Vertical-organic-nanocrystal-arrays for crossbar memristors with tuning switching dynamics toward neuromorphic computing

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Abstract
Memristors proposed by Leon Chua provide a new type of memory device for novel neuromorphic computing applications. However, the approaching of distinct multi-intermediate states for tunable switching dynamics, the controlling of conducting filaments (CFs) toward high device repeatability and reproducibility, and the ability for large-scale preparation devices, remain full of challenges. Here, we show that vertical-organic-nanocrystal-arrays (VONAs) could make a way toward the challenges. The perfect one-dimensional structure of the VONAs could confine the CFs accurately with fine-tune resistance states in a broad range of 10^3 ratios. The availability of large-area VONAs makes the fabrication of large-area crossbar memristor arrays facilely, and the analog switching characteristic of the memristors is to effectively imitate different kinds of synaptic plasticity, indicating their great potential in future applications.

Key words
c unknowing filament, memristor, organic electronics, organic single crystal
1 | INTRODUCTION

Memristors, devices that are capable of tuning resistance states as proposed by Chua in 1971,1 provide a new type of memory device, unlike today’s existing memories.2 Ideally, the existing state variable in memristors can accurately correspond to the resistance state of the device, that is, it can operate outside of “0” and “1” beyond the conventional memory, showing unique analog switching characteristics.3,4 Until 2008, Strukov et al.5 After that, memristors based on transition metal oxides,5–7 inorganic solid electrolytes,8,9 ferroelectric tunnel junctions,10,11 phase change materials,12,13 and organic materials14–19 have emerged and progressed rapidly. However, it remains a challenging issue to control inherent state variables and achieve corresponding ideal resistance tuning, especially for memristors based on filamentary switching mechanism.20–22 Indefinite defect positions in the amorphous medium lead to the stochastic formation of conducting filaments (CFs) in filamentary memristors, seriously affecting the performance of switching uniformity and controllability.9,22–24 Many strategies have been developed to confine and/or assist the CFs formation, for example, engineered dislocations of crystalline epitaxial layer to restrict CFs into dislocation pipes,25 self-assembled nanoscaffold structure with vertical heterointerfaces to create oxygen vacancy switching channels,26 or constructing oxygen-poor/rich bilayer to locate CFs into a few-nanometer-thick high-resistance region.27 Indeed, these optimization strategies have driven the continuous advancement of neuromorphic computing applications. Nevertheless, the memristor is still limited by the implementation of ideal CF control properties, specifically on orientation randomness and location uncertainty,9,24,28–30 and thus, new strategies for better CF control and resistance tuning are urgently needed. In this study, we demonstrate that vertical-organic-nanocrystal-arrays (VONAs) provide a novel strategy to design and control CFs and is an ideal candidate for high-performance memristor arrays. Vertical nanocrystals not only provide abundant active metal ions for CF formation, but also restrict the orientation of CFs. Crossbar memristor arrays based on VONAs are fabricated successfully and result in many promising properties, for example, continuous resistance tuning in a large resistance range, controllable formation of CFs, mimicking rich synapse plasticity, and so forth, paving the way to develop organic crystalline materials for memristors and neuromorphic applications.

2 | GROWTH AND CHARACTERIZATION OF VONAS

CFs are generally formed between the bottom and top electrodes in the memristor.19–21,28 The uncontrollability of CFs in the amorphous switching medium makes it easy to grow into an unpredictable dendritic morphology, which will adversely affect the performance.9,24,30 Here, a unique structure of VONAs is developed to assist the formation of CFs, which is achieved by a combined technique of chemical vapor deposition and physical vapor transport using organic charge-transfer complex, copper tetracyanoquinodimethane (CuTCNQ)31–33 (Figure 1A). Large area well-aligned VONAs with uniform size are densely and vertically grown on Cu substrates (Figures 1B–D and S1). Moreover, VONAs is allowed to fabricate into any desired pattern, overcoming the challenges of organic materials being unable to approach the photolithography process owing to their inability to withstand high temperatures and solvents (Figure S2). The diameters, lengths, and density of the nanocrystals are around 40, 600, and 10^10 cm⁻², respectively. X-ray diffraction (XRD) patterns of the nanocrystal arrays are well assigned to the Phase-I structure of CuTCNQ (Figure 1E).33 Transmission electron microscope (TEM) combined with selected-area electron diffraction (SAED) characterization suggest that the nanocrystal grows along the a-axis direction of the phase-I structure and have good crystallinity,32,33 and the tight π–π stacking of TCNQ⁻ radicals along a axis results into the one-dimensional morphology (Figure 1F,G).

