An electrically and optically controllable memristor with synaptic plasticity based on scalable monolayer ReS$_2$/WS$_2$ heterostructure

Yaping Wu (✉ ypwu@xmu.edu.cn)
Fujian Provincial Key Laboratory of Semiconductor Materials and Applications, Department of Physics
https://orcid.org/0000-0001-9325-2212

Huang Feihong
Xiamen University

Congming Ke
Xiamen University

Li Chen
Xiamen University
https://orcid.org/0000-0002-8013-5508

Jun Yin
Xiamen University
https://orcid.org/0000-0003-4551-3515

Xu Li
Xiamen University
https://orcid.org/0000-0002-0377-2925

Zhiming Wu
Chunmiao Zhang
Xiamen University

Feiya Xu
Xiamen University

Junyong Kang
Xiamen University

Article

Keywords:

Posted Date: September 6th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2006369/v1

License: ☕️ This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

Memristors with non-volatile storage performance and simulated synaptic functions are regarded as one of the critical devices to overcome the bottleneck in traditional von Neumann computer architecture. van der Waals heterostructures integrating excellent properties of two-dimensional semiconductor materials, possessing controllable optoelectronic properties and high compatibility with conventional microelectronic technology, have paved a new way for the development of advanced memristors. Herein, we demonstrate a two-dimensional planar memristor with both electrical and optical controllability based on ReS$_2$/WS$_2$ van der Waals heterostructure. The device shows a typical unipolar non-volatile behavior with a high $R_{on}/R_{off}$ ratio, multiple tunable resistance states, and desirable endurance and retention. It also successfully realizes biological synaptic functions and plasticity, including spike rate-dependent plasticity and paired-pulse facilitation. Furthermore, the developed device shows a significant gate controllability and a remarkable optical tunability. The superior performance is attributed to the unique optoelectronic property and the interlayer interaction in the heterostructure. The research presented here demonstrates the potential of two-dimensional van der Waals heterostructures for high-performance memristor applications and further developments in modelling biological synapses.

Introduction

Recent years have witnessed a spurt of progress in computing and communications technology. As traditional silicon-based microelectronic devices have struggled to scale up further according to Moore's Law, advanced storage technologies require new materials and device design. Memristors can maintain the internal resistance state created by the applied voltage and current, making them viable to implement memory computing systems without any program and having attracted tremendous research attention. The preliminary study of memristors mainly involved traditional three-dimensional (3D) materials, which are challenging to reduce the size to meet the stringent requirements of future big data and artificial intelligence for high-density integration and low power consumption. Two-dimensional (2D) semiconductors are considered be a focal point for future research due to their ultra-thin thickness, high flexibility, and intriguing optoelectronic properties. Rhenium disulfide (ReS$_2$) is a promising 2D material with unique physical and chemical properties. The soft Re-S covalent bonds are more likely to produce sulfur (S) vacancies, providing an intensive possibility for the development of 2D memristors. The S vacancies have an even lower forming energy and more evident movement under the applied bias, which are beneficial to improve the switching performance of memristors. Sifan Li et al. demonstrated a double-ended lateral memristor based on few-layer ReS$_2$, realizing an amnestic block function with a cycle count of over 100 and a switching ratio of $10^2$. Besides, a simulation of synaptic plasticity was further implemented.

Nevertheless, the retention and durability of memristors based on a single 2D material may be relatively lower than that of traditional 3D devices. Heterostructures can integrate the properties of different materials becoming an alternative to enhance the performance of memristors. In order to take
advantage of the excellent properties of 2D materials, and also consider the compatibility with conventional microelectronic technology, attention has been targeted on 2D/2D heterostructures with steep potential gradient at the atomic level. The stacked layers in the heterostructure are no longer restricted by lattice matching due to their van der Waals interface. Zhang et al. designed a 2D/2D memristor based on few-layer MoS\(_2\)/WS\(_2\) heterostructure, implementing a resistive switching mechanism based on the band structure modulation with a switching ratio of \(10^4\).\(^{17}\) Its higher stability, larger memory window, and superiority in high-density integration further confirm the great potential of 2D van der Waals heterostructures for the memristor applications.

