Mediating short-term plasticity in an artificial memristive synapse by the orientation of silica mesopores

Li, Bin; Liu, Yaqing; Wan, Changjin; Liu, Zhiyuan; Wang, Ming; Qi, Dianpeng; Yu, Jiancan; Cai, Pingqiang; Xiao, Meng; Zeng, Yi; Chen, Xiaodong

2018

Li, B., Liu, Y., Wan, C., Liu, Z., Wang, M., Qi, D., . . . Chen, X. (2018). Mediating short-term plasticity in an artificial memristive synapse by the orientation of silica mesopores. *Advanced materials*, 30(16), 1706395-. doi:10.1002/adma.201706395

<https://hdl.handle.net/10356/138663>

<https://doi.org/10.1002/adma.201706395>

© 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved. This paper was published in *Advanced Materials* and is made available with permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Downloaded on 26 Apr 2023 07:52:49 SGT

Mediating Short-term Plasticity in Artificial Memristive Synapse by the Orientation of Silica Mesopores

Bin Li, Yaqing Liu, Changjin Wan, Zhiyuan Liu, Ming Wang, Dianpeng Qi, Jiancan Yu, Pingqiang Cai, Meng Xiao, Yi Zeng, and Xiaodong Chen*

Dr. B. Li, Dr. Y. Liu, Dr. C. Wan, Z. Liu, Dr. M. Wang, Dr. D. Qi, Dr. J. Yu, Dr. P. Cai, Dr. M. Xiao, Dr. Y. Zeng, Prof. X. Chen
School of Materials Science and Engineering, Nanyang Technological University, 50
Nanyang Avenue, 639798, Singapore
E-mail: chenxd@ntu.edu.sg

Keywords: artificial memristive synapse; short-term plasticity; orientation; mesopores; silica

Abstract: Memristive synapses based on the resistive switching are promising electronic devices that emulate the synaptic plasticity in neural system. Short-term plasticity (STP), reflecting a temporal strengthening of the synaptic connection, allows artificial synapses to perform critical computational functions, such as fast response and information filtering. To mediate this fundamental property in memristive electronic devices, the regulation of the dynamic resistive change is necessary for an artificial synapse. Here, we demonstrate that the orientation of mesopores in the dielectric silica layer can be used to modulate the STP of artificial memristive synapse. The dielectric silica layer with vertical mesopores could facilitate the formation of conductive path, which underlies a lower set voltage (~ 1.0 V) compared to these with parallel mesopores (~ 1.2 V) and dense amorphous silica (~ 2.0 V). Also, the artificial memristive synapses with vertical mesopores exhibit the fastest current increase by successive voltage pulses. Finally, the oriented silica mesopores is designed for varying the relaxation time of memory, and thus the successful mediation of STP is achieved. The implementation of mesoporous orientation provides a new perspective for engineering artificial synapse with multilevel learning and forgetting capability, which is essential for neuromorphic computing.

Learning and memory are postulated to be performed by dynamic change of connection strength between vastly interconnected networks of biological synapses.^[1] Artificial synapses, imitating the fundamental principles of synaptic behaviors, are thought to be the hardware implementation for neuromorphic computing system with ultralow power consumption.^[2] Two terminal memristive devices have been demonstrated as the promising candidates of artificial synapse,^[3] in which a dense dielectric layer is sandwiched between two electrodes.^[4] Under a burst of voltage pulses, the conducting pathways between electrodes form randomly in the dense dielectric film, which results in the gradual conductance change. Such gradual resistive switching phenomenon shows great resemblance to the synaptic weight modification by pre/post-synaptic spikes - known as the synaptic plasticity.^[5] Especially, short-term plasticity (STP), which originates from temporal response to the external spike and strongly relates to the ions transfer dynamic, is vital for the synapses to achieve fast response and information filtering.^[6] Mediating STP process in an artificial memristive synapse offers a wide range of opportunities for designing of specific functions with multilevel responding rate and information processing priority.^[7] Although the mediation of STP is achieved by tuning external programmed voltage pulse in the memristive synapse with dense dielectric layer,^[8] the lack of intrinsic mediation of STP based on the inherent modulation of ionic transfer dynamics in the dielectric layer restricts the fulfillment of fidelity and diversity of desired STP functions, which are necessary for neuromorphic computing.

