ABSTRACT: Interest in biodegradable and transient electronics is gaining due to their potential use in green electronics, biomedical devices, and sustainable solutions for e-wastes. In this paper we employed Protamine Sulfate (PS) as the active layer to demonstrate biodegradable transient resistive memory devices. The Au/PS/ITO device exhibits nonvolatile resistive switching with write-once-read-many (WORM) memory behavior. The observed WORM memory performance was very good with high memory window (4.57×10^3), data retention (experimentally >10^6 s, extrapolated >10^8 s), device yield (~87.5%), read endurance (>3.6 × 10^5), and device stability (>210 days). Bias induced charge trapping followed by conducting filament formation was the key to such switching. The electronic as well as optical behavior completely disappeared after 8 min of dissolution of the device in aqueous solution. As a whole this work suggests that the PS based WORM memory device may be a potential candidate toward designing biodegradable transient memory devices.

KEYWORDS: WORM, biodegradable, transient electronics, data retention, protamine sulfate, resistive memory

INTRODUCTION

Biomaterials have been extensively used for the realization of Green Chemistry. Owing to their vast advantages, the electronics industry is heading toward a sustainable solution involving biomolecules.1,2 Most of the present electronic devices mostly use inorganic elements as their structural ingredients, which has the physical limitation of downsizing the size and has a hazardous impact on their degradation in the environment. According to a recent study, India alone produced 53 million tons of electronic waste by the end of 2020 which is 40% of the global share.3 Countries like India with high population density have a larger probability of becoming affected by the hazardous elements leaching out from the improper decomposition of such e-waste materials. Therefore, alternate solutions are highly demanded. Electronic devices based on biomaterials have additional merits like bioabsorbability, biocompatibility, biomedical implantation, and obviously the large domain of choice of materials.4–6 Additionally, the transient nature of the biomolecules is the added advantage.

In addition, the scientific community is hopeful that the emergence of transient electronics may resolve the environmental issues arising from the rapid growth of consumer electronics.7,8 Transient electronics employ materials, devices, and systems that can be dissolved in biofluids or an aqueous environment and degrade into nontoxic products that can be absorbed by the surrounding medium when their operation is over.9,10 Biodegradability along with transient nature may be highly desired for the sustainable solution of e-waste disposal.

In addition, this kind of system is very useful for biomedical applications.10 The digital universe is becoming known for the information and data that is generated at an amount of millions of gigabytes (GB) every year.11 The emerging arenas of big data, cloud computing, AI, and so forth require high performance memory devices for data storage. Hence, in the near future data storage devices will be at a premium in the world of electronics. The resistive switching phenomenon can play a key role in the utilization of data storage devices as an alternative to the existing Si-based memory devices.12,13 Resitive switching is a popular characteristic in a molecule where resistance states can be switched between two levels upon application of suitable electric field. Depending upon the nature of the switching, volatile and nonvolatile characters can be observed. Such devices have important features like low cost, easy fabrication, down scalability, flexibility, high data retention, and so forth, which make them extremely useful for memory applications.14,15 Unlike Si-based memory devices, here a wide variety of materials can be employed ranging from organics, polymers, biomaterials, and so forth. A huge study has been accelerating for the need for high performance memory behavior using a
diverse range of molecules. Due to the biodegradability, resistive switching using biomolecules has attracted much attention. This could be a sustainable solution for data storage devices. Resistive switching in proteins, carbohydrates, starch, biopolymers, cellulose, enzyme, pectin, glucose, and even leaves have been studied by different research groups across the globe. A completely biodegradable memory device consisting of chitosan as the active layer and biodegradable magnesium as the electrode has also been reported. This is a very important and nice work from the biodegradable memory devices point of view. In the near future, we shall try to design a biodegradable memory device using biodegradable electrodes in addition to a biodegradable active layer.

