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Photoinduced write-once read-many-times memory device based on DNA biopolymer nanocomposite

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We demonstrate a photoinduced write-once read-many-times (WORM) organic memory device based on DNA biopolymer nanocomposite. The device consists of a single biopolymer layer sandwiched between electrodes, in which electrical bistability is activated by *in situ* formation of silver nanoparticles embedded in biopolymer upon light irradiation. The device exhibits a switching effect to high conductivity above a threshold of 2.6 V and a good retention property. This facile technique, taking advantage of DNA's affinity for metals and solution processing, can optically manipulate the properties of DNA nanocomposite thin films, which holds promise for optical storage and plasmonic applications. © *2011 American Institute of Physics.* [doi:10.1063/1.3671153]

There is a growing interest to develop functional memory elements for information technology, where data storage components are employed as building blocks. Data storage can be realized using devices that exhibit two states of different conductivities at the same applied voltage, a phenomenon known as electrical bistability. The use of organic materials for memory devices associated with solution processing pave the way for cost-effective and large-area implementation.[1,2] A number of approaches have been proposed for constructing the active layer of organic memory devices. One configuration is based on polymer-nanoparticle (NP) system, in which electrical bistability is observed for polymer incorporated with metal NPs.[1,3] Such polymer-NPs configurations are attractive as functional materials for many applications as the optical and electrical properties can be tailored by changing the composition and size/shape of the nano elements.[4]

On the other hand, deoxyribonucleic acid (DNA) is well-known as a good template for metal NP synthesis due to its affinity to the metal ions.[5] Recently, DNA has also been shown to be a promising optical material with the material processing fully compatible with conventional polymer for thin-film optoelectronic applications.[6,7] In this study, we demonstrate a photoinduced write-once read-many-times (WORM) organic memory device based on DNA biopolymer nanocomposite, taking advantage both of the DNA's affinity for silver ions and the ease of DNA film formation by spin-coating. Presented device consists of a single biopolymer layer sandwiched between two electrodes, in which memory-switching is functionalized by *in situ* photoreduction of Ag salt to produce Ag NPs embedded in biopolymer. Although DNA-templated fabrication based on a variety of metals is widely applied in biomolecular science,[8] we demonstrate that such feature can be combined with existing DNA biopolymer processing for the development of functional organic devices via facile and rapid photoinduced reduction of metal precursor in DNA biopolymer.

DNA from salmon testes purchased from Sigma-Aldrich (D1626) was fragmented by sonication to 1500 kDa. A cationic surfactant, cetyltrimethylammonium (CTMA) chloride, was used to form DNA biopolymer DNA-CTMA, rendering the DNA soluble in organic solvents. The detailed synthesis procedures of DNA-CTMA has been reported elsewhere.[9] Silver nanoparticles were formed via a photochemical synthesis using Irgacure-2959 ((1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one)) (I-2959). I-2959 produces ketyl radicals upon UV irradiation and the radicals then function as reducing agents for reduction of silver ions, leading to silver nanoparticle formation.[10] The as-synthesized DNA-CTMA biopolymer was dissolved in ethanol, mixed with silver trifluoroacetate, and stirred for one day at room temperature. I-2959 was then added to the mixed solution, in which the molar ratio of DNA biopolymer:silver trifluoroacetate:I-2959 was controlled to be 5:1:5. The solution was filtered through a syringe filter with a pore size of 1 μm prior to use. An illustration of the fabricated device is depicted in Fig. 1. The filtered solution was spin-coated on a patterned indium tin oxide (ITO) substrate at 3000 rpm for 20 s. The thickness of the active layer was 90 nm. The biopolymer layer was irradiated using UV light at 365 nm with an intensity of 3.5 mW/cm^2 for 1, 5 and 10 min. The wavelength of 365 nm was employed since it
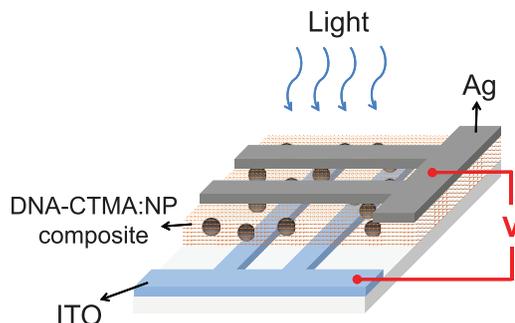

FIG. 1. (Color online) An illustration of the memory device consisting of a thin DNA biopolymer film sandwiched between electrodes. The memory-switching effect is activated upon light irradiation.

