Compliance Current-dependent Dual-functional Unipolar and Threshold Resistive Switching in Silver Nanowires-egg Albumen Composites-based Device

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Abstract. The continued exploration of novel synthetic memristive materials with multifunctional properties is critical for future synapse-emulating circuits and electronic devices in the field of next-generation neuromorphic computing applications. In this work, the silver nanowires (AgNWs)-Egg albumen composites have been integrated as a resistive switching layer in the Ag/AgNWs-Egg albumen/Ag planar structure and exhibits both unipolar (memory) switching and threshold switching functions. The device in unipolar switching regime demonstrates an ON/OFF ratio above 10⁵, a low resistance state of about 1.2 KΩ and a high resistance state of about 120 MΩ. Finally, a mechanism in combination with the conductive filament theory and a tunnelling conduction mechanism is proposed to explain the resistive switching behavior. The devices are prepared by simple and low-cost techniques, which make such devices appealing for future electronic applications.

1. Introduction
With the enormous growth in data and internet of things, the next-generation memory devices able to be scaled beyond the Moore’s law are developing more rapidly where memory and processing are better collocated.[1, 2] The emerging memristor which presents a variable resistance that can be controlled by applying a voltage has become a dominant candidate for information storage components and brain-inspired computing.[3-6] In the memristor, the active layer usually changes its states from a high resistance state (HRS or OFF-state) to a low resistance state (LRS or ON-state) and vice versa upon application of voltage amplitudes. Depending on the polarity of the voltage required, the switching process is mainly categorized as bipolar (BRS) and unipolar switching (URS), corresponding to nonvolatile memory switching (MS). Besides the aforesaid MS, there exists another type of switching, threshold switching (TS), which exhibits volatile resistive switching from HRS to LRS at a particular voltage and switches to HRS once the applied voltage is smaller than a critical value.[7, 8]
The use of composite materials in memristor devices has the potential to outperform conventional materials. Their fascinating properties are also favorable for the development of future multifunctional memristor devices. Silver nanowires (AgNWs) have attracted considerable interest in the use of composite materials for memristor technology, where the switching action is controlled by the properties of both the electrodes using AgNWs as core and the dielectric materials coating on the
surface of AgNWs that comprise these devices.[9-15] As a typical natural biomaterial, egg albumen (or egg white) has shown promise as the resistive switching layer in the memristors with sandwiched structure.[16, 17] Meanwhile, from the perspective of biological applicability, egg albumen is also biocompatible, implantable, and cheaply produced. Silver nanowire and Egg albumen have already been widely explored, respectively, but to date, the electrical behaviors of AgNWs-Egg albumen composites have not been described.

In this work, we describe the unique electrical properties that emerge by combining the two materials into composites for the first time. Typical memristor cells are constructed as Ag/AgNWs-Egg albumen/Ag planar structure and have displayed a wealth of resistive switching behaviors including the coexistence of both URS and TS, which is distinct from the normal resistive switching behavior of memristor device using egg albumen as the resistive layer. The dual-mode switching behaviors in the devices were thoroughly investigated by controlling the compliance current of the device. On the basis of the results, we propose a switching mechanism in a combined tunneling conduction mechanism and the filament theory to explain the resistive switching behaviors.

2. Experimental Section

2.1. Materials
Silver nitrate (AgNO₃, weight-average molecular weight (Mw) = 169.87) was purchased from Shanghai Shenbo Chemical Co., Ltd. Polyvinyl pyrrolidone (PVP, Mw = 1 300 000) was purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Sodium chloride (NaCl, Mw = 58.4) and ethylene glycol (EG, ρ = 1.036 g/mL) were purchased from Chengdu Kelong Chemical Co., Ltd. Egg albumen was obtained from a fresh chicken egg. All chemicals except eggs were used without further purification. Ultrapure, deionized water was used in all experiments.

2.2. Fabrication of the resistive switching device based on AgNWs-Egg albumen composites
The AgNWs were synthesized by a salt-mediated polyol process. In a typical synthesis, ethylene glycol containing PVP was first heated with magnetic stirring at 160 °C for 30 min and then NaCl was added. After cooling to room temperature, AgNO₃ was added and then heated at 150 °C for 5 h. Finally, the as-prepared AgNWs were obtained by centrifugation and washed with water and ethanol three times before finally being dispersed in deionized water. Egg albumen was collected by breaking the shell of a fresh, precleaned chicken egg. Some egg albumen can be filtered out by a stainless-steel mesh spoon. Then, extract the sample (volume: 1 mL) from the egg albumen solution using a pipette and mixed with 15 mL of AgNWs solution to synthesize a thin film for device fabrication. The mixed solution was stirred for 30 min. The as-prepared AgNWs-Egg albumen solution was spin-coated onto the precleaned glass substrates with prepatterned Ag electrodes at 1500 rpm for 10 s and 2500 rpm for 20 s. The distance between counter electrodes and width of the electrodes were both about 200 μm for the network device. The device was then baked at 105 °C for 10 min.

2.3. Materials and device characterization
Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 scanning electron microscope. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were observed with Titan 80-300 transmission electron microscope. The crystal structures of the as-synthesized AgNWs were analysed using X-ray diffraction (XRD) with Cu-kα radiation. The electrical properties of the devices based on the AgNWs-Egg albumen composites was tested by a Keithley 4200 Semiconductor Characterization System connecting with a probe station.