3 | CROSSBAR MEMRISTOR ARRAYS BASED ON VONAS

Crossbar memristor arrays over a large area based on the nanocrystal array are shown in Figure 2A,B, which is an essential massive parallelism architecture in neuromorphic systems.34,35 Resistance tuning capability is primarily performed for the VONAs memristors. There are two general strategies to realize multilevel resistance states in CF memristors, that is, programming compliance current (I_CC) during set process and negative differential resistance (NDR) region during reset process.30,22 Significantly, the VONAs memristor can be precisely tuned in a broad resistance range using both methods. As shown in Figure 2C, the device current is continuously increased by increasing I_CC during set process. Seven resistance levels in 10³ ratios are achieved based on the applied maximum I_CC from 10 µA to 5 mA. Moreover, the VONAs memristor exhibits more elaborate
modulation in the NDR region (Figures 2D and S3). Twenty-one resistance levels are achieved by applying gradually increased reset voltage amplitude from 4 to 15 V, which, to our knowledge, is the finest resistance tuning using DC testing mode in currently reported memristors.7,20–22,36 Furthermore, the performance difference between array devices is small, indicating the uniformity of resistance control (Figure S4).

Principally, the fine adjustment of the resistance state is attributed to the precise control of the quantity or width of CFs in memristors.9,20,24,28 Indeed, thirty-level resistance states are achieved by programming reset voltage sweeps from 3.4 to 9.0 V with every step of 0.2 V (Figure S5), demonstrating the advantages of VONAs in CF control. Attractively, the VONAs memristors can demonstrate a transition from bistable to analog switching characteristics by controlling $I_{CC}$ during CF electroforming (Figure 2E). The current jump with a high on/off ratio of $10^4$ is exhibited when low $I_{CC}$ (i.e., 10 $\mu$A) is applied. With $I_{CC}$ increasing, the current jump disappeared especially at the NDR region owing to the increasing quantity of metal atoms joining in CFs (Figure S6). Endurance and retention properties are examined in a representative current range, in which reliable switching behavior can operate for at least 200 cycles, and each data is retained for at least $10^3$ s (Figure S7). Thus, careful selection of suitable set $I_{CC}$ and reset voltage amplitude can enable the VONAs memristor to operate in a selected current range, thereby satisfying various requirements in practical applications. Figure 2F shows that once the device is set into identical on-states, multilevel storage is well demonstrated by varying the reset voltage amplitude.

**FIGURE 1** Growth and characterization of vertical-organic-nanocrystal-arrays (VONAs). (A) Schematic growth process of VONAs. (B) Schematic view of VONAs. (C,D) Scanning electron microscopy images of VONAs with the side view and the top view. Scale bar = 500 nm. (E) X-ray diffraction spectra of VONAs. (F) Transmission electron microscopy image and its corresponding selected-area electron diffraction pattern of an individual nanocrystal. Scale bar = 100 nm. (G) Molecular stacking of the Phase-I structure of CuTCNQ along the $a$ axis.
Flexible memristors are prospective for flexible electronics. Polyimide (PI) substrates are chosen owing to the permissible processing temperature for crystal growth as well as the inherent compatibility with organic materials. Attractively, VONAs are grown on PI substrate successfully, and then for flexible memristor array (Figure 3A). The fabrication of crossbar memristor array on a flexible substrate is similar to that of on SiO₂ substrate. The flexible devices work well under bending state, and exhibit reliable switching operations and the obvious NDR region even with a curvature radius of 1.6 mm (Figure 3B). By programming set and reset switching processes, the flexible device also demonstrates good resistance tuning characteristics (Figure 3C). A maximum of 12 resistance states is available in the NDR region. Figure 3D shows the reliability test of the flexible memristor under continuous bending operations, which shows excellent bending durability over $10^4$ cycles, indicating the bright future of VONAs for flexible neuromorphic electronics.