In addition, most of the existing memristors are solely based on the electrical modulation. It does not completely match the practical human stimuli, including vision, hearing, touch, smell and so on. Light as an extra stimulus may also supply a way to fill the gap between the visual system and brain function.\(^{18}\) Beyond pure electronic devices, further introducing the optical signals as information carriers during the device working has advantages in terms of high bandwidth, low crosstalk, and high connectivity. The optical programmability also facilitates the application in the field of neuromorphic vision.\(^{19}\) Therefore, developing a memristor with both electrical and optical controllability is significantly crucial. In this regard, van der Waals heterostructures possess another advantage on modulating the optical absorption and exciton recombination through the design of their band alignment.\(^{20-22}\)

In this work, a 2D memristor with planar structure is fabricated based on ReS\(_2\)/WS\(_2\) heterostructure through an alignment transfer of chemical vapor deposition (CVD) grown monolayers. The lattice configuration, stacking structure and band alignment are determined by Raman scattering, transmission electron microscopy (TEM), time-resolved photoluminescence (TRPL) and Kelvin atomic force microscopy (KPFM). The memristor properties, such as resistance states, switching ratio, cycle number, and retention time are studied at room temperature, and the synaptic functions of short-term plasticity (STP), spike rate-dependent plasticity (SRDP), and double-pulse (PPF) dissimilation are simulated. Moreover, the special gate and optical control over the resistive switching is achieved, and the related mechanism is further revealed.

Results

Morphological, structural, and electronic properties of the ReS\(_2\)/WS\(_2\) heterostructure

For the development of ReS\(_2\)/WS\(_2\) memristor, the properties of ReS\(_2\)/WS\(_2\) heterostructure are studied at first. The heterostructure is prepared through an alignment transfer of CVD grown ReS\(_2\) and WS\(_2\) monolayers (detailedly in Methods). The optical microscopy in Fig. 1a shows a clear surface all around the sample, and the heterostructure area is vertically stacked with triangular WS\(_2\) on top of hexagonal ReS\(_2\). The crystal and electronic structures of the ReS\(_2\)/WS\(_2\) region are characterized through the Raman and photoluminescence (PL) measurements. As shown in Fig. 1b, the Raman spectrum of heterostructure region is coincident with the combination of characteristic peaks from the two monolayers, where the
peaks located at 164 cm$^{-1}$ and 216 cm$^{-1}$ respectively correspond to the in-plane ($E_{12g}^{1}$) and out-of-plane ($A_{1g}$) vibrational modes from ReS$_2$, and the two peaks at 359 cm$^{-1}$ and 420 cm$^{-1}$ are identified as from monolayer WS$_2$. Different from the superposition of the Raman peaks, the PL spectrum for the heterostructure demonstrates an obvious intensity decay and a 5 nm blue shift with respect to the monolayer WS$_2$ (625 nm), as shown in Fig. 1c, which suggests an interlayer charge transfer and stress interaction. The intensity mappings of Raman and PL peaks further reveal the good uniformity of the structures (Figure S1a-c in SI). Accordingly, we infer that a type II heterostructure may be formed between ReS$_2$ and WS$_2$. The atomic force microscope (AFM) image (Figure S1d in SI) also indicates an existence of interlayer interaction.

