Negative Photoconductance Effect: An Extension Function of the TiO$_x$-Based Memristor

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The negative photoconductance (NPC) effect, defined as an increase in resistance upon exposure to illumination, holds great potential for application in photoelectric devices. A prepared memristor with the structure of Ag/graphene quantum dots (GQDs)/TiO$_x$/F-doped SnO$_2$ exhibits typical bipolar resistive switching (RS) memory behavior. The NPC effect is impressively observed in the high resistance state branch of the RS memory, enabling the memristor function to be extended to both memory logic display and multistate data storage. The observed NPC effect is attributed to the excitation, migration, and compensation of oxygen vacancy at the GQDs/TiO$_x$ interface, at which the electron transportation is efficiently restricted because of the variation in the charge distribution and electrostatic potential under illumination. Experiments, theoretical calculations, and physical models are used to provide engineer the interface with the aim of building the NPC effect in the memristive device. These results unveil a new horizon on extending the functionality of the memristor.

The memristor, which is the resistance switch, is an emerging electronic device, whose internal conductance states depend on the history of the electrons and/or the ions it has experienced. The programmable conductance states make it possible to use a memristor for neuromorphic computing, data storage, and memory logic hardware. Memristors require a small size (< 2 nm), fast switch speed (< 1 ns), and low energy consumption (< 10 fJ) to be computationally efficient.

Two different types of resistive switching (RS) mechanisms have emerged and depend on the memristor structure involved in the redox process: i) an active electrode metal (i.e., Cu, Ag, or Mg) in the case of electrochemical metallization memories (ECMs) and ii) an oxide layer as the solid electrolyte in the case of valence change memories (VCMs). The performance of the RS memory (in terms of the $R_{on}/R_{off}$ ratio, power consumption, and cycling endurance) of TiO$_x$- and HfO$_x$-based ECMs was enhanced by improving the design of the active electrode and by modulating the redox reaction. VCMs, which are often associated with the growth of conduction

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/advs.202003765

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DOI: 10.1002/advs.202003765
The cross-section of the FE-SEM image reveals the thickness of approximately 10 nm with an average diameter of logic display and multistated storage is thus feasible.

The NPC effect, characterized by an increase in resistance under illumination, has been extensively investigated because of its great potential for application in photodetector, nonvolatile memory, and leakage current compensation. In 1983, the NPC effect was theoretically predicted to exist in semiconductors according to the compensation of minority carriers at the band edge under illumination. Two years later, the NPC effect was observed in a GaAs|AlGaAs heterojunction as a result of elaborate engineering of the compensation process.

In 2003, an NPC-based electron avalanche photo-detector was developed. Subsequent years witnessed the proliferation of applications based on the NPC effect in 2D materials because of the strong compensation of the electrons and holes in the band edge.

A pseudo-NPC effect was observed in a graphene-doped SnO$_2$ nanoparticle by utilizing the intensive electron scattering. Gao has stressed that a great potential of application is desired in the memory device with the pseudo-NPC effect. This milestone work has essentially orientated both physical mechanisms and applications. Hot carrier trapping and de-trapping processes were partially responsible for the observation of the NPC effect, even though the positive photoconductance (PPC) effect was possibly triggered during these processes.

Liu and Li have emphasized that the co-occurrence of the PPC and the NPC should be received concern, despite the PPC has been extensively studied in a variety of memory devices. Baraban pointed out that the concentration of impurity dopant is an important approach to understand the co-occurrence of the PPC and NPC.

Miao and Wang reported that a gate-tunable transition between the PPC and the NPC is feasible in the van der Waals heterostructure of ReS$_2$|h-BN|MoS$_2$.

However, the coexistence of the PPC and NPC in the same RS memory device is adverse to conductance programming and variable control. Here, we report an interface engineering, which involves the excitation, migration, and reaction of oxygen vacancies and electrons at the interface of graphene quantum dots (GQDs)|TiO$_2$| to construct the TiO$_2$-based memristor with only NPC effect. Directly utilizing the coexistence of the RS memory behavior and the single NPC effect to realize the memory logic display and multistate data storage is thus feasible.

