SURFACTANT-FREE SILVER NANOFLUIDS AS LIQUID SYSTEMS WITH NEUROMORPHIC POTENTIAL

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Abstract

Neuromorphic engineering is a rapidly developing branch of science that aims to implement the unique attributes of biological neural networks in artificial devices. Most neuromorphic devices are based on the resistive switching effect, which involves changing the device's conductivity in response to an external electric field. For instance, percolating nanoparticle (NP) networks produced by gas aggregation cluster sources (GAS) show collective spiking behavior in conductivity reminiscent of brain-like dynamics. Nevertheless, the problem of dynamic spatial reconfiguration in solid-state neuromorphic systems remains unsolved. Herein, novel nanofluids with resistive switching properties are proposed as neuromorphic media. They are produced by depositing silver NPs from GAS into vacuum-compatible liquids (paraffin, silicon oil, and PEG) without the use of surfactants or other chemicals. When the electric field is applied between two electrodes, the migration of NPs toward biased electrode is detected in all liquids. The electrophoretic nature of the NP movement was proved by means of ζ-potential measurements. Such movement led to the self-assembly of NPs in conductive paths connecting the electrodes and, as a result, to resistive switching. The electrical response was strongly dependent on the dielectric constant of the base liquid. The Ag-PEG nanofluid demonstrated the best switching performance reproducible during several tens of current-voltage cycles. The growth of flexible and reconfigurable conductive filaments in nanofluids makes them suitable media for potential realization of 3D neural networks.

Keywords: Nanofluid, gas aggregation cluster source, ζ-potential, electrophoresis, resistive switching

1. INTRODUCTION

The growing demand of modern society for big data processing and storage requires the search for innovative computational techniques. For example, the rapidly developing Internet of Things requires collecting data from an enormous number of sensors and exchanging them with other devices, which represents a very complex task [1]. Conventional computers based on the von Neumann architecture can still handle it; however, high energy costs and low processing speed make them increasingly unprofitable. On the other hand, the brain is the most powerful computational system on the Earth, which can solve highly complex tasks, such as image and speech recognition, with an extremely low power consumption of a few tens of watts. The attempts to imitate the neurons and synapses employing artificial devices formed the basis of the fast-growing branch of knowledge named neuromorphic engineering [2].

Memristors are widely used building blocks in neuromorphic systems. Similarly to biological synapses, these two-terminal devices change their state from insulative to conductive in response to external stimuli. The conventional memristor represents the sandwich-like structure consisting of two metal electrodes with a thin (typical thickness of tens of nm) dielectric film in between [3]. The redox processes occur in the dielectric under the action of a strong electric field, leading to the migration of charged species and the formation of conductive filaments [4,5]. The device switches from an insulative to a conductive state. The filament can stochastically rupture, leading to switching back from a conductive to an insulative state. The main advantages of memristors include high switching speed, high endurance, low power consumption, as well as the opportunity to be organized in cross-bar arrays for potential in-memory computing. In a recent publication in Nature, authors from IBM presented the memristor-based system for energy-efficient speech recognition and transcription [6].

Despite all the benefits of conventional memristor-based cross-bar systems, their architecture is far from the real 3D and hierarchical organization in biological neural networks. Moreover, the fabrication process of such complex systems is expensive and complicated. Therefore, the search for alternative approaches in neuromorphic engineering continues. Recently, it was found that the self-organized networks of nanowires and nanoparticles demonstrate resistive switching effects [7-9]. In these systems, switching occurs due to the formation and rupture of nanoscale filaments in the interparticle gaps. Such percolative networks can be easily produced by the top-down approach of cluster-beam deposition. Moreover, the characteristic spiking behavior in network resistance was recently detected, which strongly resembles neural firing patterns in biological systems [8,9]. Nowadays, intensive research is performed to implement the benefits of these systems in computational devices. Nevertheless, randomly distributed interparticle gaps still limit the transition of electrical signals in the nanoparticle networks. They are far from mimicking self-ordered, interconnected, and highly mobile neural networks. In this work, we propose metal nanofluids (colloidal solutions of metal NPs in base liquids) as alternative nanoparticle-based systems with the potential to be used as neuromorphic materials.

2. EXPERIMENTAL PART

Linker- and surfactant-free silver nanofluids were prepared in vacuum by direct deposition of silver NPs into vacuum-compatible liquids. The details of this technique are described elsewhere [10]. Briefly, the NPs were synthesized using a magnetron-based gas aggregation cluster source. The Petri dish filled with the base liquid was placed on the way of the cluster beam, and the deposition was performed. The concentration of NPs in the fluid was regulated by the deposition time. Following the fabrication process, the homogenization of the resulting nanofluid was carried out in the ultrasonic bath to disintegrate micro-sized agglomerates.