Interlayer interaction related to the band alignment of WS$_2$ and ReS$_2$ monolayers is closely associated with the electronic property of the heterostructure. To gain an insight into their band alignment, KPFM is employed to detect the work function ($\phi_s$) of a 60° stacked ReS$_2$/WS$_2$ heterostructure on an Au-plated SiO$_2$/Si substrate. As shown in Fig. 1d and Figure S2a,b in SI, a clear variation of $\phi_s$ between ReS$_2$, WS$_2$, and the heterostructure areas is observed, in well agreement with the optical contrast. By measuring the potential change in ReS$_2$/Au and WS$_2$/Au steps, the $\phi_s$ difference is determined to be about −21 mV between ReS$_2$ and Au, and about −66 mV between WS$_2$ and Au, which indicates a higher Fermi energy level of WS$_2$ than that of ReS$_2$ (seeing detail in Figure S2c,d in SI). HRTEM characterization (detailedly in the Methods) is further performed to investigate the lattice and stacking structures of the ReS$_2$/WS$_2$ heterostructure. As measured in Fig. 1e, the space between two Re atoms in the Re4-chain (0.27 nm) is smaller than that of adjacent two Re atoms (0.32 nm), consistent with a 1T'-ReS$_2$ structure, while the distance between neighboring W atoms (0.29 nm) corresponds to 2H-WS$_2$. The FFT image (insert in Fig. 1e) and SAED patterns (Fig. 1f) contain two set of six-fold symmetrical lattices, corresponding to the lattice spacings of 5.5 Å and 2.8 Å, respectively. The lattice structures are identified to the (010) planes of monolayer WS$_2$ and ReS$_2$, respectively, confirming a 60° vertical stacking of the heterostructure.

Photoinduced interfacial charge behavior is studied through the TRPL measurements (Fig. 1g). The heterostructure area exhibits a significantly faster intensity decay than that of pristine WS$_2$. Fitting the TRPL curves by the multi-exponential function:

$$D(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}$$

where $D(t)$ is the exciton concentration, $\tau_i$ ($i = 1, 2, 3$) are the time constants, and $A_1$, $A_2$, $A_3$ symbolize the changes in exciton density due to surface states recombination, radiative recombination, and charge transfer, respectively, the lifetime of ReS$_2$/WS$_2$ heterostructure (about 134 ps) is found significantly shorter than that of monolayer WS$_2$ (about 700 ps) (seeing detail in Table S1 in SI). Further considering the intensity decay in the PL spectrum (Fig. 1c and Figure S1c), the type II band alignment is confirmed for the ReS$_2$/WS$_2$ heterostructure. Accordingly, the band structure is schematically shown in Fig. 1h,
where the conduction band minimum and valence band maximum locate in WS₂ and ReS₂, respectively. The facilitated interlayer charge transfer strongly predicts a possibility for electrical modulation for the heterostructure.

**Resistive switching behavior of the ReS₂/WS₂-based memristor**

Based on the understanding of the electronic properties, the ReS₂/WS₂-based planar memristor is constructed on a SiO₂/Si substrate using Au as the source and drain electrodes. Each electrode is in contact with both the ReS₂ and WS₂ monolayers simultaneously, as the schematic diagram and the optical image shown in Fig. 2a,b. The I-V measurements of the device exhibit a typical resistive switching behavior, as shown in the blue curve of Fig. 2c. A compliance current is set at 50 µA, followed by a voltage sweeping from 0 V to 4 V. At an applied voltage of about 3 V, the current increases abruptly, completing the "SET" process from high resistance state (HRS) to low resistance state (LRS); after a voltage sweeping from 4 V to 0 V, the device remains LRS. As removing the compliance current setting and performing a voltage sweep from 0 V to 2 V, the device shifts from LRS to HRS at an increasing current, corresponding to the "RESET" process; and the device maintains HRS at the reversed sweep from 2 V to 0 V. Similar performance of the device is found under the negative voltages, as shown in Figure S3 in SI. This electrical property confirms a typical unipolar resistive switching behavior. Different from the previous reported ReS₂ memristor that only exhibited bipolar resistive switching behavior,¹⁴,³²,³³ the ReS₂/WS₂ unipolar memristor predicts higher switching ratio, higher integration density, and more simplified control circuit. Good reliability is demonstrated during the repeated 100 times switching cycles (the brown cycle curves in Fig. 2c). The set voltage ($V_{set}$) is extracted and depicted in the histogram in Fig. 2d. A Gaussian fit suggests that the $V_{set}$ generally distributes around 2.90 V.

For comparison, the electrical properties of the planar memristors based on pristine monolayer ReS₂ and WS₂ are also studied and shown in Figure S4 and S5 in SI, respectively. The ReS₂-based device exhibits a typical unipolar memristive property that, the resistance jumps from HRS to LRS at a statistical $V_{set}$ of about 3.19 V, as depicted in the histogram in Fig. 2e. While for the WS₂-based device, the HRS is maintained without significant change even when the voltage exceeds 7.0 V. Obviously, the ReS₂ plays a key role in the resistive switching for the heterostructure, since the ReS₂ and WS₂ layers are in parallel connecting to the Au electrons. By comparison, the ReS₂/WS₂-based planar memristor has a decreased and a more stable $V_{set}$ value than that of monolayer ReS₂.