The HR-TEM image shows that the GQDs range from 2 to 10 nm with an average diameter of $\approx$ 3 nm (Figure 1a). The lattice constant of 0.243 nm originating from the graphene is demonstrated in the enlarged region of the HR-TEM image (Figure 1b). The cross-section of the FE-SEM image reveals the thickness of TiO$_2$ to be 85 nm (Figure 1c). The UV–Vis spectrum of the carbon dot solution shows an obvious absorption at the wavelength in the range 250–500 nm, and the PL emission spectrum excited at the wavelength of 300 nm presents emission peaks near 400, 430, and 460 nm (Figure 1d). The expected fluorescence is observed for the carbon dot solution under UV illumination (inset of Figure 1d). Thus, the GQDs are well prepared.

The GQDs solution was spin-coated onto the TiO$_2$ surface to construct the interface of GQDs|TiO$_2$. The UV–Vis absorption varies negligibly between TiO$_2$|F-doped SnO$_2$ (FTO) and TiO$_2$|GQDs|FTO samples, but it does exhibit a small red shift for the GQDs|TiO$_2$|FTO sample (Figure 1e). The GQDs solution spin-coated on the TiO$_2$ surface possibly facilitates the absorption of visible light.

The Mulliken charge distribution mapping of the GQDs in the ground state demonstrates that the oxygen was mainly absorbed by the central defeat region rather than the edge region and that mainly contributes to the electron distribution. The red and blue regions stand for the electron and hole distribution, respectively. Most of the holes are closely distributed at the sites of the carbon atoms and around the edges of the GQDs (Figure 1f). The electric potential of the GQDs is dominated by the distribution of holes and electrons. The front, back, and lateral view electrostatic potential mapping of the GQDs demonstrates that the positive electrostatic potential is mainly distributed on the front side, whereas the negative electrostatic potential distributes on the back and along the edges of the GQDs (Figure 1g–i). Therefore, the electrostatic potential calculation is consistent with the charge distribution results.

The electrons, holes, and ions are activated by applying a bias voltage and illumination, resulting in a redistribution of the electric potential. First-principle calculations were employed to study the charge and potential re-distribution. Twenty eight excited states of the GQDs were calculated for the redistribution of electrons and holes (Figure S1, Supporting Information).

In the 1st excited state, the electrons and holes distribute on the same region of the GQDs and 0.308 electrons are transferred (Figure 1j). As the GQDs entering the 14th excited state, distribution of electrons and holes can be distinguished, but the electron transfer decreases (0.283 e) compared with the 1st state (Figure 1k). The holes and electrons are completely identified in difference region for the 22nd excited state and 0.729 electrons are transferred (Figure 1l). Thus, the electrostatic potential is triggered by charge redistribution, which has a restrictive effect on the GQDs.

Figure 2a shows a schematic diagram of the device with the structure of Ag|GQDs|TiO$_2$|FTO under illumination. The AFM image demonstrates that the GQDs are well distributed on the TiO$_2$ surface (Figure 2b). Current voltage (I–V) measurements were conducted on the memristor under dark and illumination conditions. The current clearly decrease under illumination at the wavelength of 550, 365, and 254 nm (Figure 2c), which is the so-called NPC effect.

To further verify the existence of the NPC effect in the Ag|GQDs|TiO$_2$|FTO device, cyclic voltammetry curves were recorded under dark and illumination (Figure 2e). Typical bipolar RS memory behavior was observed in the device both of these conditions. The device is not a free-forming memristor. The as-prepared memristor is in a low resistance state (LRS) state. A sweeping bias voltage (0 → 2 → 0 → 2 → 0 V) was applied to the fresh memristor in order to complete the forming process, in which a complex ion migration and redox reaction were involved (Figure S2a, Supporting Information). A normal RS memory behavior with clockwise switching direction was observed after
Figure 1. a) HR-TEM image of GQDs and b) an enlarged region. c) Cross-section of FE-SEM image of GQDs|TiO$_x$|FTO sample. d) The UV–Vis and PL absorption spectra of the GQDs solution. The inset is an optical photo of the GQDs solution under UV illumination. e) The UV–Vis absorption spectra of the TiO$_x$|FTO, TiO$_x$|GQDs|FTO and GQDs|TiO$_x$|FTO samples. f–i) Theoretical calculation on the charge distribution and electrostatic potential mapping of the GQDs. j–l) Charge transfer and distribution of the 1st, 14th, and 22nd excited state.

completing the forming process (Figure S2b, Supporting Information). In the 1st stage (0 → ≈1.5 V), the current of the LRS branch gradually increases to the highest value. In the 2nd stage, (1.5 → 2 → 0 V), the memristor switches from the LRS to a high resistance state (HRS). In the 3rd stage (0 → −1 → −2 V), the memristor gradually switches from the HRS to the LRS. In the 4th stage (−2 → 0 V), the memristor is in the LRS state.