In the neural system, an electrical synapse composed of precisely aligned and paired channels (1.2 to 2.0 nm) in the gap junctions between two neurons can provide quick STP responding function and short memory retention time compared with chemical synapse (**Figure 1a and b**).^[9] Inspired by the nature structure of electrical synapses, we propose to tune the orientation of nanopores in the dielectric layer to realize the inherent modulation on STP behaviors (**Figure 1c**). Ordered mesoporous silica thin film fabricated by the solution-processed and surfactant-templated strategy can provide tunable pore size (2 ~ 50 nm), high

porosity ($\sim 75\%$), and large-scale area ($\sim \text{cm}^2$).^[10] More importantly, the orientation of mesopores to the substrate in the film is readily programmable, which is beneficial for the modulation of the diffusion dynamics of guest species (ions, molecular, cluster, etc.) from one side to another accordingly.^[11] These intriguing properties are of great potential for realizing inherent STP modulation which is mediated by the diffusion dynamics within the dielectric layer.^[12]

In this paper, we present a new design for the mediation of STP in an artificial memristive synapse by the optimal orientation of silica mesopores in the dielectric film. The resistance-switching property of artificial memristive synapse is highly correlated to the orientation of mesopores in the silica film between the electrodes. The dielectric silica layer with vertically oriented mesopores provides directional channel for resistive switching at a lower set voltage ($\sim 1.0\text{ V}$) compared to these with parallelly oriented mesopores ($\sim 1.2\text{ V}$) and dense amorphous silica ($\sim 2.0\text{ V}$). As a result, the artificial memristive synapses with vertical mesopores exhibit the fastest current increase by successive voltage pulses. The oriented silica mesopores is capable of varying the relaxation time of memory. Thus, the mediation of STP emulation has been successfully realized. Our strategy provides a new perspective to adjust the resistance-switching property of memristive synaptic devices, which could open up a new insight into the design of versatile artificial synapses for building neuromorphic computation systems.

In a typical experiment, artificial synapses are constructed in a two-terminal Ag/Ag₂S/vertical-silica/ITO configuration (**Figure 2a**). A mesoporous silica thin film of $\sim 100\text{ nm}$ thickness with vertical orientation to the ITO substrate is deposited through a Stöber solution growth method according to the literature.^[13] The mesopores are oriented vertically throughout the cross-sectional film and the ends are fully opened (Figure 2b). The mesoporous silica film possesses a space group $p6mm$ with hexagonal symmetry (Figure S1a). This is in good accordance with that of mesoporous silica MCM-41 (Mobil crystalline

material).^[14] The film shows a pore size of ~ 2.4 nm with a narrow distribution (Figure S1b and S1c). Ag₂S is introduced due to its ionic/electronic conductive property and has been investigated in the fabrication of synaptic device.^[3b, 15] Ag₂S provides a platform for the formation of metallic conductive species.^[16] Ag₂S layer with thickness of ~ 100 nm (Figure S2a and S3) stems from the sulfuration of Ag layer pre-deposited through thermal evaporation on the mesoporous silica thin film. The orientation of mesopores in thin silica film can be adjusted through different sol-gel process. Silica mesopores paralleled to the electrode are obtained by a spin-coating method according to the previous report.^[10a] A thin film with thickness of ~ 100 nm and average pore size of ~ 8.5 nm are achieved (Figure 2c, S4 and S5). It should be noted that the nanopores (< 2 nm in diameter) are located in the walls of mesopores, due to the penetration of surfactant into the walls of mesopores.^[17] For comparison, dense amorphous silica film with thickness of ~ 100 nm is also fabricated through a physical sputtering method (Figure 2d) to construct the same device configuration with the Ag₂S film.

