WORM Memory Effects in Gold Nanoparticles Loaded Aloe Vera Gel Films

Z.X. Lim¹, K.Y. Cheong¹

¹Electronic Materials Research Group, School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia
Email: srcheong@usm.my

Abstract. A bio-organic memory device based on a thin layer of gold nanoparticles (AuNPs) loaded Aloe vera gel is demonstrated. The device functions in analogous to an electric fuse, in which the irreversible dielectric breakdown in the A. vera gel film causes permanent switching from a high-resistance state to a low-resistance state. The concentrations of AuNPs loaded in the A. vera gel film can alter its optical bandgap, thereby affecting the device operational properties. The demonstration further expands the electronic application of naturally occurring A. vera gel.

1. Introduction

Rapid changing consumer behaviors and growing environmental awareness have driven a paradigm shift in the way natural resources are being utilized. The immediate impact would be the ongoing dominance of inorganic materials, notably Si, Ge, and GaAs, for a wide variety of electronic applications. Technological evolution over the past decades has enriched mankind with various electronic devices that are being massively produced at rock bottom costs. Consequently, the useful lifespan electronic devices are getting shorter, as they are considered obsolete when new devices with more advanced functionality start to make inroads to the market [1-3]. This planned obsolescence of electronic devices will eventually lead to the sustainability issues when massive amounts of electronic waste are being piled up at landfill sites around the world [4-6]. The impending Internet of Things that encompasses almost every aspects of daily lives requires new functional materials which are biocompatible, biodegradable, renewable, energy-efficient, and low-cost to ensure a sustainable ecosystem within the electronics manufacturing industry.

The paradigm shift toward sustainable electronics has opened up new opportunities for bio-organic materials [7-11], which are generally derived from living or once-living organisms that are found in abundance in the nature. These materials are not only renewable, biodegradable, biocompatible, and environmentally friendly for addressing the environmental issues concerning with electronic waste hazards, but also exotic for next-generation electronics realization. One such natural bio-organic materials is the gel extracted from Aloe barbadensis Miller (Aloe vera), a succulent plant that has been widely cultivated throughout the world. While A. vera gel is commonly used for various medical, cosmetic, and nutritional purposes [12-15], its solid-state electronic application remains largely unexplored. A. vera plant has been demonstrated to show responses toward various electrical signals in vivo [16-18], making it a promising candidate for utilization in solid-state
electronics. Our research group has attempted to develop solid-state electronics on the basis of *A. vera* gel thin films as both passive and active layers [19-26].

Here, we demonstrate write-once-read-many (WORM) memory effects in a simple metal-insulator-metal (MIM) device with *A. vera* gel film functioning as the middle insulating layer. The device works in analogous to an electric fuse. Owing to the dielectric properties of the *A. vera* gel film, the pristine device is in its high-resistance state (HRS). Upon undergoing dielectric breakdown, the device is electrically switched to a low-resistance state (LRS). Because dielectric breakdown is an irreversible process, a recovery back to the initial HRS is impossible. The effect of gold nanoparticles (AuNPs) loading in the *A. vera* gel film on the device operational properties is systematically studied.

2. Experimental Procedure

*A. vera* gel was extracted from *A. vera* leaves measuring about 30–50 cm in length cut from a 3-year-old plant that is cultivated in the garden of School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia Engineering Campus, Penang, Malaysia (Figure 1). Freshly harvested leaves were washed thoroughly with flowing distilled water to remove surface dirt and sap. After removing the spikes along the margins, the epidermis of the leaves was separated from the inner parenchyma using a knife and spoon. The epidermis was discarded, while the parenchyma were washed with distilled water to remove exudate before being homogenized in a food processor (Philips, The Netherlands) at low speed for about 5 min. Then, the homogenized *A. vera* slurry was centrifuged (Rotina 38, Hettich, Germany) at 3,000 rpm for 30 min to separate heavy fibers from the supernatant, which contains the *A. vera* gel. The *A. vera* gel was recovered and vacuum filtered through a filter paper in a sintered glass funnel. The centrifugation and vacuum filtration steps were repeated for at least 10 times to obtain the fiber-free *A. vera* gel for use in subsequent device fabrication.

The device has a simple metal-insulator-metal (MIM) structure, which were fabricated bottom-up according to the following procedure. First, a glass slides was cut into a dimension of 1.5 cm × 1.5 cm for use as the substrates, which were cleaned sequentially in an ultrasonic bath containing acetone (CMOS grade, J.T. Baker), ethanol (95 v/v%, Merck Millipore), and deionized water for 30 min each. Then, 10 mL *A. vera* gel was added with different volumes of (0.2, 0.5, 0.7, and 1 mL) gold nanoparticles (AuNPs) that was purchased from Sigma-Aldrich (Cat. No. 741949-100ML, 5 nm, OD = 1). The mixture was homogenized ultrasonically and was spin-coated onto the glass substrates pre-coated with a layer of 100-nm Al. The *A. vera* gel-AuNPs film was dried subsequently in an oven (UNB100, Memmert, Germany) at 90°C for 5 min before an array of 100-nm Al as the top electrodes was thermally evaporated (K950X, Quorum Emitech, UK) at a base pressure of ~10^-4 Torr via a metal mask (feature size 1 mm in diameter).