Under dark condition, the behavior of the RS memory was effectively limited by the compliance current (CC) of 10$^{-2}$ A, but it is self-limited when the CC exceeds 10$^{-2}$ A (Figure S3a, Supporting
Information). In addition, the RS memory behavior was enhanced when the bias voltage magnitude increased from ±2 to ±3 V, but it reached saturation when the bias voltage exceeded ±3 V (Figure S3b, Supporting Information). The resistance of the HRS branch clearly tends to decrease an obvious decreasing tendency as the bias voltage scan rate increasing from 0.5 to 8.0 V s\(^{-1}\) under dark (Figure S4, Supporting Information). The high response speed and time evolution of the ions (i.e., \(V^+_O\), OH\(^-\)) at the interfaces dominate the variation.

It is worth noting that the current in the LRS branch under goes a negligible variation, whereas it obviously decreases in the HRS branch when illuminated by 550 nm light. This confirms that the NPC effect occurs in the Ag|GQDs|TiO\(_x\)|FTO memristor. In addition, the power consumption, defined as \(W = i \cdot dv + \int vdi\), is efficiently reduced by the observed NPC effect. An energy band was built to enable the NPC effect observed in the memristor of Ag|GQDs|TiO\(_x\)|FTO to be fully comprehended.

The energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are −3.91 and −4.43 eV for the 3 nm GQDs with an O/C ratio of 9.6%, respectively. Therefore, the energy gap between the HOMO and LUMO is 0.52 eV for the GQDs (Figure S5, Supporting Information). Therefore, the energy gap between the HOMO and LUMO is 0.52 eV for the GQDs (Figure S5, Supporting Information).

Our previous work demonstrated that the concentration of charged oxygen vacancies (\(V^+_O\)) gradually decreased from the interface of the TiO\(_x\)|FTO to surface.\(^{[43]}\) The \(V^+_O\) were driven to migrate from the high-concentration to the low-concentration region when a positive bias voltage was applied to the FTO electrode. In this case, the electrons are synchronously injected
from the Ag electrode to the TiO$_2$|GQDs interface, where the $V^*_o$ interacted with the injected electrons. This interactive process is described as follows:

$$V^*_o + e^- \rightarrow V_o$$  \hspace{1cm} (1)$$

According to Equation 1, the $V^*_o$ at the TiO$_2$|GQDs interface are partially recombined to be $V_o$ under dark conditions (Figure 2f). The $V^*_o$ migration outweighs the recombination, resulting in the current in the HRS branch gradually increasing. By comparison, it is necessary to point out that three processes occur under illumination: i) the Schottky barrier originating from the Ag|TiO$_2$ contact changes from the down-bending to up-bending; ii) the recombination process is weakened; and iii) the Coulomb blockade effect and electron scattering is enhanced. The $V_o$ is re-excited after absorbing $h\nu$ energy, which is described as follows:

$$V_o + h\nu \rightarrow V^*_o + e^-$$  \hspace{1cm} (2)$$

According to Equation 2, $V^*_o$ accumulates at the interface of the TiO$_2$|GQDs and the electrons jump to the conduction band of the TiO$_2$ films under light illumination. Simultaneously, photo excitation process of the GQD occurs according to the following equation:

$$\text{GQDs} + h\nu \rightarrow \text{GQD (} \epsilon^- + h^+ \text{)}$$  \hspace{1cm} (3)$$

Based on Equation 3, the holes and electrons are separated upon exposure to illumination, resulting in the polarization of the GQDs. In this case, the scattering effect, which is induced by the holes and $V^*_o$, is built at the TiO$_2$|GQDs interface, and then weakens the recombination of the $V^*_o$. In addition, the Coulomb blockade effect, which originates from the electrons of GQDs and the injection electrons, is enhanced as the Equation 3 continues to proceed.\(^{[72,73]}\) Therefore, the injected electrons are partially forbidden and the electron induced by the polarization of the GQDs possibly falls back to the Ag electrode (Figure 2g).

The aforementioned theoretical calculations and analysis serve to explain the observation of the NPC effect in the Ag|GQDs|TiO$_2$|FTO memristor. The electrons injected from the Ag electrode are partially restricted or their paths are even reversed because of quantum confinement, scattering, and the Coulomb blockade effect under illumination, which naturally results in the NPC effect (Figure 2d).