A positive voltage was applied to the top Ag electrode (Figure 2b) under current compliance of 1 mA. Current-voltage (I - V) curves of the synaptic device with vertical silica mesopores show typical resistance-switching characteristics (**Figure 3a**). During voltage sweep from zero to a positive set voltage of ~ 1.0 V, the synaptic device switches from high resistance state (HRS) to low resistance state (LRS); similarly, the resistance for the synaptic device with parallel mesopores is switched from HRS to LRS at a set voltage of ~ 1.2 V (Figure 3b). On the contrary, the synaptic device with dense amorphous silica shows the highest set voltage of above 2.0 V (Figure 3c). Moreover, the statistics of set voltage for device-to-device distribution also shows an increase in the order of vertical, parallel and then amorphous (Figure 3d), indicating the orientation of mesopores affects the resistance switching behavior of memristive synaptic device. Furthermore, the set voltage can be tuned

from ~ 0.5 to ~ 0.1 V in the synaptic device with vertical mesopores by reducing its thickness from ~ 50 to ~ 20 nm (Figure S6).

The resistive switching mechanisms rely on the formation and transfer of the electrically conductive filament induced by electrical field.^[4a, 18] Ag_2S , as a kind of chalcogenides with both ionic/electronic conductive properties, allows faster ion transport.^[19] Electrochemical metallization induces the formation of filament composed of metal atoms, which comes from the surface of Ag_2S phase.^[20] Since SiO_2 is a dielectric layer, the filament nucleation and transfer strongly depend on the local microstructure and electric field distribution.^[21] The equation (1) gives the free enthalpy for the nucleation and diffusion of filament in the dielectric film:^[22]

$$\Delta G (N_c) = N_c e \Delta \phi + \Phi (N_c) + N_c \varepsilon \quad (1)$$

Where ΔG is the free enthalpy of filament nucleation; N_c is the number of atoms constituting the nucleus; $\Delta \phi$ is the voltage drop; Φ is the surface energy contribution and ε is the strain energy per atom. The voltage drop ($\Delta \phi$) depends on the applied voltage and the position of the filament.^[23] At the same applied voltage, the nucleation and diffusion of filament is strongly related to the microstructure of dielectric layer ^[21a] and we assume this item is the same for the devices in our work. The surface energy contribution (Φ) is closely coherent with interfacial surface area between the filaments and dielectric film.^[24] Due to the introduction of mesopores in the dielectric film, the amount of interfaces included in the filament nucleation and transfer process is different, resulting different total surface energy ($N_c \Phi$). Atom strain energy (ε) stems from the internally atomic rearrangement of filaments, which is strongly related to the interface interaction between filament and dielectric film during the electrochemical metallization process.^[25] It has also been reported that a feature void formed in the dense SiO_2 film at the interface after sustainable amounts of Ag filaments passed.^[21b] Since the formed Ag filament transfer towards the inert electrode, new filament can fill in the void with reduced strain energy (equation 1), inducing the filament growth

towards the inert electrode. The mesopores in silica film could facilitate the filament transfer from active Ag_2S side to inert electrode since the filament is inclined to grow in the way with reduced strain energy. In our work, tremendous mesopores are introduced into the dielectric film. The mesopores can provide sufficient voids for the filament growth with low interfacial energy and atom strain energy. In the device with vertical mesopores, the filaments are supposed to pass the directional channel preferably. Therefore, the interface between the filaments and silica is not considerable, resulting low interfacial energy and low atom strain energy. In the parallel mesopores, the pathway is not straight. More interfaces are included during the nucleation and diffusion of filaments, resulting in higher interfacial and atom strain energy than that in the vertical mesopores. For the dense amorphous silica film, the filaments are supposed to nucleate and diffuse in a random and tortuous way. Thus, tremendous interfaces are assumed to be existed between the filament and dielectric film, leading the highest interfacial and atom strain energy compared with that in the vertical and parallel mesopores. The atom strain energy may also lead to the increased mechanical stress, leading to the plastic deformation in the dielectric film.^[26] To qualitatively verify these hypothesis, the electric field distribution of vertical and parallel mesopores in the silica film were stimulated as shown in Figure 3e. The electric field intensity in the mesopores is larger than that in the walls, indicating that the conducting filament is preferred to pass through mesopores. The electric field in the vertical mesopores is straight, which facilitate the filament transfer. However, due to the nanopores (1 ~ 2 nm) randomly distributed on the wall of parallel mesopores, the electric field distribution is more random than that in vertical mesopores, resulting in the filament transfer is not straight. Thus, more energy is needed for filament transfer from one side to another, resulting in a higher set voltage than that in the vertical mesopores. In summary, the orientation of mesopores can tune the growth and migration of the filament inside dielectric layer, resulting in different resistive switching behavior.