The NPs were characterized using transmission electron microscopy (TEM, JEOL JEM 2200FS). The size, chemical composition, and crystalline structure were determined for the NPs deposited on copper grids with carbon coating (SPI Supplies).

The water content in base liquids was determined using the integration of peaks in ^{1}H nuclear magnetic resonance (NMR, Bruker Avance 500) spectra.

The ζ-potential of Ag NPs in nanofluids was measured by the electrophoretic light scattering method using a device of Zetasizer NanoZS ZEN3600 and a universal cell with closely spaced parallel electrodes.

Characterization of the electric field-driven phenomena in nanofluids was performed by a two-point method using a home-built probe station and a commercial probe station (BD-6, Everbeing). The 1 μl nanofluid droplet was placed on the silicon chip equipped with the system of platinum electrodes. The current-voltage characteristics were recorded between a couple of electrodes – one biased and one grounded, using the source meters Keithley 2450 or Keithley 2400. The migration of NP agglomerates in nanofluids was monitored in situ using an optical microscope (PSM-1000).

3. RESULTS AND DISCUSSION

First, the morphology, structure, and size of Ag NPs were characterized by TEM in detail. As can be seen in **Figure 1a**, the NPs are of spherical or multifaceted shape. The high-resolution TEM image revealed their polycrystalline structure (**Figure 1b**). The STEM-EDS mapping of the individual nanoparticle presents the chemical composition in **Figure 1c**. NPs consist of silver (green), which is only slightly oxidized on the surface (blue). The size distribution (**Figure 1d**) was constructed based on the selection of 150 NPs. It is relatively broad and can be approximated by the lognormal function. The mean diameter of nanoparticles was determined to be 60 ± 16 nm.

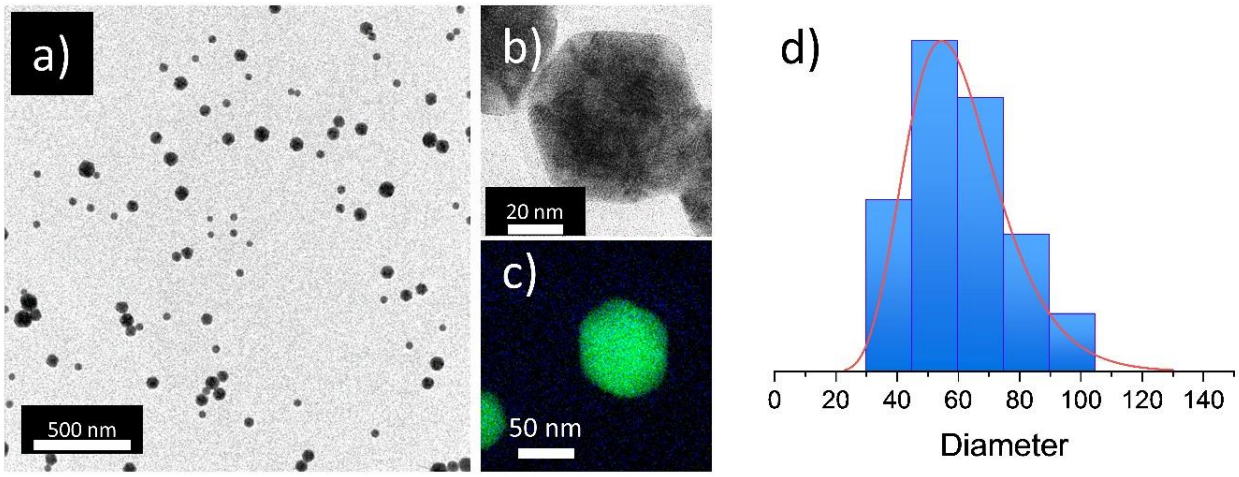

Figure 1 TEM characterization of Ag nanoparticles deposited on carbon-coated copper grid: **a)** overview image; **b)** high resolution TEM image; **c)** EDS map of individual nanoparticle (green – Ag, blue - O); **d)** size distribution.

Ag NPs were deposited into three vacuum-compatible liquids: poly(ethylene glycol) (PEG), pentaphenyl trimethyl trisiloxane (PTT), and paraffin (Par), each withstanding vacuum of 1×10^{-3} Pa. They can be attributed as dielectrics with dielectric constants summarized in **Table 1**. However, it is well known that the dielectric constant of a material can be affected by impurities. The base fluids used in this research have a purity chemical grade, but they can absorb water from the ambient atmosphere. For the estimation of the water content in nanofluids, NMR measurements were performed, and resulting spectra were integrated. The results showed that only the Ag-PEG nanofluid contains 3 wt. % of water (see Table 1), which is negligible from the point of view of the dielectric properties. In turn, PTT and paraffin are moisture-free according to NMR. Finally, the colloidal stability of nanofluids was examined. The value of the ζ-potential exceeding ±30 mV is typically taken as a rule of thumb to mark the stability of nanofluids. It was revealed that all three nanofluids have different colloidal stability. The ζ-potential of Ag NPs in paraffin was -15 mV, which may indicate the intensive agglomeration processes. The opposite situation was detected in Ag-PTT nanofluid with the ζ-potential of -56 mV. Finally, the Ag-PEG sample showed the intermediate value of the ζ-potential that was decisive for the electrical response, as demonstrated later.