The CF control in memristors depends on the appropriate induced orientation and forming location. In the crossbar array, Al top electrode with low work function (4.0–4.3 eV) is easily oxidized to generate the AlOₓ interface layer between the nanocrystal array and Al electrode (Figure S8). A resistance ratio of $10^9$ (Figure 4A) is found after putting the fresh device in the atmosphere for 1 day, indicative of the formation of well-defined AlOₓ interface. After that, the device can return to the initial low resistance state through a typical electroforming process, which covers a broad current range from $10^{-12}$ to $10^{-1}$ A (Figure S9). Notably, the electroforming $I$–$V$ characteristics of device arrays show very high device-to-device uniformity (Figure S10). A series of distinct on states can be achieved by continuously increasing $I_{CC}$ from 1 to 10 mA on electroforming processes, representing the gradual strengthening of CFs (Figure 4B). The corresponding reset processes show that the device conductance clearly concentrates on several discrete values under opposite polarity (Figure 4C).
FIGURE 3  Flexible memristor arrays fabricated on polyimide substrates. (A) Optical image of flexible memristor arrays; scale bar = 1 cm. (B) Consecutive I–V curves of the memristor at bending state. The compliance current and reset voltage amplitude adopted 1 mA and 8 V, respectively. (C) Gradual resistance tuning is achieved during set/reset process under a sequence of increased compliance current and reset voltage sweeps. (D) Endurance performance under $10^4$ bending cycles with a curvature radius of 2.4 mm, read voltage is $-1$ V and scale bar = 1 cm.

FIGURE 4  Conducting filaments (CFs) control and working mechanism of the vertical-organic-nanocrystal-arrays (VONAs) memristors. (A) The contrast of I–V characteristics for the device in neutral (N$_2$) atmosphere and in air after 24 h. (B) A series of on states obtained by continuously increasing $I_{CC}$ from 1 to 10 mA on forming process, representing the gradual strengthening of CFs. (C) The reset process corresponding to these on states shows a pronounced negative differential resistance region from 4 to 15 V, representing the gradual dissolution of CFs. (D) Thermal activation energy of $E_a$ for $T$ variation from 160 to 300 K at several representative resistance levels. The resistance values were extracted from Figure S11 at $-1$ V. (E,F) Conductive atomic force microscopy (AFM) electrical characteristics of the nanocrystal and the nanocrystal/Al heterostructure. Inset is the corresponding AFM surface morphology.
As the applied voltage increases (approximately greater than 4 V), pronounced NDR regions appear and remain until 15 V, which is broader and more continuous than that of today’s available memristors,\textsuperscript{7,21,25–27,41} showing the effectiveness of VONAs in controlling CFs. To further reveal the metal filament mechanism in VONAs memristors, the relationship of resistance–temperature (R–T) is performed at several representative resistance states (Figures 4D and S11). Metallic behaviors with linear electrical characteristics and negative activation energy can be exhibited when applying high $I_{CC}$ on the electroforming process, confirming the existence of metal CFs in devices. Semiconducotor nonlinear electrical characteristics are demonstrated when the applied $I_{CC}$ is reduced. The activation energy increases from 61 to 92 meV with a controlled increase of initial resistance states. The activation energy in the higher initial resistance state is close to that of CuTCNQ itself,\textsuperscript{33} implying that at this time CFs are mainly localized in the AlO$_x$ insulating interface (Figure S12). Therefore, a schematic model is provided to illustrate the advantages of VONAs on CF control (Figure S13), in which the main effect of VONAs is their orientation constraint and interface positioning for CFs formation.