Devices with the structures of Ag|TiO$_2$|FTO and Ag|TiO$_2$ |GQDs|FTO were constructed to further verify the existence of NPC effect. As expected, the typical bipolar RS memory behavior was observed in all devices in darkness and under illumination, yet the NPC effect neither appeared in Ag|TiO$_2$|FTO nor in Ag|TiO$_2$|GQDs|FTO (Figure 3a,b). More specifically, we discovered that the NPC effect does not appear in the memristor of the Ag|GQDs|TiO$_2$|FTO when the light wavelength is longer than 550 nm (Figure 3c). At shorter wavelengths, the NPC was again observed in the Ag|GQDs|TiO$_2$|FTO memristor upon illumination at 550, 365, and 254 nm, respectively (Figure 3d).

Therefore, enough $h\nu$ energy is necessary for the reaction of Equation 2 and the Equation 3 to proceed. The TiO$_2$ function layer was post-annealed at 550 °C for 30 min to obtain the anatase TiO$_2$. This led us to surmise that the absence of the NPC effect from the Ag|TiO$_2$|GQDs|FTO memristor resulted from the deactivation of the GQDs, the structure of which could have been destroyed by the high-temperature annealing. To verify this hypothesis, titanium tetrasopropoxide was spin-coated onto the GQDs|FTO device to enable the Ag|TiO$_2$|H$_2$Cl$_2$|GQDs|FTO device to be prepared at room temperature. This device exhibited stable RS memory behavior under dark conditions, and the NPC effect with a wide modulation range was detected upon exposure to illumination (Figure S6, Supporting Information). These results suggest that the NPC effect is dominated by the activation of the GQDs.

Because the activation of the GQDs is intensively influenced by the annealing temperature, it was necessary to investigate the temperature-dependency of the RS memory behavior and the NPC effect. Prior to this investigation, it was necessary to demonstrate the stability of the device. Three hundred consecutive $I$–$V$ profiles were recorded to demonstrate that the Ag|GQDs|TiO$_2$|FTO memristor has excellent cycle-to-cycle stability; thus, the stochastic switching process is suppressed (Figure 3e). The $I$–$V$ sweep curves were obtained by using one hundred memristors, demonstrating that the observation of RS memory behavior and the NPC effect has good device-to-device stability; thus, the TiO$_2$ film is uniformly fabricated (Figure 3f). The retention time of the Ag|GQDs|TiO$_2$|FTO memristor was measured under dark and illuminated conditions. The Ag|GQDs|TiO$_2$|FTO memristor was programmed to the HRS state in the dark and then read out at 0.2 V. The HRS state at $\pm$2.5 mA ($\pm$0.8 mA) is well maintained under darkness (illumination), whereas the LRS state is maintained at $\pm$30 mA either under darkness or under illumination (Figure 3g). Therefore, multilevel storage with photoelectric control can be realized in the Ag|GQDs|TiO$_2$|FTO memristor. The $\pm$2.5 mA decreases to $\pm$0.8 mA under illumination, which is consistent with the NPC effect previously observed in the Ag|GQDs|TiO$_2$|FTO memristor.

The temperature-dependency of the RS memory behavior of the Ag|GQDs|TiO$_2$|FTO memristor was measured in situ at 300, 320, 340, 360, 380, and 400 K under darkness and illumination. Interestingly, the current in the HRS branch increases as the temperature increases under dark conditions (Figure 3h), whereas the current has a decreasing tendency under illumination (Figure 3i). The values of $ln (I/V)$ versus $1/ KT$ were extracted from the HRS branch under darkness and illumination, as shown in Figure 3j,k. The slope of the $ln (I/V)$ versus $1/ KT$ plot denotes the activation energy ($E_a$) under different bias voltages. The $E_a$ versus $V^{1/2}$ was calculated to extract the trap energy ($E_t$), that is, the intersection on the $y$-axis at zero bias voltage.

In our previous work, we demonstrated the value of $E_t$ to be 0.26 eV for the Ag|TiO$_2$|FTO memristor.\(^{[41]}\) By comparison, this value increases slightly (0.265 eV) after insertion of the GQDs into the Ag|TiO$_2$ interface, whereas it decreases to 0.162 eV in the dark (Figure 3i). This confirms that the Ag|GQDs|TiO$_2$|FTO memristor is sensitive to temperature variation, indicating that the RS memory behavior is dominated by the inherent traps and the NPC is efficiently modulated by the Joule heat.