However, more intense research is still required to explore the underlying mechanism in such memory devices. Also, a wide variety of materials need to be investigated. Among various resistive switching based memory devices, the write-once-read-many (WORM) memory device is non-volatile and is not rewritable. So, once the data is written into the WORM memory, it cannot be modified later. This makes WORM memory useful for several applications, where data security, reliability, and long-term storage is important, such as archival storage devices, permanent storage, secure databases, and electronic labels and so forth. There exist several reports of resistive switching devices employing biomaterials. However, among them WORM memory using biomaterials has only been observed in very few cases. WORM memory employing DNA with an ON/OFF ratio of $\sim 10^4$ and a data retention time over $10^5$ seconds has been demonstrated. Another DNA based WORM memory showed a very good ON/OFF ratio after more than 100 switching cycles and with a retention time of more than $10^5$ seconds. Wang and co-workers investigated WORM devices based on silk fibroin with a very high ON/OFF ratio $\sim 10^8$ and a retention time of more than $10^5$ seconds.

In this work, we have studied the resistive switching behavior of protamine sulfate (PS) which is a protein naturally found in salmon. PS is typically utilized as a medicine for coagulation. PS is also studied for its exclusive antimicrobial activity. Hence PS has a great deal of bio-absorbability with almost no harmful impact on the environment. A literature survey reveals that most of the Protamines consist of 50-110 amino acids which consist of a large number of amino linkages and carboxylic groups. These may act as trapping sites during carrier conduction and hence are expected to show resistive switching phenomenon. However, electronic applications of PS are hardly reported. Our investigations revealed that PS can be used to design a WORM device with high data retention characteristics, high stability, and good ON/OFF ratio. Also more importantly, the PS film could be completely dissolved in aqueous medium within 8 min. This indicates the application potential of PS based WORM devices toward biodegradable transient electronics.

**EXPERIMENTAL SECTION**

We purchased ITO coated glass substrate of resistivity 15-25 $\Omega$/Sq. from Sigma-Aldrich. Protamine sulfate was purchased from Sigma-Aldrich and used as received without any further modification. Ultrapure (18.2 MΩ-cm, Milli-Q) water was used to make the solution of Protamine Sulfate. Chloroform (spectroscopic grade, SRL, India) and isopropyl alcohol (spectroscopic grade, SRL, India) were used to wash the ITO-coated slides. FESEM (Sigma 300 model, Zeiss Pvt., Ltd.) operating at a 5 kV acceleration voltage was used to record the images for the surface morphology as well as the cross-sectional view of the device.

In order to fabricate the memory device, a PS solution in water (0.5 mg/mL) was deposited onto a cleaned ITO coated glass substrate using the drop-casting method. The purity of the ITO was checked by measuring the current-voltage ($I-V$) characteristics of the blank ITO slides. The film was then kept in a vacuum chamber for 24 h under ambient conditions. The vacuum deposition technique has been used to deposit gold electrodes onto the PS film using a mask system. For the Au/PS/ITO device, ITO acts as the bottom electrode and Au acts as the top electrode. A source meter (Keithley-2401) and a homemade probe station were used to measure the $I-V$ characteristics of the device. The device was kept inside of a homemade vacuum chamber with a temperature control facility to measure the $I-V$ curve at different temperatures.
RESULTS AND DISCUSSION

The surface as well as cross-sectional morphology of the PS film and Au/PS/ITO device have been investigated using field emission scanning electron microscopy (FESEM). Corresponding images have been shown in Figure 1. SEM images suggest that PS formed a uniform, smooth, and continuous film on the glass substrate. However, the ITO, PS layer, and Au electrode are clearly distinguishable in the Au/PS/ITO device as seen from the cross-sectional SEM image of the device in Figure 1b. Therefore, SEM investigation gives visual confirmation about the formation of the PS film as well as the Au/PS/ITO device.