Except for the $V_{set}$, another crucial factor determining the overall performance of a memristor is the memory window that reflected as $R_{ON}/R_{OFF}$ ratio between HRS and LRS. As shown in Fig. 2f, the ReS₂/WS₂-based memristor exhibits a notable $R_{ON}/R_{OFF}$ ratio higher than $10^6$, which is superior to most of the existing 2D memristors.¹⁴,²⁹,³⁴-³⁶ This value is more than an order of magnitude larger than that of pure ReS₂ ($10^5$), indicating a larger memory window when forming the heterostructure. Moreover, the ReS₂/WS₂-based device possesses multiple adjustable resistance states within $5 \times 10^2 \sim 8 \times 10^4 \text{ Ω}$ by varying the compliance current from 1 µA to 100 µA, as shown in Fig. 2g, demonstrating its great
potential for multi-level data storage and multi-state neuromorphic computing. Subsequently, a
switching cycling test of the heterostructure memristor is conducted over 200 times (Fig. 2h),
which shows a reliable resistive switching performance with a clear memory window. A
desirable stability of the memristor is also evidenced by the retention time of over $10^4$ s for
each HRS and LRS state, as seen in Fig. 2i.

**Gate modulation and its mechanism of the ReS$_2$/WS$_2$-based memristor**

Furthermore, the electrical modulation capability is examined by the three-terminal FET
configuration (Fig. 3a). The $I$-$V$ curves measured under different gate voltages ($V_g$) are shown
in Figures S6 and S7 in SI, and the $V_g$ dependent $V_{set}$ is summarized in Fig. 3a. As is shown,
opposite variation trends for the $V_{set}$ are found under different $V_g$ directions. For a positive
gating ($V_g > 0$), the $V_{set}$ increases from 2.9 V to 3.5 V when increasing the $V_g$ from 0 V to 2 V.
As the positive $V_g$ increases to 3 V, 4 V, and 5 V, the device is always in a HRS state within
the voltage sweep range of 0 ~ 5 V, as shown in Fig. 3b, i.e., the device is blocked from turning
on. To be more specific, a negative gating ($V_g < 0$) significantly reduces the $V_{set}$ of
the device, which is decreased from 2.9 V to 1 V when changing the $V_g$ from −5 V to −8 V.
While in the $V_g$ range of 0 ~ −5 V, the $V_{set}$ is relatively stable. Therefore, the ReS$_2$/WS$_2$-based
memristor not only possesses a high $R_{ON}/R_{OFF}$ ratio, multiple adjustable resistance states,
good endurance and desirable retention, but also demonstrates a significant gate controllability.

The mechanism of resistive switching and gate modulation in the ReS$_2$/WS$_2$-based planar
memristor is described in Fig. 3c. Monolayer ReS$_2$ and WS$_2$ grown by the CVD method have been
demonstrated to possess n-type conductivity with intrinsic S vacancies and additional electrons.
When forming the heterostructure, the electrons will transfer from WS$_2$ to ReS$_2$ owing to the
type II band alignment (the top panel in Fig. 3c). By applying a forward bias and a compliance
current, electrons in the ReS$_2$ layer transport to the conducting channel to form a current.
When the bias voltage reaches a threshold, the conducting channel meets the condition for rapid
migration of electrons between electrodes, and the device jumps from HRS to LRS ("SET" process,
the middle panel in Fig. 3c). Hence, the formation of conducting filaments by S vacancies is the
primary conduction mechanism in the memristor. As grown ReS$_2$ generally possesses a lower
stoichiometric ratio than that of WS$_2$, and thus has greater possibility to generate S vacancies.
As such, the resistive switching is dominant by the ReS$_2$ layer during the device working,
while the WS$_2$ layer maintains HRS. The large accumulation of electrons near the head of
the conducting channel causes a noticeable reduction of interface electrons in the ReS$_2$ layer.
Therefore, more electrons will transfer from WS$_2$ to ReS$_2$, which explains the faster conductance
change of ReS$_2$/WS$_2$-based device than that of ReS$_2$. Simultaneously, owing to the addition of
electrons, the resistance at LRS of ReS$_2$/WS$_2$-based device is an order of magnitude lower (Fig. 2f),
resulting in its higher $R_{ON}/R_{OFF}$ ratio. When the voltage with the same polarity is scanned again
with no applied compliance current, the effect of Joule heating is greater than that of the voltage
between electrodes. As
a result, the conducting channel breaks and the S vacancies gradually return to their original state. The device resistance jumps back to the HRS ("RESET" process).