The observation of the NPC effect is characterized in situ by the current-sensing atomic force microscope (CS-AFM). Figure 4a presents a schematic diagram of the CS-AFM measurement of the GQDs|TiO$_2$|FTO sample. The AFM image shows that the
Figure 3. Investigation of the NPC in the memristor with the structure of a) Ag|TiO$_x$|FTO, b) Ag|TiO$_x$|GQDs|FTO, and c) Ag|GQDs|TiO$_x$|FTO. No NPC effect is observed in the memristor of Ag|TiO$_x$|FTO and Ag|TiO$_x$|GQDs|FTO. d) An obvious NPC effect is observed in the memristor of the Ag|GQDs|TiO$_x$|FTO under illumination with wavelengths of 550, 365, and 254 nm, respectively. The NPC effect does not appear in the memristor of the Ag|GQDs|TiO$_x$|FTO when the light wavelength is longer than 550 nm. The stability of e) the cycle-to-cycle and f) the device-to-device for the Ag|GQDs|TiO$_x$|FTO memristor. g) Retention time measurement of the Ag|GQDs|TiO$_x$|FTO memristor under illumination of 550 nm. h,i) Temperature-dependency of the RS memory behavior of the Ag|GQDs|TiO$_x$|FTO memristor under dark and illumination of 550 nm, respectively. j,k) Ln (I/V) versus 1/KT of the Ag|GQDs|TiO$_x$|FTO memristor under dark and illumination, respectively. l) Activation energy (E$_a$) versus V$^{1/2}$ under dark and light in order to extract the trap energy, the intersection on the y-axis at zero bias voltage.

average roughness ($R_a$) of the GQDs|TiO$_x$|FTO sample is 1.01 nm (Figure 4b), verifying that the GQDs|TiO$_x$ sample was developed with a high-quality surface.

It should be noted that a Pt probe served as the top electrode during the CS-AFM measurement, with the current from the FTO electrode to the Pt probe defined as the positive direction. The sensing current is not detected at 0 V. A slight sensing current emerges at bias voltage of 0.1 V, but it is difficult to distinguish between the dark and illuminated states. An obvious sensing current is observed in certain regions when a bias voltage of 0.2 V is applied. An increasing current is clearly observed as the bias voltage increases from 0.5 to 1.0 V, and the current under dark conditions is higher than that under illumination (Figure 4c), indicating that the NPC is confirmed in situ by the CS-AFM measurement.

A memristor with a state of time-series and space dependency was employed to realize memory logic. In the case of time-series memory logic, a single memristor cell, which was timely programmed to take on the different states the memory logic gate requires (“AND,” “OR,” and “NOT”), was extensively investigated.$^{[15,59]}$ The case of space-dependency memory logic, memristor point arrays or crossbar arrays were either synchronously or asynchronously programmed to take on different states, acting as the memory logic display.$^{[66,74–77]}$
Figure 4. a) Schematic diagram of the CS-AFM measurement of the GQDs|TiO$_x$|FTO sample. b) The AFM image of the GQDs|TiO$_x$|FTO sample, an average roughness is 1.01 nm. c) CS-AFM image of the GQDs|TiO$_x$|FTO sample operated at a bias voltage of 0, 0.1, 0.2, 0.5, and 1.0 V under dark and illumination. The NPC effect is verified by the CS-AFM image.

Figure 5. a) Schematic diagram of Ag|GQDs|TiO$_x$|FTO memristor point array under dark and illumination. b) Current–time (I–T) relation under dark and illumination. c) Light programming process with the binary code. Uppercase letters of the “S” “W” “U” are display according to the ASCII code.
Based on the observation of RS memory behavior and the NPC effect in the Ag|GQDs|TiO$_2$|FTO memristor, a memristor point array was fabricated and tested in a memory logic display. Figure 5a presents a schematic diagram of the Ag|GQDs|TiO$_2$|FTO memristor point array that was programmed by illumination with a wavelength of $<550$ nm. This memristor point array (with eight columns and three rows), which was initially programmed to be in the HRS state by applying closed-loop bias voltage ($0 \rightarrow -2 \rightarrow 0 \rightarrow 2 \rightarrow 0$ V), was designed for the memory logic display. The current-time ($I$–$T$) curve indicates that the $\approx800$ and $\approx200$ $\mu$A currents, which are respectively defined as the logic states “1” and “0,” are well maintained under dark and illumination (Figure 5b). The eight memory cells in the 1st, 2nd, and 3rd row were respectively programmed to have the logic states of “0 1010011,” “0 1010111,” and “0 101 0101,” reflecting the upper-case letters “S,” “W,” and “U” according to the American Standard Code for Information Interchange (ASCII) (Figure 5c).