Figure 2a shows the current–voltage ($I-V$) characteristics of the designed memory with (PS) as the active layer while applying a voltage sweep in the positive direction. The Au electrode was given positive bias while ITO was kept grounded. The bias voltage was optimized as 0 to $\pm 2$, and the compliance current (CC) as 10 mA. The scanning direction was 0 $\rightarrow$ +2 $\rightarrow$ 0 $\rightarrow$ -2 $\rightarrow$ 0 $\rightarrow$ +2 with a step voltage of 0.02 V. Interestingly, it has been observed that while scanning initially the device remains at a high resistance state (HRS), i.e., the OFF state and then suddenly the current increases sharply at 1.27 V. This is the typical threshold voltage ($V_{Th}$) at which the device switches from its low conducting state (HRS) to its high conducting state (LRS), i.e., ON state. This process is typically referred to as the writing process in the memory device.37,38 Interestingly it has also been observed that once the device is switched ON, it remains in the ON state and cannot be restored to the HRS (OFF state) by applying the bias voltage in either direction. The LRS state can also be preserved even when the electrical power is disconnected. Therefore, the observed switching phenomena between HRS (OFF state) and LRS (ON state) is irreversible and nonvolatile. The ON/OFF ratio was found to be $4.57 \times 10^3$. The observed results suggest that it is possible to design a memory device with PS as the active layer and the corresponding Au/PS/ITO device exhibits Write Once Read Many (WORM) like memory behavior.28 It has also been observed that this WORM like behavior can also be realized even when the initial scanning bias direction is reversed (scanning of direction 0 $\rightarrow$ -2 $\rightarrow$ 0 $\rightarrow$ +2 $\rightarrow$ 0 $\rightarrow$ -2) in Figure 2b. In that case, the $V_{Th}$ is found to be negative, whereas the...
ON/OFF ratio remains almost the same. This suggests that the observed switching behavior is independent of the voltage scanning direction. Again during scanning when \( V_{\text{max}} \) exceeds \( \pm 2.5 \) V, the device did not show any switching behavior but rather ohmic characteristics were observed. This indicates that the device may be short circuited through damage to the PS layer due to heating when the \( V_{\text{max}} \) exceeds a certain limiting value. So the maximum allowed scanning voltage range for the present device is \( \pm 2.5 \) V.

In order to have practical as well as commercial applications, reproducibility and sustainability of the designed memory device are highly required. Investigation of retention behavior may shed light in this regard. This gives an idea about the ability of the memory device to retain stored data into it, i.e., how long the device can maintain a particular state (HRS or LRS). In order to do that, the designed device Au/PS/ITO has been switched to its ON state and the LRS of the device was recorded on an average of 10 times per day up to 25 days at a read voltage of 0.6 V. Interestingly even after 25 days (2.16 \( \times \) 10\(^8\) s) the device maintained its ON state under ambient conditions as shown in Figure 3a. As far as the literature survey is concerned such long retention time using organic/biomolecules has never been reported. A cumulative probability of the ON state resistance (LRS) has also been shown in the inset of Figure 3a. The results suggested that the LRS values show very good stability even after 25 days with a standard deviation 3.6%. Therefore, our experimental data showed that the device can retain its ON state even after 25 days with negligible degradation. Hence in order to have an idea about the projected lifetime of the device, the retention characteristics have been extrapolated beyond 25 days.\(^{42}\) Interestingly the extrapolated data based on the LRS measured up to 25 days showed that the ON/Off window can be clearly discriminated even after 3.15 \( \times \) 10\(^8\) s, i.e., 10 years. Therefore, data retention as well as extrapolation of the experimental data suggested that the WORM device made with the use of the PS molecule can hold the stored data for at least up to 10 years. Such a value is very good in terms of the lifetime of the memory device with respect to the application point of view.

Besides data retention characteristics, the idea of the data endurance is also very important for sustainable applications of such devices. Reading endurance gives an idea of the number of times the stored data can be read for a particular device.\(^{36}\) In the present case once the device is ON, the LRS of the device is measured continuously at an interval of 1 s at a read voltage of 0.6 V. The corresponding results shown in Figure 3b revealed that at least 3.6 \( \times \) 10\(^4\) times read operation can be performed successfully with almost negligible distortion in the memory window.