![Figure 1. The workflow from *A. vera* gel extraction to device fabrication.](image)

The surface morphology and thickness of the *A. vera* gel-AuNPs film were characterized using scanning electron microscopy (SEM; Supra 35VP, Zeiss, Germany). The optical properties of the *A. vera* gel-AuNPs film were studied using UV-visible spectroscopy (Cary 50, Varian, USA). The current–voltage (I–V) characteristics of the device was measured using a semiconductor parameter analyzer (4156C, Agilent Technologies, USA).
3. Results and discussion

Figure 2 shows the surface morphology of the *A. vera* gel film loaded with different concentrations of AuNPs. The *A. vera* gel film forms a flat and smooth surface when being deposited on the glass substrate (Figure 2a). However, the surface morphology becomes bumpy with the addition of different volumes (0.2–1.0 mL) of AuNPs (Figure 2b–e). The uneven surface structures mimic the shape of nanoparticles with diameters ranging 3.5–18.5 nm. Obviously, the AuNPs are well-dispersed throughout the film as there is no indication of agglomeration. It has been reported that *A. vera* gel film loaded with nanoparticles demonstrated better insulating properties that render its application as the dielectric layer in electronic devices [19-21,26]. The addition of nanoparticles can result in the creation of defects in the form of grain boundaries, local strains, impurities, broken or cross-linked biopolymer chains. Consequently, more localized states serving as electronic charge traps present in the film leading to better insulating properties.

![Figure 2](image1)

**Figure 2.** Surface morphology of the *A. vera* gel film loaded with (a) 0 mL, (b) 0.2 mL, (c) 0.5 mL, (d) 0.7 mL, and (e) 1.0 mL of AuNPs.

Figure 3 shows the cross-sectional SEM images of the *A. vera* gel film loaded with different amount of AuNPs on a glass substrate. The thickness of each film is measured from the SEM images and is summarized in Table 1. The addition of AuNPs appears to have no effect on the film thickness, as there is only a difference of 12.3 nm between the thickest (*A. vera* gel + 0.5 mL AuNPs) and thinnest (*A. vera* gel + 1.0 mL AuNPs) films.

![Figure 3](image2)

**Figure 3.** Cross-sectional SEM images showing thickness of the *A. vera* gel film loaded with (a) 0 mL, (b) 0.2 mL, (c) 0.5 mL, (d) 0.7 mL, and (e) 1.0 mL of AuNPs.
Table 1. Thickness of the A. vera gel film loaded with different amount of AuNPs.

| Sample                        | Thickness 1 (nm) | Thickness 2 (nm) | Average Thickness (nm) |
|-------------------------------|------------------|------------------|------------------------|
| A. vera gel                   | 226.8            | 229.6            | 228.2                  |
| A. vera gel + 0.2 mL AuNPs    | 232.2            | 227.8            | 230.0                  |
| A. vera gel + 0.5 mL AuNPs    | 234.5            | 241.2            | 237.9                  |
| A. vera gel + 0.7 mL AuNPs    | 216.6            | 243.4            | 230.0                  |
| A. vera gel + 1.0 mL AuNPs    | 230.0            | 221.1            | 225.6                  |

Figure 4a shows the current–voltage (I–V) characteristics of the device measured using a single DC voltage sweep from 0 to 15 V at 0.01 V/step under ambient conditions. Notice the occurrence of dielectric breakdown in the A. vera gel film without AuNPs loading at 9.36 V, corresponding to an electric field strength of (9.36 V)/(228.2 nm) = 0.41 MV/cm. This breakdown voltage shifts to higher values, i.e. 9.93 V and 10.34 V, when the AuNPs loading is increased to 0.2 mL and 0.5 mL respectively. However, as the AuNPs loading in the film is further increased to 0.7 mL and 1.0 mL, the breakdown voltage is shifted toward lower values, i.e. 8.76 V and 7.83 V, respectively. Figure 4b shows the UV-visible spectra of the A. vera films with different AuNPs loading. Apparently, the A. vera gel films display UV opacity attributes, due to their high absorbance of wavelengths that fall within the range of 200–400 nm. Their optical energy bandgap can be extracted from the UV-visible spectra (Figure 4b) using Tauc’s relation: $(\alpha h c/\lambda)^{1/2} \propto (h c/\lambda)$, where $\alpha$, $h$, $c$, and $\lambda$ refer to the absorbance, Planck’s constant, speed of light, and wavelength respectively. Figure 4c presents the optical bandgap of the A. vera gel films as a function of AuNPs loadings. The maximum optical bandgap is achieved by the A. vera gel film loaded with 0.5 mL AuNPs. As the optical bandgap increases, the breakdown voltage is shifted to a higher value.