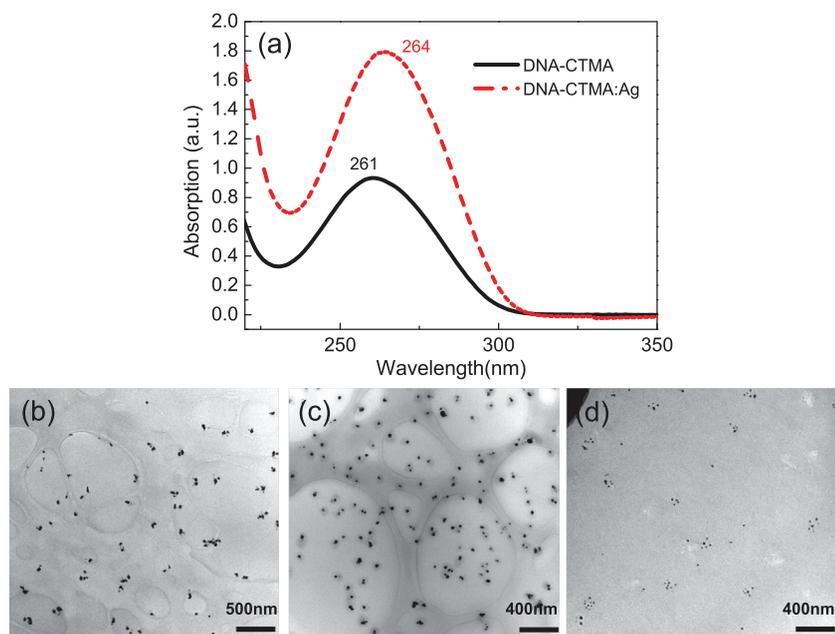a)Electronic mail: ychung@ee.nthu.edu.tw.

FIG. 2. (Color online) (a) UV-VIS spectra of DNA-CTMA and photoinduced DNA-CTMA:Ag. (b) TEM image of Ag NPs grown in DNA biopolymer under irradiation for 1 min, (c) 5 min, and (d) 10 min.

falls within the absorption band of the photoinitiator I-2959 and is transparent to DNA biopolymer. Top electrode was deposited by thermal evaporation in a vacuum chamber with 4×10^{-6} Torr. The devices were then encapsulated using an epoxy resin and a glass plate. The area of the device is 4×4 mm^2. The photoinduced DNA biopolymer nanocomposite was characterized by a UV-VIS spectrometer (PerkinElmer Lambda 35) and the TEM images were obtained using an electron microscope (Philips CM200 FEG/ST).

DNA-templated process was characterized by the formation of DNA-complexed metal ion. Upon silver ions complexation and reduction, the absorption maximum of DNA biopolymer exhibited a spectral shift from 261 nm to 264 nm as shown in Fig. 2(a), which was attributed to the DNA structural changes induced by the silver nanoclusters.[11] Figs. 2(b)–2(d) show the TEM images of the DNA biopolymer complexed with silver ions under irradiation for 1, 5, and 10 min. Photoinduced Ag NPs were formed in all cases with almost uniform distribution of NPs, although variation in size and distribution can be observed in samples under different irradiation durations. This can be explained by a thermally driven process of light induced growth. It has been shown earlier that strong electromagnetic field is induced around Ag NP, which causes further aggregation.[12] Aggregates which are forming from initial small Ag seeds absorb light and convert it to thermal energy, which enables further growth and particle coalescence. However, there are also strong indications that this process is not only thermally driven but O$_2$ might play an important role in the initial stages of seed formation.[13]

The fabricated devices were measured using an Agilent B1500A semiconductor device analyzer. Fig. 3 shows the current-voltage (I-V) curves for devices under irradiation for 1, 5, and 10 min, driven by a voltage scan between 0 and 6 V and a reverse scan between 0 and −6 V. In a case when device was not irradiated, the current traces did not exhibit any bistable phenomenon during the full voltage scan as shown in the inset figure. The electrical switching effect was observed for device under 1 min of irradiation and was most

pronounced for device with 5-min exposure time. The device demonstrated a low-conductivity state (OFF-state) with a current scale approximately at the order of 10^{-4}–10^{-5} A. Current increased dramatically to the order of 10^{-2}–10^{-1} A as the supplied voltage was slightly above a threshold amount of 2.6 V, and the threshold value increased for a thicker thickness of the active layer. This condition indicates that a high-conductivity state was attained, corresponding to the ON-state of a memory device. The ON/OFF ratio is $\sim$233 at 1 V. In the subsequent scan, the device remained in the high-conductivity state (ON-state) and did not return to the low-conductivity state by applying a high voltage in either polarity. Such device can be employed for the application of write-once read-many-times (WORM) memory element. For device under longer irradiation (e.g., 10 min), the switching behavior became less evident.