The synaptic behaviors of STP characteristics are emulated in the artificial memristive synapse. STP reflects a temporal strengthening of synaptic connection, which then fades away to its initial state if external stimulus is not continuous. Paired-pulse facilitation (PPF) is a physiological phenomenon related to STP, in which a previous stimulus enhances a followed response of stimulus.^[6] In an electrical synapse, its simplicity results in a faster response than the chemical synapses with a more complex information transfer process. Analogously, the current in our artificial memristive synapse is increased when a pair of successive simulated presynaptic potentials (0.8 V, 30 ms) is applied (**Figure 4a**). The facilitation ratio is defined by A_2/A_1 , where A_1 and A_2 are the peak amplitudes of current from the first and second pulse potentials, respectively. As illustrated in Figure 4b, the facilitation ratio decreases gradually with the increasing of pulse interval. For the synaptic device with vertical mesopores, the PPF facilitation ratio decreases obviously from 1.28 to 1 as the pulse interval increase from 50 to 500 ms. The maximum A_2/A_1 of 1.06 and 1.01 are achieved in the synaptic device with parallel mesopores and dense amorphous silica, respectively. It should be noted that the applied pulse voltage was selected a little smaller than the set voltage of the synaptic devices with vertical porous in order to mimic the short-term plasticity using intermediate conducting states. As reported in some two-terminal artificial synapses, the intermediate conducting state is dependent on the pulse amplitude compared to the set voltage as well as duration and pulse number.^[3a, 27] Therefore, the synaptic devices with parallel mesopores and dense amorphous silica show much weaker facilitation behaviors. In this case, the PPF behavior could be modulated through intended orientation of the mesopores in such kind of devices. When the time interval between pulses is 100 ms and the simulated presynaptic potential is 0.8 V with 10 ms width, the current of the synaptic device increases as the number of pulses increases (Figure 4c). For the synaptic device with vertical mesopores, the amplitude of postsynaptic current (I_t) reaches as high as 38 times larger than the current (I_1) triggered by the first pulse ($I_t/I_1 = 38$) after 4 s continuous pulse sequence, which is analogous

to the high memory level acquirement through the repeated rehearsal. However, the low memory level of 1.13 and 1.02 can only be achieved in the synaptic devices with parallel mesopores and dense amorphous silica, respectively, under the same pulse sequence. In psychology, the higher memory level achieved through certain times of rehearsal means the better learning capability.^[28] Therefore, these results indicate that the intended design of the mesopores orientation could shape the learning ability of such artificial synapses. The STP process emulation is strongly related to the migration and diffusion of conductive filaments. The vertical mesopores in the artificial synapse can facilitate the filament migration to render the artificial synapse with a fast response.

In addition, upon a simulated presynaptic potential with a higher voltage (1.5 V) and larger width (0.7 s) under the current compliance of 100 μ A, the synaptic devices exhibit a switching to the LRS and relax back to the HRS after a characteristic time as the simulated presynaptic potential ends, as shown in Figure 4d. The synaptic devices with vertical and parallel mesopores both show a sharp switch (< 0.02 s). However, the synaptic device with dense amorphous silica shows a delay time of ~ 0.1 s (Figure S7). This is related to the growth dynamics of conducting filaments to eventually form conductive channels. In the synaptic device with vertical and parallel mesopores, the filaments are supposed to pass through the meso-channels with reduced strain energy, resulting in a fast switch. In the dense amorphous silica, high Ag atom strain energy may lead to slow growth of conductive channel, resulting a delay time of switch. As seen in Figure 4d and 4e, the relaxation time is around 0.5 s in the synaptic device with vertical mesopores. The synaptic device with parallel mesopores shows a longer relaxation time of around 3 s. The synaptic device with dense amorphous silica exhibits longest time (> 10 s). Such relaxation of the conductive paths in memristive devices depends on the stability of filament, which is function with diffusion potential, interfacial energy, operation history and device geometry.^[4c, 29] As discussed above, the filaments are inclined to transfer in the mesopores with reduced atom strain energy. After

the applied voltage is removed, the atom diffusion could also be facilitated due to the low strain energy in bidirectional way, which may lead the filaments with high diffusion potential. In our design, the vertical mesopores may provide a directional channel with the lowest grain boundaries compared with that in the parallel mesopores and amorphous silica. These boundaries can serve as the energy barrier for the diffusion.^[30] Consequently, without external applied voltage, the spontaneous diffusion of the atoms is easier in the vertical mesopores compared with that in the parallel mesopores and amorphous silica. Therefore, this may result into the shortest relaxation time in the devices with vertical mesopores than the other two types.