Concentration of AuNPs (mL)

0.0 0.2 0.4 0.6 0.8 1.0 1.2
Optical Bandgap, $E_g$ (eV)

3.2 3.3 3.4 3.5 3.6 3.7 3.8

Figure 4. (a) I–V characteristics of the device. (b) UV-visible spectra of A. vera gel films loaded with AuNPs. (c) Optical bandgap of the film extracted from the UV-visible spectra.

4. Conclusion

WORM memory effects in AuNPs loaded A. vera gel films are demonstrated using a simple MIM device structure. The AuNPs loading modifies the surface morphology of the A. vera gel film so that it becomes rough and uneven, but it does not affect the film thickness. The breakdown voltage increases when 0.2–0.5 mL of AuNPs is loaded into the A. vera gel film. Conversely, the breakdown voltage decreases when 0.7–1.0 mL of AuNPs is loaded. The AuNPs loading can alter the optical bandgap of the A. vera gel film causing the changes in breakdown voltage.
Acknowledgements

This work was financially supported by the Malaysian Ministry of Higher Education (MOHE) and Universiti Sains Malaysia (USM) under the Fundamental Research Grant Scheme (203/PBAHAN/6071301), Research University–Individual Grant (1001/PBAHAN/814216), and Postgraduate Research Grant Scheme (1001/PBAHAN/8036018). ZX Lim gratefully acknowledges MOHE for supporting his graduate study in USM under MyBrain15–MyPhD scholarships program. The authors acknowledge the financial aid provided by the School of Materials & Mineral Resources Engineering, USM to attend RCM & AMC 2017.

References

[1] Bauer S and Kaltenbrunner M 2014 ACS Nano 8 5380
[2] Geyer R and Blass VD 2010 International Journal of Advanced Manufacturing Technology 47 515
[3] Robinson BH 2009 Science of The Total Environment 408 183
[4] Irimia-Vladu M, Glowacki ED, Voss G, Bauer S and Sariciftci NS 2012 Materials Today 15 340
[5] Savage N 2015 IEEE Spectrum 52 18
[6] Cucchiella F, D’Adamo I, Koh SCL and Rosa P 2015 Renewable and Sustainable Energy Reviews 51 263
[7] Mühl S and Beyer B 2014 Electronics 3 444
[8] Irimia-Vladu, Troshin PA, Reisinger M, Shnygileva L, Kanbur Y, Schwabegger G, Bodea M, Schwödiauer R, Mummyatov A, Fergus JW, Razumov VF, Sitter H, Sariciftci NS and Bauer S 2010 Advanced Functional Materials 20 4069
[9] Irimia-Vladu M, Sariciftci NS and Bauer S 2011 Journal of Materials Chemistry 21 1350
[10] Raeis-Hosseinei N and Lee JS 2017 Journal of Electroceramics 39 223
[11] Jung YH, Chang TH, Zhang H, Yao C, Zheng Q, Yang VW, Mi H, Kim M, Cho SJ, Park DW, Jiang H, Lee J, Qiu Y, Zhou W, Cai Z, Gong S and Ma Z 2015 Nature Communications 6 7170
[12] Eshun K and He Q 2004 Critical Reviews in Food Science and Nutrition 44 91
[13] Rodriguez RE, Martin JD and Romero CD 2010 Critical Reviews in Food Science and Nutrition 50 305
[14] Hamman J 2008 Molecules 13 1599
[15] Capasso F, Borrelli F, Capasso R, Di Carlo G, Izzo AA, Pinto L, Mascolo N, Castaldo S and Longo R 1998 Phytotherapy Research 12 S124
[16] Volkov AG, Reedus J, Mitchell CM, Tucket C, Forde-Tuckett V, Volkova, MI, Markin VS and Chua L 2014 Plant Signaling and Behavior 9 e29056
[17] Volkov AG, Nyasani EK, Tuckett C, Scott JM, Jackson MMZ, Greeman EA, Greenidge AS, Cohen DO, Volkova MI and Sh tessel YB 2017 Bioelectrochemistry 113 60
[18] O’Neal L, Ebere LC, McIntyre R, Volkova-Gugeshavili MI, Markin VS and Volkov AG 2013 ECS Transactions 50 7
[19] Khor LQ and Cheong KY 2013 Journal of Materials Science: Materials in Electronics 24 2646
[20] Khor LQ and Cheong KY 2013 Advanced Materials Research 858 74
[21] Khor LQ and Cheong KY 2013 ECS Journal of Solid State Science and Technology 2 P440
[22] Lim WF, Quah HJ, Sreenivasan S and Cheong KY 2015 Materials Technology: Advanced Performance Materials 30 A29
[23] Lim ZX and Cheong KY 2015 Physical Chemistry Chemical Physics 17 26833
[24] Lim ZX, Sreenivasan S, Wong YH, Zhao F and Cheong KY 2016 MRS Advances 1 2513
[25] Lim ZX, Sreenivasan S, Wong YH, Zhao F and Cheong KY 2017 Procedia Engineering 655
[26] Lim ZX, Sreenivasan S, Wong YH and Cheong KY 2017 AIP Conference Proceedings 1865 050006