In summary, the fabricated memristive devices with the structures Ag|TiO$_2$|FTO, Ag|GQDs|TiO$_2$|FTO, and Ag|TiO$_2$|GQDs|FTO exhibit bipolar RS memory behavior. An obvious NPC was observed in the HRS branch of the Ag|TiO$_2$|GQDs|FTO memristor under illumination. Multistate data storage and low power consumption are feasible because of the coexistence of the NPC and RS memory behavior. This coexistence was exploited by mapping the memory logic display to the memristor point arrays. The NPC effect is attributed to the compensation of the oxygen vacancies, the restriction of injected electrons, and the variation in the electrostatic potential.

**Experimental Section**

*TiO$_2$ Fabrication:* The FTO substrate was processed by air plasma (PDC-32G-2) for 30 s to remove possible contaminants. The precursor solution was obtained by mixing titanium isopropoxide (350 $\mu$L), isopropanol (5 mL), and hydrochloric acid (25 $\mu$L). The precursor solution was allowed to cool to room temperature naturally and adjusted to pH 7 with an aqueous solution of NaOH (20 wt%). Finally, the solution was sonicated for 72 h at 60 °C and stirred for 24 h at 100 °C. The stirred solution was continuously stirred for 12 h in a N$_2$ atmosphere.

The initial TiO$_2$ film was formed by spin coating the precursor solution onto the plasma-processed FTO substrate at 4500 rpm for 45 s. The anatase TiO$_2$ film was developed by post-annealing the films at 550 °C in air for 3 h.

*GQD Fabrication:* Graphene samples (1.0 mg) were added to 60% HNO$_3$ (1 mL) and 95% H$_2$SO$_4$ (3 mL) to form a solution. The solution was sonicated for 72 h at 60 °C and stirred for 24 h at 100 °C. The stirred solution was allowed to cool to room temperature naturally and adjusted to pH 7 with an aqueous solution of NaOH (20 wt%). Finally, the developed solution was dialyzed in a dialysis bag (retained molecular weight: 2000 Da for 72 h).

**Supporting Information**

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

**Acknowledgements**

G.D.Z. is especially grateful for funding from the Postdoctoral Program for the Innovative Talent Support of Chongqing (CQBS201806), Natural Science Foundation of Chongqing (No. cstc2020jcyj-msxmX0648), and Natural Science Foundation of Guizhou Province ([2020]1Y024). This work was also supported by the National Natural Science Foundation of China (Nos. 11774293, 11776046, 11704426, 61976246). The authors sincerely thank the experts Hongbin Zhao, Yanqing Yao, Jun Dong, Gaobo Xu, Jiayu You, Haiwei Liu, Jia Yan, Yue Zhou, Xiaoyan Fang, Xusheng Zhao, Jinggao Wu, Lijia Chen, Xiude Yang, and Ping Li for the important guidance on the language expression.

**Conflict of Interest**

The authors declare no conflict of interest.

**Author contributions**

G.D.Z., B.S., X.H., L.S., Z.Z., B.X., and W.Q. contributed equally to this work. G.Z. and B.S. conducted all experiments, analysis, and wrote the manuscript. X.H. and L.W. measured the spectra of the graphene quantum dots. L.S. and Z.Z. built the band energy structure of the memristor. X.B. and J.C. built the calculation of the 3 nm graphene quantum dot. W.Q. and S.Z. calculated the distribution of charge and electrostatic potential. J.H. and L.L. synthesized the precursor solution of TiO$_2$. L.X., G.X., and L.X. measured the temperature-dependency data. B.W. and C.X. conducted the infrared spectroscopy and AFM measurement. S.D. and Q.S. gave key guidance on the physical models of the NPC.

**Data Availability Statement**

The data used to support the findings of this study are available from the corresponding author upon request.

**Keywords**

graphene quantum dots, memory logic display, negative photoconductance effect, TiO$_2$-based memristor

Received: October 2, 2020
Revised: December 18, 2020
Published online: May 6, 2021

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