When applying a positive $V_g$ during the "SET" process, some electrons in the device are attracted to the interface of ReS$_2$ and SiO$_2$ substrate due to the electrostatic equilibrium effect (the bottom panel in Fig. 3c). Fewer electrons could jump around the conducting channel made up of S vacancies, causing an increased $V_{\text{set}}$ threshold required for the resistive switching (Fig. 3a). As the $V_g$ increases further, the consumption of electrons finally blocks out the device from turning on (Fig. 3b). In contrast, by applying a negative $V_g$, the electrostatic equilibrium effect causes the holes to accumulate at the interface near the SiO$_2$ substrate. In a small gating range of 0 ~ ~ 5 V, the consumed holes in ReS$_2$ may be supplemented by those transferred from WS$_2$, leading to a relatively stable $V_{\text{set}}$. Further consumption of holes results in more left electrons for the conduction. The left electrons are active to the conducting channel formed by S vacancies, and the required $V_{\text{set}}$ threshold thus gradually decreases (Fig. 3a).

**Simulated synaptic properties of the ReS$_2$/WS$_2$-based memristor**

The superior electronic performance of the ReS$_2$/WS$_2$-based planar memristor sheds light on exploring of its potential applications. We demonstrate that it can simulate partial neuron-based biological synaptic functions, as shown in Fig. 4a. When a presynaptic neuron is stimulated and conducted to a synaptic vesicle, the synaptic vesicle fuses tightly with the presynaptic membrane and causing a rupture. The neurotransmitters within the synaptic vesicles are released into the synaptic space, diffuse to reach the postsynaptic membrane, and thereby induce excitatory or inhibitory modifications in the postsynaptic membrane. For the ReS$_2$/WS$_2$-based planar memristor, the S vacancies are comparable to neurotransmitters in biological synapses.

To simulate the biological synaptic plasticity, conductance of ReS$_2$/WS$_2$-based memristor is modulated by applying a pulse voltage, with the pulse parameters such as amplitude, width, and interval varied to adjust the synaptic weights. As shown in Figure S8 in SI, at a 1 V reading voltage and a fixed 5 V amplitude, the device current tends to saturate with the continuous application of pulse, when the pulse width and interval increase in equal proportion. This performance exhibits a typical memristor characteristic. Accordingly, the device property is analyzed by acquiring the conductance at the saturated currents for different pulse amplitudes, widths, and intervals. As the results shown in Fig. 4b, the conductance is increased when simultaneously increasing the pulse width and interval from 0.5 s to 5 s, indicating a positive response to a continuously longer stimulation. The conductance can also be modulated by individually adjusting the pulse width or interval. An enlarged pulse width increases the upward trend of the conductance, while an opposite trend is found when increasing the pulse intervals, as shown in Fig. 4c,d. Modulating the memristor characteristics by adjusting pulse width and interval is recognized as the biological synapse SRDP.