This kind of relaxation time is basis for the implementation of STP. After the volatile conductive filament forms via the stimulation, the filaments tend to dissolve and the device relaxes toward its insulating state soon after the removal of voltage. The similar filament evolution process has been directly observed by *in situ* TEM observations.^[29b] Such evolution process shows a significant similarities to the Ca^{2+} dynamics in synapses, which underlies short-term plasticity and responsible for learning and forgetting behaviors.^[31] Interestingly, in our design, the relaxation time can be tuned by the orientation of mesopores in the dielectric film. In other words, the forgetting rate in the synaptic device with vertical mesopores is faster than that of others. Hence, the forgetting rate and information retention time can also be mediated by the orientation of mesopores in the silica film. These kinds of characteristic may be involved in several tasks, including simple learning and sound-source localization, in which the response needs to be fast and the information is not necessary for long time storage.^[32]

In summary, we have successfully demonstrated that the orientation of mesopores in the dielectric silica layer can mediate the STP in an artificial memristive synapse. The synaptic device with vertical mesopores can be switched from HRS to LRS at a lower set voltage (~ 1.0 V) compared to these with parallelly mesopores (~ 1.2 V) and dense amorphous silica ($\sim$

2.0 V). Hence, at an identical simulated presynaptic potential, the artificial synapse with vertical mesopores can achieve the fastest learning compared with other devices with parallel mesopores and dense amorphous silica. Furthermore, the retention time of memorized information can also be tuned by the orientation of mesopores in the dielectric silica layer. These kinds of characteristics can pave the way for engineering devices with different artificial synaptic behavior. Cascading device with multilevel response rate and forgetting capability is one of the most promising strategies aiming at the realization of neuromorphic computing to meet the imperative demand on information processing in the forthcoming big data era.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the financial support from Singapore Ministry of Education (MOE2014-T2-2-140 and MOE2015-T2-2-060) and the National Research Foundation, Prime Minister's Office, Singapore under NRF Investigatorship (NRF2016NRF-NRFI001-21).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] a) W. Gerstner, H. Sprekeler, G. Deco, *Science* **2012**, 338, 60; b) Y. Liu, K. He, G. Chen, W. R. Leow, X. Chen, *Chem. Rev.* **2017**, 117, 12893.
- [2] a) M. Prezioso, F. Merrih-Bayat, B. D. Hoskins, G. C. Adam, K. K. Likharev, D. B. Strukov, *Nature* **2015**, 521, 61; b) P. A. Merolla, J. V. Arthur, R. Alvarez-Icaza, A. S. Cassidy, J. Sawada, F. Akopyan, B. L. Jackson, N. Imam, C. Guo, Y. Nakamura, B. Brezzo, I. Vo, S. K. Esser, R. Appuswamy, B. Taba, A. Amir, M. D. Flickner, W. P. Risk, R. Manohar, D. S. Modha, *Science* **2014**, 345, 668.