In recent years resistive memory using organics as well as biomolecules have been very promising and are expected to be a replacement for the existing Si-based memory devices.\(^{16}\) However, the long-term stability of such devices remains a serious concern to date.\(^{33,44}\) In the present case in order to check the physical device stability, the \( I-V \) curves of the designed device have been recorded with the passage of time. Interestingly, it has been observed that almost reproducible switching behavior was observed even after 210 days from the days of device manufacture (Figure S1a of the Supporting Information, SI). The cumulative standard deviation of the switching voltage (\( V_{\text{Th}} \)) recorded with the passage of time has been found to be 14.38% (Figure S1b of the SI). As far as the literature survey is concerned, stability on the order of greater than 210 days is very good for practical applications. Although we measured the device stability up to 210 days, however, we expect that the present device will show stable reproducible memory behavior for an even longer time.

In order to investigate the device to device distribution of LRS, HRS as well as threshold voltage (\( V_{\text{Th}} \)), we have prepared 32 (8 \( \times \) 4 array) switchable independent devices in a PS layer deposited onto ITO glass. Thus, we get 32 devices with almost similar structure having a configuration of Au/PS/ITO. The physical picture of the same has been shown in the inset of Figure 4a. Interestingly, out of a total of 32 independent measurements, 28 devices showed reliable switching behavior with device yield of the order of 87.5%. The cumulative distribution of the switching voltage (\( V_{\text{Th}} \)) and the device to device variation of the OFF and ON resistances corresponding to this study have been shown in Figure 4a and b, respectively. The HRS resistance ranges from 2 \( \times \) 10\(^8\) to 4.5 \( \times \) 10\(^8\) ohms, whereas, the LRS resistance ranges from 64 to 100 ohms. The memory window extracted from these results ranges from 3.1\( \times \) 10\(^4\) to 4.5\( \times \) 10\(^5\), which is well within the acceptable limit for practical applications. The switching voltage (\( V_{\text{Th}} \)) ranges from...
1.15 to 1.63 V with a standard deviation of 14.3%. These results suggest that it is possible to design reproducible WORM devices using PS as the active layer. Different switching parameter/memory characteristics as extracted for the $I$–$V$ curves of the Au/PS/ITO device along with recently reported results have been listed in Table 1.

A close look at Table 1 reveals that in the present work, the data retention is higher compared to most of the earlier reported results. Also the device switched ON to a lower threshold voltage, which is also advantageous with respect to lower power consumption. The long stability of the device using biomaterials is always challenging, but in the present work we obtained the physical stability more than 210 days which is rarely reported for any resistive switching memory using bio-materials.

We tried to explore the underlying conduction mechanism behind such observed switching. Accordingly, $I$–$V$ characteristics of the Au/PS/ITO device have been measured at different temperatures ranging from 293 to 343 K. At all temperatures, the device showed almost reproducible switching behavior. However, the LRS resistance of the device decreased with an increase in temperature (Figure S2 of the SI). This observation negates the possibility that the observed switching is due to the formation of a conducting metal filament.46 Usually LRS resistances increase for such metallic filament formation.47 The role of an electrochemical oxidation–reduction process in the observed switching has also been investigated by cyclic voltammetry (CV) measurement. However, the absence of any distinct oxidation–reduction peaks in the CV curve of the PS deposited onto electrode eliminates the involvement of an oxidation–reduction process in the observed switching.47 To check the effect of the device thickness on switching, an Au/PS/ITO device has been prepared with the PS films having two different thicknesses, and their $I$–$V$ curves were recorded. An increase in $V_{th}$ has been observed with the increase in the PS layer thickness (Figure S3 of the SI), indicating the involvement of electric field driven conduction in the switching process.48

To further investigate the conduction mechanism of the WORM memory device, $I$–$V$ curves were analyzed using standard theories.26,29 $I$–$V$ curves of the HRS showed a linear change in the plot of $\ln(I)$ vs $V^{1/2}$, with a slope of 5.25 (Figure S4 of the SI). This suggests that the carrier transport in HRS follows Schottky’s emission.48