Table 1 Basic properties of the silver-based nanofluids investigated in this study

Base liquid	Dielectric constant	Water content (from NMR), wt. %	ζ potential of Ag NPs, mV
PEG	14.1	3	-32
PTT	2.8	0	-15
Paraffin	2.3	0	-56

The electrode arrangement used for the electrical characterization of the nanofluids is schematically depicted in **Figure 2a**. In the first phenomenological experiment, the red electrode was under +4 V bias voltage, the blue electrode was under -4 V bias voltage, the black electrode was grounded, and the grey electrodes were under floating potential. The optical microscopy images of the three nanofluids prior to the applied bias are demonstrated in the left column of **Figure 2b**. As expected from ζ-potential measurements, the biggest agglomerates are visible in the Ag-PEG nanofluid. When the electric field was applied, the movement of nanoparticle agglomerates in the nanofluids was observed. In the Ag-PEG system, negatively charged agglomerates migrated toward the positive electrode and self-organized into a filamentary-like structure filling the gap between the positive and the grounded electrodes. A similar transport of agglomerates was observed in the Ag-PTT system. However, the particles do not form filaments in this case, probably due to their high colloidal stability.

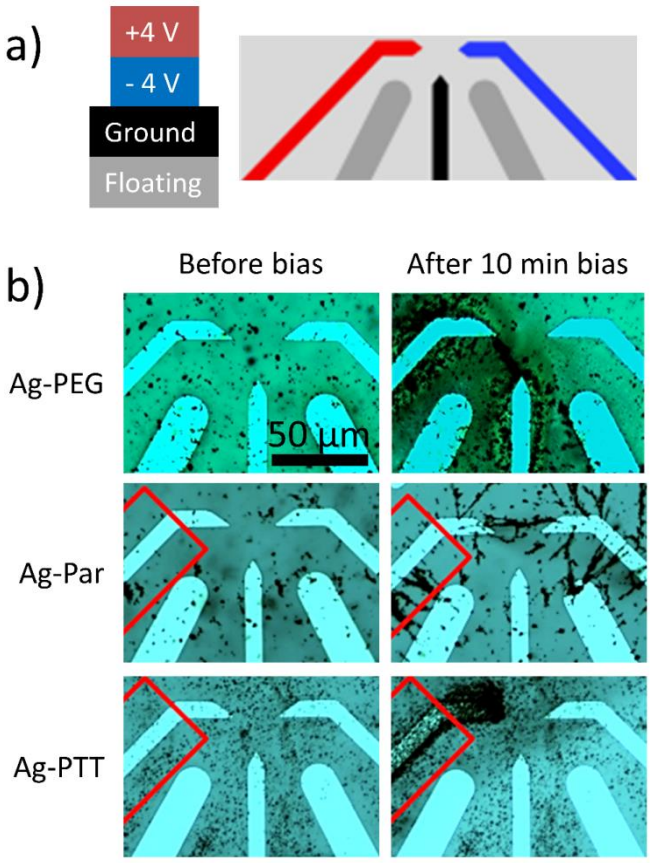

Figure 2 a) Scheme of the electrodes arrangement used for the electrical characterization of the nanofluids; b) Optical microscopy images of the nanofluids before (left) and after (right) the electric field was applied.

The striking difference in the NP behavior was revealed in the Ag-paraffin nanofluid. NPs moved toward both negatively- and positively-biased electrodes and formed dendrite-like structures. We associate this effect with the low value of ζ-potential. They could be subjected to the dielectrophoretic force when the NPs with zero net charge become dipoles and can migrate in the direction of electrodes of both polarities.