- [3] a) T. Chang, S.-H. Jo, W. Lu, *ACS Nano* **2011**, *5*, 7669; b) T. Ohno, T. Hasegawa, T. Tsuruoka, K. Terabe, J. K. Gimzewski, M. Aono, *Nat. Mater.* **2011**, *10*, 591; c) B. Zhu, H. Wang, Y. Liu, D. Qi, Z. Liu, H. Wang, J. Yu, M. Sherburne, Z. Wang, X. Chen, *Adv. Mater.* **2016**, *28*, 1559; d) H. Ling, M. Yi, M. Nagai, L. Xie, L. Wang, B. Hu, W. Huang, *Adv. Mater.* **2017**, *29*, 1701333.
- [4] a) Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, C. Xu, Z. Xu, S. Li, W. Huang, F. Huo, X. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 8884; b) Y. Liu, Z. Liu, B. Zhu, J. Yu, K. He, W. R. Leow, M. Wang, B. K. Chandran, D. Qi, H. Wang, G. Chen, C. Xu, X. Chen, *Adv. Mater.* **2017**, *29*, 1701780; c) H. Wang, Y. Du, Y. Li, B. Zhu, W. R. Leow, Y. Li, J. Pan, T. Wu, X. Chen, *Adv. Funct. Mater.* **2015**, *25*, 3825; d) P. Cheng, K. Sun, Y. H. Hu, *Nano Lett.* **2016**, *16*, 572; e) H. Wang, B. Zhu, H. Wang, X. Ma, Y. Hao, X. Chen, *Small* **2016**, *12*, 3360; f) Y. Qian, X. Zhang, L. Xie, D. Qi, B. K. Chandran, X. Chen, W. Huang, *Adv. Mater.* **2016**, *28*, 9243; g) D. Son, S. I. Chae, M. Kim, M. K. Choi, J. Yang, K. Park, V. S. Kale, J. H. Koo, C. Choi, M. Lee, J. H. Kim, T. Hyeon, D.-H. Kim, *Adv. Mater.* **2016**, *28*, 9326.
- [5] a) W. Xu, H. Cho, Y.-H. Kim, Y.-T. Kim, C. Wolf, C.-G. Park, T.-W. Lee, *Adv. Mater.* **2016**, *28*, 5916; b) T. Tuma, A. Pantazi, M. Le Gallo, A. Sebastian, E. Eleftheriou, *Nat. Nano.* **2016**, *11*, 693.
- [6] L. F. Abbott, W. G. Regehr, *Nature* **2004**, *431*, 796.
- [7] a) S. D. Brenowitz, W. G. Regehr, *Neuron* **2005**, *45*, 419; b) D. Kuzum, R. G. D. Jeyasingh, B. Lee, H. S. P. Wong, *Nano Lett.* **2012**, *12*, 2179.
- [8] a) Z.-H. Tan, R. Yang, K. Terabe, X.-B. Yin, X.-D. Zhang, X. Guo, *Adv. Mater.* **2016**, *28*, 377; b) L. Hu, S. Fu, Y. Chen, H. Cao, L. Liang, H. Zhang, J. Gao, J. Wang, F. Zhuge, *Adv. Mater.* **2017**, 1606927; c) A. A. Bessonov, M. N. Kirikova, D. I.

- Petukhov, M. Allen, T. Ryhänen, M. J. A. Bailey, *Nat. Mater.* **2015**, *14*, 199; d) J. J. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nano.* **2013**, *8*, 13.
- [9] A. E. Pereda, *Nat. Rev. Neurosci.* **2014**, *15*, 250.
- [10] a) D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380; b) K.-C. Kao, C.-H. Lin, T.-Y. Chen, Y.-H. Liu, C.-Y. Mou, *J. Am. Chem. Soc.* **2015**, *137*, 3779; c) J. Kim, B. Kim, C. Anand, A. Mano, J. S. M. Zaidi, K. Ariga, J. You, A. Vinu, E. Kim, *Angew. Chem. Int. Ed.* **2015**, *54*, 8407; d) N. L. Torad, H.-Y. Lian, K. C. W. Wu, M. B. Zakaria, N. Suzuki, S. Ishihara, Q. Ji, M. Matsuura, K. Maekawa, K. Ariga, T. Kimura, Y. Yamauchi, *J. Mater. Chem.* **2012**, *22*, 20008.
- [11] a) Y. Liu, D. Shen, G. Chen, A. A. Elzatahry, M. Pal, H. Zhu, L. Wu, J. Lin, D. Al-Dahyan, W. Li, D. Zhao, *Adv. Mater.* **2017**, *29*, 1702274; b) J. Gao, W. Guo, D. Feng, H. Wang, D. Zhao, L. Jiang, *J. Am. Chem. Soc.* **2014**, *136*, 12265; c) D. Feng, Y. Lv, Z. Wu, Y. Dou, L. Han, Z. Sun, Y. Xia, G. Zheng, D. Zhao, *J. Am. Chem. Soc.* **2011**, *133*, 15148.
- [12] S. Hestrin, *Science* **2011**, *334*, 315.
- [13] Z. Teng, G. Zheng, Y. Dou, W. Li, C.-Y. Mou, X. Zhang, A. M. Asiri, D. Zhao, *Angew. Chem. Int. Ed.* **2012**, *51*, 2173.
- [14] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
- [15] T. Hasegawa, T. Ohno, K. Terabe, T. Tsuruoka, T. Nakayama, J. K. Gimzewski, M. Aono, *Adv. Mater.* **2010**, *22*, 1831.
- [16] Z. Xu, Y. Bando, W. Wang, X. Bai, D. Golberg, *ACS Nano* **2010**, *4*, 2515.
- [17] a) Y. Wan, D. Zhao, *Chem. Rev.* **2007**, *107*, 2821; b) Y. Jiang, J. L. Carvalho-de-Souza, R. C. S. Wong, Z. Luo, D. Isheim, X. Zuo, A. W. Nicholls, I. W. Jung, J. Yue, D.-J. Liu, Y. Wang, V. De Andrade, X. Xiao, L. Navrazhnykh, D. E. Weiss, X. Wu, D. N. Seidman, F. Bezanilla, B. Tian, *Nat. Mater.* **2016**, *15*, 1023.