To understand the conduction mechanism further, the $I$–$V$ curves are replotted on double logarithmic scales and linearly fitted as shown in Figure 5. A close look at the figure elucidates that at low bias (HRS, slope $\sim$1, regime-1) the current is almost linearly proportional to the voltage and follows Ohm’s law. Here the applied bias voltage is very small and the number of injected carriers across the device is also very small. Most of the free charge carriers are thermally generated. The current density,

$$ J = \frac{q \mu n V}{d} $$

where $q$ is the charge of carrier, $n_0$ is the free carrier density, $\mu$ is the current mobility, $V$ is the voltage, and $d$ is the active layer thickness. With an increase in the bias voltage, the slope of the log ($I$) vs log ($V$) becomes 2.15 (regime-2). This indicated that the current through the active layer of the device is governed by the build of the charges injected from the source electrode. Here initially the current is controlled by trap centers existing in the active layer. Slowly the trap centers are occupied by the injected carriers. Space-charge-limited-conduction (SCLC) theory demonstrated that a typical space-charge effect leads to a current–voltage relationship like $I \propto V^2$ (slope-2) just after the ohmic region. However, a slight variation in the slope may be observed based on the depth of the trap centers in the active layer.29,50 In the Au/PS/ITO device, the trapping centers could be formed just below the conduction band due to the defects in the PS film or chemical composition of PS molecules, such as the carbonyl group and the amino linkage. Generally, the carbonyl group and amino linkage have been reported to act as the nucleophilic or electrophilic sites.51 At $V_{th}$, the traps are almost completely filled up and a sharp rise in the current occurred due to the further injection of carriers. Accordingly, the device is switched from its HRS to LRS. Here the slope is much greater than 2 (regime-3).52 When the

<table>
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<tr>
<th>device configuration</th>
<th>threshold voltage (V)</th>
<th>OFF state currents (Amp)</th>
<th>ON state currents (Amp)</th>
<th>ON/OFF retention time (s)</th>
<th>references</th>
</tr>
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<tr>
<td>Ag/Silk Fibroin/Au</td>
<td>1.3–3.4</td>
<td>$10^{-4}$ to $10^{-10}$</td>
<td>$10^{-1}$ to $10^{-2}$</td>
<td>$10^{-4}$ to $10^{4}$</td>
<td>33</td>
</tr>
<tr>
<td>PEDOT:PS/DNA/</td>
<td>−2</td>
<td>$10^{-10}$</td>
<td>$10^{-6}$</td>
<td>$10^{-4}$</td>
<td>31</td>
</tr>
<tr>
<td>PEDOT:PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag/albumen/ITO</td>
<td>2.2</td>
<td>$10^{-9}$</td>
<td>$10^{-2}$</td>
<td>$2.0 \times 10^{-7}$</td>
<td>26</td>
</tr>
<tr>
<td>PFN/PBS-5</td>
<td>1.6</td>
<td>$6.0 \times 10^{-5}$</td>
<td>$10^{-3}$</td>
<td>$10^{2}$</td>
<td>45</td>
</tr>
<tr>
<td>PFN/PBS-10</td>
<td>1.6</td>
<td>$2.0 \times 10^{-7}$</td>
<td>$10^{-5}$</td>
<td>$10^{2}$</td>
<td>45</td>
</tr>
<tr>
<td>Au/PS/ITO</td>
<td>1.33</td>
<td>$1.75 \times 10^{-6}$</td>
<td>$8 \times 10^{-3}$</td>
<td>$4.57 \times 10^{5}$</td>
<td>present work</td>
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</table>

Figure 5. Double logarithmic plot of the $I$–$V$ curve of the Au/PS/ITO device.
device is at LRS during the reverse voltage sweep, the slope was found to be $\sim 1$ (regime $-4$). This indicates the formation of a conducting filament in the ON state where the $I-V$ relationship obeys Ohm’s law ($I \propto V$).

The proximity of the electrode work function with the LUMO or HOMO level designates the type of charge carriers flowing to the active layer of the device. The work function of the ITO is $\sim -4.7$ eV, and the work function of the Au is $\sim -5.1$ eV. The HOMO and LUMO energy levels of the PS molecules are around $-9.128$ and $-4.758$ eV, respectively. A close look at these values indicates that the LUMO levels of the PS molecule are very close to the electrode work functions.