3. Results and discussion
SEM and TEM micrograph of the AgNWs is presented in figure 1a and b, respectively. The as-synthesized AgNWs had an average length of about 20 μm and an average diameter of 80 nm. A 3 nm thick PVP coating can be observed in the HRTEM image shown in figure 1c. The AgNWs exhibit a pure face-centered-cubic (fcc) structure (JCPDS File No. 04-0783), as shown in figure 1d.[11]
Figure 1. (a) SEM image, (b) XRD pattern, (c) TEM image, and (d) HRTEM image of AgNWs.

Figure 2a shows the current-voltage (I-V) of AgNWs-Egg albumen composites-based device with planar Ag/AgNWs-Egg albumen composites/Ag structure under repetitive positive and negative voltage sweeps with a compliance current ($I_{CC}$) of 1 µA in linear scale. For the first voltage sweep under positive region, the device starts transition from HRS to LRS at a threshold voltage, $V_{th} = +1.16$ V, and again switches to HRS for voltage less than a certain voltage, known as the hold voltage, $V_{hold} = +0.06$ V. The observed behavior corresponds to TS behavior, as the LRS can hardly be maintained after removal of the applied voltage.[18, 19] Symmetric resistive switching behavior was also observed with the opposite polarity bias, showing that the threshold switching is bidirectional in nature. Figure 2b shows the multilevel I-V curves of the device under different $I_{CC}$ values, ranging from 10 to 500 µA. It is worth noting that volatile TS behavior cannot be changed here by a higher applied $I_{CC}$ until increased up to 500 µA. After a higher compliance current (500 µA), during the positive voltage sweep, the current gradually increased, and then, abrupt change of the current was observed at about $V_{th} = 0.64$ V. However, when the voltage was swept back to 0 V, the device was remained in the LRS. In the negative bias region, the device with switchable resistance was then changed into a resistor, and the devices became conductive. When the compliance current was removed, at a voltage, $V_{RESET} = 3.88$ V, the device revert to HRS as shown in figure 2c, consistent with RESET process of unipolar resistive switching operation.

Figure 2. (a) I-V curve of AgNWs-Egg albumen composites-based device in linear scale. The compliance current ($I_{CC}$) is 1 µA. (b) Multilevel I-V curves of the device operated for four $I_{CC}$ values ($I_{CC} = 10, 50, 100, 500$ µA) in log scale. (c) I-V curves with $I_{CC}$ being removed for RESET.
Figure 3a shows the typical MS property of the AgNWs-Egg albumen composites-based device in the unipolar regime. During the forming and SET processes, a $I_{CC}$ level of 500 µA is set to prevent the device from switching back to the HRS at zero bias. The device switches from the HRS ($\sim$ 120 MΩ) to LRS state ($\sim$ 1.2 KΩ) at a SET voltage of $V_{set} = +1.88$ V. A RESET process was required to bring the device from the LRS to HRS. Thus, $I_{CC}$ is removed, and the RESET process happened at 1.1 V. Figure 3b depicts the data retention capability of the device up to 550 s at a read voltage of 0.5 V, which signifies the nonvolatile property of the memory device. Although little variation in OFF and ON-state can be observed, a steady ON/OFF ratio of $10^5$ is maintained in the switching device.

Figure 3. (a) MS property of the AgNWs-Egg albumen composites-based device in the unipolar regime. (b) Retention characteristics of the device.

Figure 4. Double logarithmic I−V curves of the AgNWs-Egg albumen composites-based device during the (a) SET and (b) RESET process.

To understand the conduction mechanism of the AgNWs-Egg albumen composites-based device, the I−V characteristic was replotted on the $\text{Ln}(I)$ vs $\text{Ln}(V)$ graph, as shown in figure 4. During the SET process (Figure 4a), the I−V relationship with a slope of $\sim$1.4 in HRS was observed. After the abrupt increase in the current, switching from HRS to LRS occurred. As shown in figure 4b, LRS showed a nearly linear dependence of current on voltage ($\sim$1.0), indicating the ohmic conduction. An obvious RESET process occurred at a lower voltage, and the device was completely switched back to HRS with a slope of $\sim$1.5. It is very common to see two or even three different mechanisms dominate the resistive switching behavior.[20] As a consequence, we propose a possible conduction mechanism based on two different phenomena: i) electron tunnelling over the physical distance of extremely close silver nanowires; and ii) conductive filament formed in the egg albumen. As the applied voltage increases, starting from zero bias at the HRS, the transition to the LRS occurs at a certain threshold voltage due to an abrupt electron tunnelling between close silver nanowires. Besides, as the temperature of the system increases due to Joule heating, thermally-activated electrons and the dissolution of the Ag metal cation from the AgNWs can be injected through the egg albumen under the combined effect of electric fields, thermal diffusion. Once the process starts taking place, it induces a further Joule heating, thus developing a chain reaction process that yields a sharp increase in current. This allows a stable conductive state as a result of conductive filament formation.

4. Conclusion
In summary, it is demonstrated that the AgNWs-Egg albumen composites-based devices display compliance current-dependent dual-functional unipolar and threshold resistive switching functions.
The TS appears for a low compliance current, whereas the MS is initiated by setting a higher compliance current. The conduction mechanism was analysed by electron tunnelling conduction and conductive filament conduction. Although further investigation into the physical mechanisms and performance-limiting factors underlying the resistive switching in this class of composites is needed, an even more significant outcome of this work is that it profoundly inspires new devices that capitalize on this responsive behavior in AgNWs-Egg albumen composites. These results also provide a foundation to better control of the two resistive switching behaviors to establish high-performance emerging devices.

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5. **References**

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