- [18] a) H. Wang, F. Meng, Y. Cai, L. Zheng, Y. Li, Y. Liu, Y. Jiang, X. Wang, X. Chen, *Adv. Mater.* **2013**, *25*, 5498; b) H. Wang, F. Meng, B. Zhu, W. R. Leow, Y. Liu, X. Chen, *Adv. Mater.* **2015**, *27*, 7670.
- [19] A. Geresdi, M. Csontos, A. Gubicza, A. Halbritter, G. Mihaly, *Nanoscale* **2014**, *6*, 2613.
- [20] a) K. Terabe, T. Nakayama, T. Hasegawa, M. Aono, *J. Appl. Phys.* **2002**, *91*, 10110; b) A. Gubicza, M. Csontos, A. Halbritter, G. Mihaly, *Nanoscale* **2015**, *7*, 4394.
- [21] a) Y. Yang, P. Gao, S. Gaba, T. Chang, X. Pan, W. Lu, *Nat. Commun.* **2012**, *3*, 732; b) Y. Yang, P. Gao, L. Li, X. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, *5*, 4232; c) C. Wu, T. W. Kim, T. Guo, F. Li, D. U. Lee, J. J. Yang, *Adv. Mater.* **2017**, *29*, 1602890.
- [22] I. Valov, G. Staikov, *J. Solid State Electrochem.* **2013**, *17*, 365.
- [23] a) I. Valov, I. Sapezanskaia, A. Nayak, T. Tsuruoka, T. Bredow, T. Hasegawa, G. Staikov, M. Aono, R. Waser, *Nat. Mater.* **2012**, *11*, 530; b) A. Milchev, *Electrocrystallization: fundamentals of nucleation and growth*, Springer Science, 2002.
- [24] E. Budevski, G. Staikov, W. J. Lorenz, in *Electrochemical Phase Formation and Growth*, Wiley-VCH Verlag GmbH, 2007, 149.
- [25] E. Budevski, G. Staikov, W. J. Lorenz, in *Electrochemical Phase Formation and Growth*, Wiley-VCH Verlag GmbH, 2007, 41.
- [26] a) I. Valov, W. D. Lu, *Nanoscale* **2016**, *8*, 13828; b) J. Sun, L. He, Y.-C. Lo, T. Xu, H. Bi, L. Sun, Z. Zhang, S. X. Mao, J. Li, *Nat. Mater.* **2014**, *13*, 1007.
- [27] R. Yang, K. Terabe, G. Liu, T. Tsuruoka, T. Hasegawa, J. K. Gimzewski, M. Aono, *ACS Nano* **2012**, *6*, 9515.
- [28] R. Lamprecht, J. LeDoux, *Nat. Rev. Neurosci.* **2004**, *5*, 45.