The performances of devices with different sizes show no obvious size dependence (Figure S14), confirming the typical CF mechanism determined by local position. Considering the high density of the vertical nanocrystals, the potential for device scalability should be great, for example, the possibility of an individual vertical nanocrystal for one memristor. Indeed, memristors based on individual nanocrystal with Cu and Al/AlO$_x$ asymmetric electrodes show typical bipolar switching behaviors (Figure S15). Moreover, conductive atomic force microscope (AFM) is used to characterize individual nanocrystal of the VONAs. As shown in Figure 4E, the nanocrystals show typical semiconductor nonlinear electrical properties, consistent with our previous reports.\textsuperscript{32} However, for nanocrystal/Al heterostructure, repeatable and reversible switching behaviors are exhibited after the electroforming process (Figures 4F and S16), suggesting that effective switching behavior can be extended to an individual nanocrystal. Considering the density of the vertical nanocrystals up to $10^{10}$ cm$^{-2}$, the memory density of the VONAs memristor has the potential to be 10 Tb·cm$^{-2}$.

### 6 SYNAPTIC PLASTICITY OF THE VONAS MEMRISTORS

For effectively emulating synaptic plasticity in neuromorphic systems (Figure 5A), it requires memristors with rich and precisely tunable switching dynamics, for example, recently combining volatile and nonvolatile characteristics in a single memristor as an accurate simulation of the human memory system.\textsuperscript{42,43} It is necessary to know the process of human brain memorization in an Atkinson–Shiffrin model,\textsuperscript{44} in which the conversion process will evolve from sensory memory (SM) to short-term memory (STM) and finally to long-term memory (LTM; Figure 5B). The VONAs memristor with effective CF controllability can be used to emulate a similar brain’s storage process. Figure 5C exhibits the typical characteristic of SM. A single spike (−9 V, 0.5 μs) is first used to trigger the memristor. The device current is immediately boosted after excitation, and then spontaneously relaxes to the initial state in 30 s. This phenomenon bears resemblance with biology synapse that a presynaptic spike will trigger an excitatory post-synaptic current (EPSC).\textsuperscript{45} When evoked by a pair of spikes with a time interval of 1 s, the current can also decay to the initial state with an extended time of 40 s (Figure 5D). The synaptic function of paired-pulse facilitation (PPF) is demonstrated,\textsuperscript{46} where the current response intensity to the second spike is stronger than that to the first spike (Figure S17).

Because pulse triggering is a weak stimulus mode, a small number of metal clusters formed by excitation tend to diffuse spontaneously after the voltage is removed, resulting in SM characteristics. The transition from SM to STM is achieved by applying multiple pulses, showing an extended relaxation time (Figure 5E). Further increasing the number of pulses, STM can be gradually converted to LTM (Figure 5F), meaning that the current cannot return to the initial state within a given time. The gradual transition from volatile to nonvolatile properties suggests the gradual strengthening of CFs.\textsuperscript{11} As shown in Figure 5G, the process of SM becoming STM and further turning into LTM is implemented by increasing the stimulus frequency from 0.5 to 10 MHz, manifested by the enhanced current intensity and longer relaxation time.

Furthermore, the synaptic weight is trained to a continuous potentiation followed by a continuous depression, which shows a relatively linear and symmetrical adjustment, laying the foundation for building an effective artificial neural network (Figure 5H). To demonstrate the potential of the proposed device in neuromorphic computing hardware, a three-layer neural network system based on passive memristor crossbars and peripheral circuits is simulated (Figure 5I, J).\textsuperscript{47} The synaptic weights in the neural network are mapped into the conductance of memristors with the reference current to implement positive and negative weights. The input $28 \times 28$ images in the
Modified National Institute of Standards and Technology (MNIST) data set are first pre-processed by cropping the edges of each image (making it $20 \times 20$ image). Then the data set is fed into the $400 \times 150 \times 10$ neural network system for online training. After 64 training epochs, the simulated memristor neural network gains an accuracy of 86.63%, which reaches over 90% accuracy of software (Figure 5K).
7 | EXPERIMENTAL SECTION

7.1 | Materials and substrate preparation

TCNQ was purchased from Sigma-Aldrich and used with one purification by physics vapor transport. Silicon with 300 nm SiO₂ wafers were used as substrates and cleaned successively with pure water, a hot solution of concentrated sulfuric acid and hydrogen peroxide (sulfuric acid/hydrogen peroxide = 2:1), pure water, isopropanol respectively for 10 min.