In addition, the impact of voltage amplitude is shown Fig. 4e, where the device conductance is increased with the enhancing pulse voltage for all the four setting pulse widths and intervals.
PPF representing the STP is an important physiological phenomenon. It is manifested as the temporal sum of biological synaptic inputs, and can be estimated from the change of synaptic weights as responding to the stimuli of two consecutive pulsed voltages.\textsuperscript{42,43} Fig. 4f shows the PPF behavior of the ReS\textsubscript{2}/WS\textsubscript{2}-based memristor, and the inset illustrates the applied pulse. The PPF can be quantitatively expressed as:\textsuperscript{44}

$$\text{PPF} = \frac{(B_2 - B_1)}{B_1} \times 100\%$$

where $B_1$ and $B_2$ are the conductance corresponding to the first and second pulses, respectively. The fitting relationship between PPF data and pulse is as follows:\textsuperscript{45}

$$y = C_1 e^{-\frac{t}{\alpha_1}} + C_2 e^{-\frac{t}{\alpha_2}}$$

which gives $\alpha_1 = 0.05$ s and $\alpha_2 = 2.9$ s, corresponding to the fast and slow decay terms, respectively. The enhancement of conductance under successive pulses stimulation tends to decay exponentially with the increasing pulse intervals, consistent with the behavior of biological synapses.

The above studies have demonstrated the effective simulation of biological synaptic function and plasticity in ReS\textsubscript{2}/WS\textsubscript{2}-based planar memristor, which are all electrical memristor characteristics. While benefiting from the interlayer coupling and charge transfer mechanisms, ReS\textsubscript{2}/WS\textsubscript{2} also displays unique photoresponsive behavior as a type II heterostructure,\textsuperscript{46} thus the optoelectronics-inspired memristor characteristics can also be expected. Since the interlayer charge transfer results in a diminution of $V_{\text{set}}$ in the ReS\textsubscript{2}/WS\textsubscript{2}-based memristor compared with that of the ReS\textsubscript{2}-based device (Fig. 2d,e), a light modulation is further performed on the two memristors under different excitation wavelengths (532 nm and 690 nm) and with various powers. The $I$-$V$ curves for all the cases are acquired, as shown in Figures S9 - S12 in SI, respectively, and the extracted $V_{\text{set}}$ values are illustrated in Fig. 4g. The results for ReS\textsubscript{2}/WS\textsubscript{2}-based memristor show an interesting wavelength-dependent conductance controllability. Under a 532 nm excitation, its $V_{\text{set}}$ drops from about 3 V to below 1 V, exhibiting a negatively correlated with the luminous power. While a 690 nm excitation basically does not affect the $V_{\text{set}}$ that is almost stable at 3 V even when the luminous power increases to 8 mW. Different from the wavelength-dependent performance for heterostructure memristor, the $V_{\text{set}}$ of ReS\textsubscript{2}-based device is basically stable at around 3.1 V under illumination with different powers at both wavelengths. The obtained $V_{\text{set}}$ values are essentially coincident with that measured without the excitation, and larger than that of the ReS\textsubscript{2}/WS\textsubscript{2}-based memristor with the same conditions. This strongly suggests that, the variation of $V_{\text{set}}$ originates from the property of ReS\textsubscript{2}/WS\textsubscript{2} rather than the inherent characteristics of ReS\textsubscript{2}. Compared with the single layer, the formation of type II heterostructure enables the optical modulation over its electrical performance. Beyond the most existing memristors which based on only electrical modulation,\textsuperscript{47,48} the above results
demonstrate an exciting behavior for the optoelectronic memristor based on the ReS$_2$/WS$_2$ heterostructure.

The light-tunable synaptic plasticity is then investigated by applying a pulse under 532 nm excitation at different luminous powers. As shown in Fig. 4h, the conductance at all luminous powers maintains an increase trend with the pulse number, and exhibiting a considerable light-sensing behavior that increases steadily with the increasing luminous power from 0 mW to 8 mW. Such power-dependent conductance control indicates the optical tunability on the synaptic weight, predicting a potential for future visual neural applications. Figure 4i exhibits an effective control over the switching time (the time of device current to stabilize when a single pulse is applied) through the modulation of luminous power. For a pulse with a reading voltage of 1 V, an amplitude of 5 V, and a pulse width and interval of both 3 s, the switching time decreases from about 1.8 s to 0.6 s under the 532 nm excitation. This hints at the advanced sensitivity of optically modulated memristor on the neuromorphic applications.