We further attempted to analyze the I-V curves of ON- and OFF-state using theoretical models for understanding the switching mechanism.[14,15] Fig. 4 shows the fitting results of the I-V curves both in OFF- and ON-state. For the OFF-state, a linear dependency with a slope of 1 was observed from the
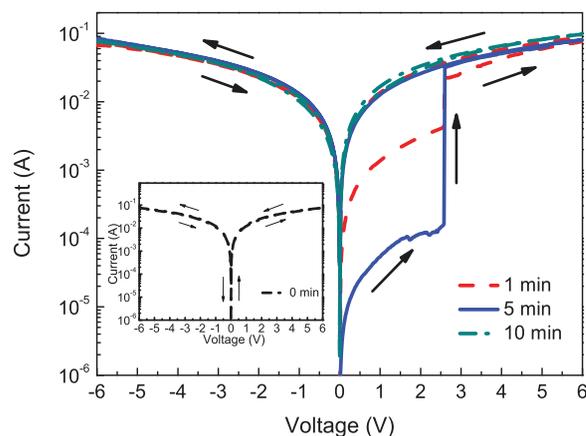

FIG. 3. (Color online) Current-voltage (I-V) curve of devices under 1, 5, and 10 min of UV exposure time. Inset: I-V curve of device without UV irradiation.
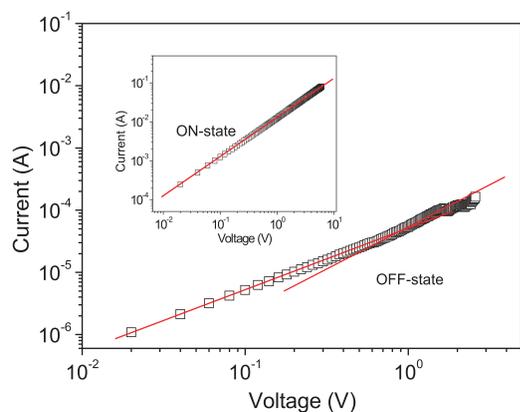
FIG. 4. (Color online) I-V curves of the device in log-log scale. The scatters are experimental data and the straight lines are the fitting curves from the theoretical models.

FIG. 5. (Color online) Retention characteristic of the OFF- and ON-state of fabricated device read at 1 V.

I-V relation and fitted well by Ohm's law. At higher driving voltages, a superlinear behavior was examined, implying that the injected charges overwhelm the transport capabilities of the biopolymer, resulting in the accumulation of positive charge near the ITO electrode. While the device was switched to ON-state, the I-V curve exhibits a linear relation with a slope of 1, suggesting the compliance of Ohmic process.

The experimental results indicate that the switching behavior is highly correlated to the size and distribution of NPs in the polymer matrix and device with relatively larger NPs shows more pronounced bistable phenomenon. Furthermore, the threshold voltage is related to the thickness of the active layer. The former feature implies that the switching mechanism is associated with the NP network topology and the latter indicates that the switching may be due to an electric field-induced effect. Not only the granular nature of metal NPs plays an important role in the manipulation of switching behavior[2,3,16] but the size of metal NPs affects the electrostatic energy, and as a consequence, larger particles tend to be more effective as traps.[3] In the OFF-state, Ag NPs result in traps in the matrix for injected carriers and a high resistance state was observed. Meanwhile, local field enhancement between nanoparticles occurred and electric field-induced filamentary paths were formed locally by defects or disorder within polymer matrix. Ag NPs were also involved in the formation of the filamentary paths.[17,18] Upon a threshold voltage, the percolation path was formed and therefore a lower resistance state was attained. This is supported by a NP network topology-dependent device performance and the Ohmic characteristic of the ON-state current, resulting from charge tunneling through filament paths induced by the electric field.[17,19]

Finally, we tested the retention property of the device, which is an important evaluation for stability of data storage. Fig. 5 shows the retention characteristic of the device measured by a semiconductor parameter analyzer (HP 4156 A). The device was read at 1 V both in ON- and OFF-state and the current was monitored every 100 s under ambient condition. The results indicate that there was no significant change of conductivity noted at both states during the testing duration for at least 10^5 s.

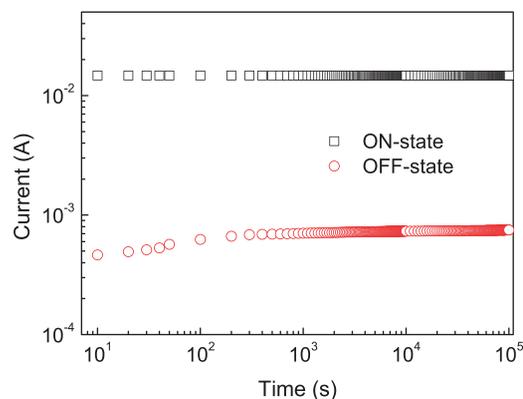To conclude, we have demonstrated a photoinduced WORM memory device based on DNA biopolymer:Ag NP nanocomposite. The memory effect was activated by photo-induced nanoparticle formation in DNA biopolymer loaded with Ag precursor. This approach combines the metallic affinity of DNA with photoinduced nanoparticle synthesis and provides a facile and convenient route for preparation of optically controlled nanoparticle-DNA biopolymers, which can be used to fabricate devices of interest by simple spin-coating process and may find broad implementation ranging from optical storage to plasmonic applications.

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