**Figure 6.** Schematic diagram of the switching mechanism of the Au/PS/ITO device.

**Figure 7.** Absorbance spectra of PS film with increasing dissolution time. Inset (a): Plot of ON/OFF ratio as a function of dissolution time. Inset (b): $I-V$ curve of the device before dissolution and after 8 min of dissolution.
This implies that a lower energy barrier for the electron to inject from the electrode to the LUMO level and hence into the active layer of the Au/PS/ITO device. Therefore, during the sweeping process electrons are injected to the PS layer. But initially they could not move freely due to the existence of the trapping centers or defects in the active layer. Hence at the initial stage of the sweep, the device displays a low conductivity OFF state with very limited increase in current. However, upon increasing the sweep voltage, electron injection increases slowly and gradually all the traps as well as defects in the PS layer are filled up. At V_{Th}, all the traps are filled up, resulting in the formation of a conducting filament across the PS layer in between the electrodes, as evidenced from the fitted Ohmic model (LRS, regime-4 in Figure 5). As a result, a sharp increase in the current is observed, and the device turns to the ON state. Upon removal of applied bias, detrapping did not occur and hence the device remains in its ON state. The injected trapped electron formed a permanent conducting filament across the PS layer in between two electrodes. The high cationic charge (+21) of protamine may also contribute to sustain the electron filament through strong electrostatic attraction within the trapping sites and the electrons. Accordingly no rupture of the filament occurred even when bias is removed.

The next time, as soon as the bias was applied, the device showed its conducting ON state following Ohm’s law and thus the Au/PS/ITO device showed nonvolatile WORM behavior.

A schematic explaining the switching mechanism has been shown in Figure 6.

In order to demonstrate the transient nature of the proposed memory device, we immersed the as prepared PS film in deionized water. Figure 7 shows a sequence of absorption spectra recorded at different dissolution times. The as prepared PS film before dissolution showed a prominent absorption band at around the 250–275 nm region. Interestingly, it was observed that with an increase in dissolution time, the absorption band intensity decreased systematically and completely diminished with a dissolution time of 8 min. This indicates the transient nature of the PS based WORM device. Digital photographs as well as the SEM images of the as prepared PS film and the same after complete dissolution also give visual evidence of the disappearance of the PS film. The corresponding images are shown in Figure S5 of the SI. To confirm further, we have conducted I–V measurement of the PS WORM memory device at different dissolution times. It has been observed that the resistance window decreases with the increase in immersion time (inset a of Figure 7). The I–V curve of the device before and after complete dissolution are also shown in inset b of Figure 7. Finally, the resistance window completely disappeared for the device with a dissolution time of 8 min or more leading to the ohmic nature of the ITO. As a whole, these results suggest that WORM memory using a PS film may find potential applications toward designing biodegradable transient memory devices.

**CONCLUSIONS**

In summary, biomaterial PS has been reported to have nonvolatile resistive switching behavior with WORM characteristics. The ON/OFF ratio of the device was found to have $4.57 \times 10^3$, whereas the read endurance was found to be $3.6 \times 10^4$. The data retention characteristics were found to be more than $2 \times 10^8$ s. Extrapolation of the retention data suggested that the proposed WORM memory device may have a lifetime of more than 10 years. The observed device stability was more than 210 days. The high device yield (87.5%) makes the device more effective for commercial purposes as well. The switching mechanism is mainly governed by the bias induced charge trapping followed by the permanent conducting filament formation. The transient characteristics of the PS based WORM device were examined to get an idea of the degradability. The absorption spectra and digital photographs, along with the I–V characteristics at different dissolution stages, confirmed the complete dissolution of the PS in deionized water within 8 min. Thus, transient and biocompatible PS could be the forefront biomaterial toward an ecofriendly solution for the next generation of memory devices.
REFERENCES


[NOTE ADDED AFTER ASAP PUBLICATION]

After this paper was published ASAP November 22, 2021, corrections were made to the TOC/abstract graphic and the Supporting Information. The corrected version was reposted December 3, 2021.