**Optical modulation and its mechanism of the ReS$_2$/WS$_2$-based memristor**

One issue that needs to be clarified is the wavelength-dependent conductance control of the ReS$_2$/WS$_2$-based planar memristor. From the perspective of band structure, the mechanism can be described in Fig. 5. Without the optical modulation, the electrons transfer from WS$_2$ to ReS$_2$, while the holes transfer in the opposite direction, forming a build-in electric field directed from WS$_2$ to ReS$_2$ (Fig. 5a). Under a 690 nm (1.80 eV) laser irradiation, monolayer ReS$_2$ with a direct bandgap of about 1.65 eV is excited, while WS$_2$ with a 2.07 eV bandgap is out of the excitation energy (Fig. 5b). Consequently, the produced photogenerated carriers distribute mainly within the ReS$_2$ layer. Driven by the build-in electric field, the electrons trend to transfer to WS$_2$, which are blocked by the interfacial potential barrier between the conduction band edges. As a result, the excited electrons and holes mostly will recombine through a radiative or nonradiative process, which essentially does not alter the net carrier distribution in the system. As a result, the $V_{\text{set}}$ of the ReS$_2$/WS$_2$-based memristor is essentially unaffected as well as that of the ReS$_2$-based device, under the modulation of 690 nm illumination and with different luminous powers (Fig. 4g, red and blue lines). For a 532 nm (2.33 eV) laser irradiation, both the ReS$_2$ and WS$_2$ layers can be excited, as shown in Fig. 5c. Since the photon energy is closer to the resonance excitation of the optical bandgap of WS$_2$, a higher excitation efficiency with more photogenerated carriers are produced in WS$_2$ than in ReS$_2$. The additional electrons will transfer from WS$_2$ into ReS$_2$ through the heterogeneous interface, while the transfer of additional holes can be blocked by the interfacial potential barrier. The increased electrons in ReS$_2$ make a positive contribution to the composition of the conductive channel by S vacancies. Consequently, the excited electrons increase with increasing luminous power under the 532 nm excitation, and thus reduces the applied voltage required for forming conducting channel in ReS$_2$/WS$_2$ heterostructure (Fig. 4g, yellow line).

**Discussion**
In summary, a scalable 2D planar memristor based on ReS$_2$/WS$_2$ heterostructure is constructed through an alignment transfer of CVD grown ReS$_2$ and WS$_2$ monolayers. The type II band structure with strong interlayer interaction is confirmed by Raman, TRPL, HRTEM and KPFM characterizations for the heterostructure. The fabricated memristor exhibits a typical unipolar resistive switching property, with the high R$_{ON}$/R$_{OFF}$ ratio up to $10^6$, tunable resistance states ($10^2$–$10^4$ Ω) for multi-level data storage, high gate controllability, clearly extended endurance, and good retention. It is also successfully in simulation of partially biological synaptic functions, including STP, SRDP and PPF, demonstrating the potential applications in neural networks and complex system. Besides the electrical modulation, optical control over the resistive switching is further achieved by tuning the wavelength and power of the exciting light. The optoelectronic property and interlayer interaction are revealed to be the mechanism for the superior performance of the heterostructure device, as well as its electrical and optical controllability. All these findings demonstrate a potential for the development of energy-efficient multi-terminal devices based on 2D van der Waals heterostructures and enable the further exploration of neurofunctional devices with optical programmability.

Materials And Methods

Preparation of ReS$_2$/WS$_2$ Heterostructure.

2D monolayer ReS$_2$ crystals are grown at atmospheric pressure, using the CVD growth methods as our previous reports.$^{49,50}$ The setup of growth systems and the growth processes are provided detailedly in Figure S13 in SI. The ReS$_2$/WS$_2$ heterostructure with special stacking configuration (60° vertical stacking) is prepared through the typical wet transfer method. The poly (methyl methacrylate) (PMMA) is used as the supporting film assisting to peel off the monolayer ReS$_2$ and WS$_2$ from mica and sapphire substrates, respectively. The transfer process is described detailedly in Figure S14 in SI.

Characterizations.