When the filament was formed, the I-V characteristics were acquired. In Ag-PEG nanofluid (**Figure 3a**), the initial current flowing through the system was 10^{-8} – 10^{-6} A. However, in the 1st cycle, the rapid growth of current by 3 orders of magnitude occurs at -5 V. This jump corresponds to the switching between the high and low resistance states. The system subsequently keeps the low-resistance state during two cycles. It switches

back to the high resistance state in the 4th cycle at +5 V. We assume that switching is related to the spatial reorganization of NPs composing the conductive path. We failed to obtain similar switching characteristics for Ag-PTT and Ag-paraffin. The current stayed low at the 10^{-11} – 10^{-10} A level even at higher bias voltages of ± 20 V (see **Figures 3b** and **3c**). This could be associated with the formation of dielectric shells surrounding NPs and preventing electronic conductance. Therefore, we continued the experiments only with the Ag-PEG system using the commercial probe station. We recorded 20 cycles demonstrating stochastic resistive switching effects at both polarities of the biased electrode in this nanofluid (**Figure 3d**). Further investigation is required for the detailed characterization of switching characteristics and investigation of the physical principles of switching in nanofluidic systems.

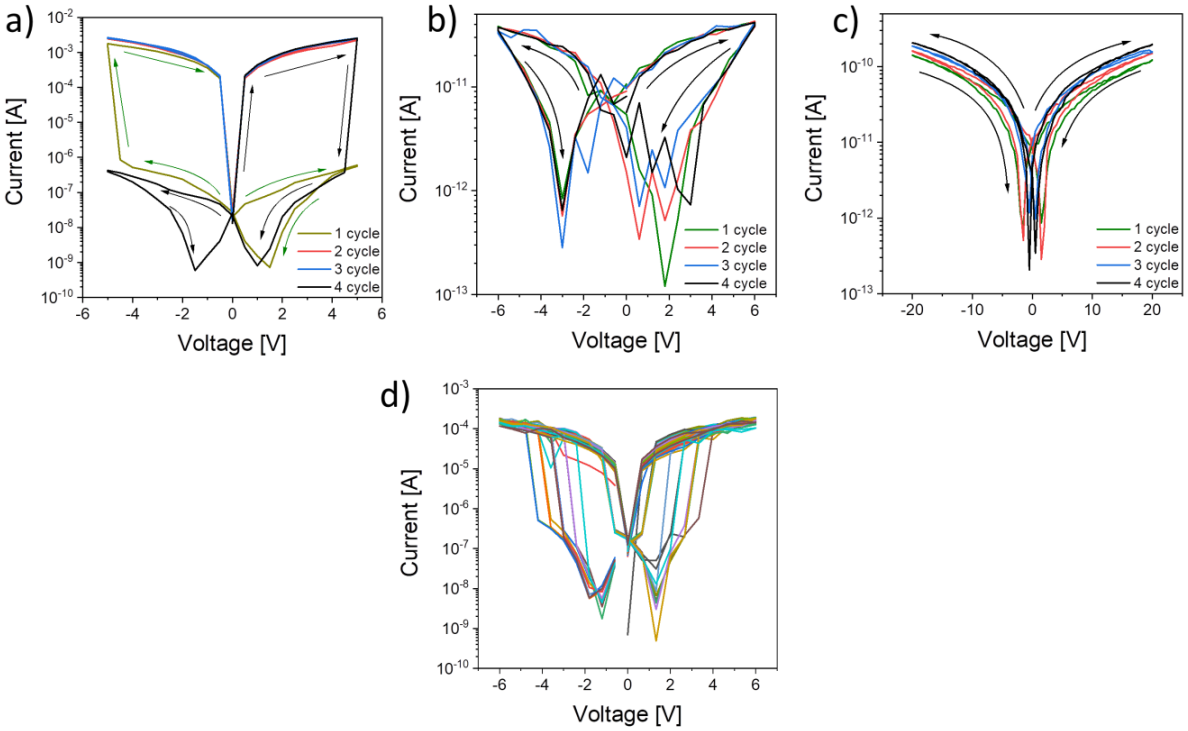

Figure 3 Current-voltage characteristics corresponding to: a) Ag-PEG nanofluid; b) Ag-PTT nanofluid; c) Ag-Par nanofluid. d) 20 current-voltage cycles demonstrating reproducibly resistive switching in Ag-PEG.

4. CONCLUSION

This research describes the perspective of using silver nanofluids for neuromorphic applications. It was shown that the nanoparticle-based conductive filament grows in Ag-PEG nanofluid between positively biased and grounded electrodes. When the path is formed, the reproducible resistive switching is detected in current-voltage characteristics. In contrast, the switching effects were not observed in Ag-PTT and Ag-Par nanofluidic systems. Such behavior is directly linked to the difference in ζ-potential of Ag nanoparticles. For Ag-PTT, the high colloidal stability prevents the formation of a stable connection between the electrodes. In Ag-Par, the dendrite-like structures grew around the electrodes of both polarity due to the dielectrophoretic effect. It can be concluded that the Ag-PEG nanofluid is the most favorable system for neuromorphic applications; however, further research into the switching mechanisms is needed.

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