- [29] a) S. La Barbera, D. Vuillaume, F. Alibart, *ACS Nano* **2015**, 9, 941; b) Z. Wang, S. Joshi, S. E. Savel'ev, H. Jiang, R. Midya, P. Lin, M. Hu, N. Ge, J. P. Strachan, Z. Li, Q. Wu, M. Barnell, G.-L. Li, H. L. Xin, R. S. Williams, Q. Xia, J. J. Yang, *Nat. Mater.* **2017**, 16, 101; c) R. Midya, Z. Wang, J. Zhang, S. E. Savel'ev, C. Li, M. Rao, M. H. Jang, S. Joshi, H. Jiang, P. Lin, K. Norris, N. Ge, Q. Wu, M. Barnell, Z. Li, H. L. Xin, R. S. Williams, Q. Xia, J. J. Yang, *Adv. Mater.* **2017**, 29, 1604457.
- [30] a) X. Liu, L. Gu, Q. Zhang, J. Wu, Y. Long, Z. Fan, *Nat. Commun.* **2014**, 5, 4007; b) I. Valov, E. Linn, S. Tappertzhofen, S. Schmelzer, J. van den Hurk, F. Lentz, R. Waser, *Nat. Commun.* **2013**, 4, 1771.
- [31] a) W. A. Catterall, A. P. Few, *Neuron* **2008**, 59, 882; b) D. E. Clapham, *Cell* **2007**, 131, 1047.
- [32] a) R. S. Zucker, W. G. Regehr, *Annu. Rev. Physiol.* **2002**, 64, 355; b) E. S. Fortune, G. J. Rose, *Trends Neurosci.* **2001**, 24, 381.

Figure 1. Proposed concept of orientation of nanopores in the dielectric layer to mediate the short-term plasticity in artificial memristive synapses: (a) Diagram illustrating the biological neuron and the coexisted chemical and electrical synapse; (b) Upon an identical stimulus for short-term plasticity, the simplicity of gap junctions channel in the electrical synapse results in a faster response and shorter relaxation time than the chemical synapses with a more complex information transfer process; (c) Inspired by gap junction channel existed in an electrical synapse, the orientation of nanopores in dielectric layer is proposed to mediate short-term plasticity.

Figure 2. (a) Schematic fabricated procedure of the artificial memristive synapse with an Ag/Ag₂S/vertical-silica/ITO configuration. (b, c, d) SEM and TEM images of the cross section for vertical-silica/ITO, parallel-silica/ITO and amorphous-silica/ITO films and detached film, respectively

Figure 3. Typical current versus voltage (I - V) curves of the Ag/Ag₂S/meso-silica/ITO device with different orientation mesopores in silica film: (a) vertical; (b) parallel; (c) amorphous; (d) device-to-device distributions (ten devices) of set voltage for device with different silica film; the time interval between the three cycles of sweeping voltage is 5 minutes; (e) simulation of electric field distribution in the vertical and parallel mesopores.

Figure 4. Short-term plasticity emulated in Ag/Ag₂S/meso-silica/ITO artificial memristive synapses. (a) The paired-pulse facilitation behavior for device with vertical mesopores. A_1 and A_2 are the peak amplitudes of the first and second presynaptic potential (0.8 V, 30 ms), respectively. (b) The facilitation ratio (A_2/A_1) plotted as a function of time interval (ΔT). (c) STP achieved by applying voltage pulses with amplitude of 0.8 V and 10 ms duration. I_1 and I_t are the amplitude of postsynaptic current triggered by the first and sequence pulses, respectively. (d) Multiple read voltage pulses (0.1 V, 10 ms) are used to study the device relaxation current after a simulated presynaptic potential (1.5 V, 0.7 s). (e) Device-to-device distribution of relaxation time.

Orientation of mesopores mediating the short-term plasticity in an artificial memristive synapse. The vertical mesopores provide directional channels for resistance switch at a lower energy consumption but faster response and shorter relaxation time upon identical simulating voltage pulses, compared to those with parallel mesopores and dense amorphous silica.

Keyword: orientation, mesopores, silica, memristive, synapse

B. Li, Y. Liu, C. Wan, Z. Liu, M. Wang, D. Qi, J. Yu, P. Cai, M. Xiao, Y. Zeng, X. Chen*

Mediating Short-term Plasticity in Artificial Memristive Synapse by the Orientation of Silica Mesopores