stored information. The endurance and retention properties of an OFET-based flash memory device with the myoglobin chargeable layer are shown in Fig. 3. The endurance test was performed by applying repeatable programming/erasing bias pulses (−70 V/+70 V for 2 s). As shown in Fig. 3(a), the V_{th} shift was retained over 100 endurance cycles: one cycle consisted of one programming bias and one erasing bias. The changes in V_{th} were preserved over 100 cycles, because the reversible redox processes of the iron ion in the heme structure occurred stably. Fig. 3(b) illustrates the stored data stability of the flash memory device with the myoglobin charge trapping layer, indicated by the variation of V_{th} as a function of time under ambient conditions. The V_{th} shift was slightly reduced to 6.36 V after 500 s, which amounts to about a 30% loss. As organic rings surrounding the heme structure play a role as tunneling insulators, our memory devices did not contain any additional tunneling insulator layer. However, the stored charge carriers are prone to release from the charge trapping sites into the semiconducting channel because the organic rings are not a dense layer. This is why the transistor memory with a solely myoglobin layer exhibits relatively short retention time. Also, the trapped charge loss corresponds to the degradation of the very thin-myoglobin layer because of the moisture in the air. The additional tunneling insulator layers are required to extend the retention time. In previous studies, the metal-oxide tunneling layer (*e.g.* HfO_2[15] or Al_2O_3[16]) was deposited by a sputtering process or atomic layer deposition for robust operation. Although the retention properties of a flash memory device with a redox protein chargeable layer were inferior to that of a memory device with inorganic materials, we believe that the memory function of redox proteins will be improved through more extensive study of the surrounding structures in redox proteins.

Other redox proteins, such as hemoglobin and cytochrome *c*, can be applied to the charge trapping elements in memory devices because they also have the heme structure. Fig. 4 demonstrates the transfer characteristics of the OFET-based memory device using (a) hemoglobin and (b) cytochrome *c* as a chargeable layer. In the flash memory device with hemoglobin and cytochrome *c*, considerable V_{th} shifts were present (the processing conditions were the same as that of myoglobin). Therefore, we were able to confirm the charge trapping effect of heme proteins through the obtained transfer properties.

In conclusion, we have shown the considerable potential of using redox proteins as a charge trapping layer for OFET-based flash memory devices. The fabricated memory devices with a charge trapping layer fabricated with various redox proteins exhibited a large memory window and good data endurance capability. These memory effects were mainly caused by the charge trapping/releasing of the heme Fe(II)/Fe(III) couples within redox proteins. We expect our attempts to represent the beginning of non-volatile memory devices based on bio-functional materials. Furthermore, various redox proteins including redox active sites could potentially be applied to other types of memory devices as well as diverse electronic devices.

This work was supported by Center for Advanced Soft Electronics under the Global Frontier Research Program (2011-0031635), the Basic Research Program (2011-0018113 and 2010-0029106) and ERC Program (R11-2005-048-00000-0) of NRF funded by Korea government (MEST).

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