7.2 | Nanocrystal array preparation

Vertical nanocrystal arrays were synthesized through a combined technique of chemical vapor deposition and physical vapor transport via a vapor–solid reaction. First, Cu substrate was first prepared by thermally evaporating 50 nm Cu thin films on the Si/SiO₂ substrate. Then, this substrate was directly placed on the top of TCNQ powders loaded in a quartz boat that was put into a horizontal quartz tube. Last, the heating zone is increased to 100°C and kept for 30 min in a vacuum environment with a pressure of 0.1 Pa. Thus, large-area vertical nanocrystal arrays were fabricated with a highly uniform morphology, which can be easily patterned into any desired shape depending on pre-prepared Cu substrates.

7.3 | Device fabrication

The fabrication process of memristors with crossbar structure was that Cu layers with the thickness of 50 nm were first thermally evaporated on Si/SiO₂ substrates by using a 100-µm stripe shadow mask. Then, vertical nanocrystals were synthesized via a solid–vapor reaction mentioned above. The unreacted Cu layers could in situ serve as the bottom electrodes and exhibit ohmic contact with nanocrystals. Last, Al top electrodes with a thickness of 200 nm were deposited in a vertical direction using the same mask. Thus, Cu/nanocrystals/Al device arrays were fabricated over a large area with an individual device area of 100 × 100 µm. Moreover, other structures of the memristor are also easily fabricated due to the advantage of easy pattern. Flexible memristor arrays were built on the PI substrate using the same fabrication processes.

7.4 | Characterizations

Nanocrystals were characterized by XRD (D/max2500), scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, Tecnai G2 F20), and atomic force microscopy (AFM; NTEGRA Solaris). Electrical characteristics of the memristors were measured by Keithley 4200 Semiconductor Parameter Analyzer and Keysight B1500A Semiconductor Device Analyzer in air conditions.

7.5 | Array simulation

The simulation is conducted on the platform “NeuroSimV3.0” under Ubuntu 18.04.2 LTS system environment. The memristor real device model is established by fitting the experimental long-term potentiation (LTP) and long-term depression (LTD) data with the Matlab script provided by the “NeuroSimV3.0” simulator. The conductance updating nonlinearity, cycle-to-cycle variation, conductance range, and the number of intermediate states are considered. The three-layer neural network is a 400 × 150 × 10 MLP (multi-layer perceptron) for MNIST image classification. The 28 × 28 MNIST images are pre-processed, making them 20 × 20 binary images with the edges cropped. The memristor neural network is then trained online using back-propagation with Adam optimizer. After 64 training epochs, the accuracy of the memristor neural network converges to 86.63%. A pure software training is also conducted with the same network structure and training parameter, and the acquired accuracy is 96.54%.

8 | CONCLUSIONS

A high-performance crossbar memristor array based on VONAs is demonstrated. Many distinct and nonvolatile intermediate resistance states in 10³ ratios are attained, and processing of the quantity of metal atoms involved in CFs allows the VONAs memristor to operate in different current regions, and exhibits bistable or analog switching behaviors. We propose that the combination of 1D structure of nanocrystals for confining and orientating CFs, and native AlOₓ interface for locating CFs, are responsible for these desired properties. Moreover, the resistance states of the VONAs memristor trained by programming pulses also show a good analog response, which enables effective implementation in mimicking diverse synapse plasticity. The results indicate an important step for high-performance memristor array, and open the door for organic crystals in
memristors, toward future high-density memories and complex neuromorphic systems.

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DATA AVAILABILITY STATEMENT
The data that support the plots within the paper and other findings of this study are available from the corresponding author upon reasonable request.

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