Raman and PL spectra are recorded using a WITec alpha 300RA confocal spectrometer system with a laser wavelength of 488 nm and a beam size of about 1 µm. The step size of the Raman and PL mapping is 800 nm. A SPA400-Nanonavi AFM is used to measure the thickness of ReS$_2$/WS$_2$ heterostructure. TEM measurements, including HRTEM and SAED, are performed on a field emission TEM (JEM-2100) at an accelerating voltage of 200 kV. Surface potential of ReS$_2$/WS$_2$ is measured by the Kelvin Probe Module of the SPA400-Nanonavi AFM after is transferred to an Au-coated SiO$_2$/Si substrate. The photoinduced interfacial charge behavior of the samples are recorded by the TRPL spectra (HORIBA, MicOS) at a PL peak of 620 nm.

Device Fabrication and Measurements.

ReS$_2$/WS$_2$, ReS$_2$ and WS$_2$ layers are transferred to SiO$_2$/Si substrates, respectively, through the above transfer method. Designed ReS$_2$/WS$_2$-based, ReS$_2$-based and WS$_2$-based devices are patterned by the
direct-write laser photolithography technique using an ML microwriter. A transmission channel with a source-drain spacing of 7 µm is defined by depositing 50 nm Au films as the source and drain in the patterned region using magnetron sputtering. The fabricated devices are annealed at 200°C in mixed Ar (a flow rate of 100 sccm) and hydrogen (H₂) (a flow rate of 3 sccm) gas environment for 30 min to improve the quality of the heterogeneous interface as well as the metal-semi-contact. The electrical properties of the devices are measured in ambient atmosphere condition at room temperature, and under dark, 532 nm and 690 nm laser irradiation conditions, respectively, using a semiconductor parameter analyzer (Agilent B2912A source-meter unit system).

Declarations

Acknowledgements

The work is funded by the National Science Fund for Excellent Young Scholars (grant no. 62022068), the National Natural Science Foundation of China (grant nos. 61874092, 61974123, and 61804129), Science and Technology Project of Fujian Province of China (grant no. 2019H0002).

Author Contributions

Yaping Wu and Feihong Huang conceived the project and designed experiments. Feihong Huang prepared samples, fabricated devices, performed Raman and PL measurements, carried AFM and KPFM measurements and measured the performance of devices. Jun Yin performed TRPL measurements. Li Chen performed TEM and SAED measurements. Yaping Wu, Zhiming Wu, Xu Li and Junyong Kang provided the Fund support. Chunmiao Zhang and Feiya Xu assisted laboratory management. Yaping Wu, Feihong Huang and Congming Ke analyzed the data. Feihong Huang and Yaping Wu wrote the manuscript. All authors discussed the results and contributed to the final version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available from Light: Science & Applications or from the author.

References


**Figures**
Figure 1

Morphology, spectroscopic and structure characterizations. (a) Optical image of a transferred ReS$_2$/WS$_2$ heterostructure on SiO$_2$/Si substrate. (b) Raman spectra of the ReS$_2$, WS$_2$, and ReS$_2$/WS$_2$ regions. (c) PL spectra of the WS$_2$ and ReS$_2$/WS$_2$ regions. (d) KPFM image of the ReS$_2$/WS$_2$ heterostructure, with the potential profile taken along the white dashed arrows. (e) High-resolved transmission electron microscopy (HRTEM) image of the ReS$_2$/WS$_2$ heterostructure, with the inset showing the fast Fourier transform (FFT) image. (f) Selected area electron diffraction (SAED) patterns of the ReS$_2$/WS$_2$ heterostructure. (g) Decay curves of the TRPL measurements for pristine WS$_2$ and ReS$_2$/WS$_2$ heterostructure (each case is repeated twice to ensure the accuracy). (h) Proposed schematic diagram of the band alignment and the charge transfer in the heterostructure.
Figure 2

Resistive switching performance of the ReS$_2$/WS$_2$-based planar memristor. (a and b) Schematic diagram and optical micrograph of the memristor based on ReS$_2$/WS$_2$ heterostructure, respectively. (c) $I$-$V$ curves of the ReS$_2$/WS$_2$-based planar memristor showing typical unipolar resistive switching behavior; the inset shows the resetting $I$-$V$ curves. (d and e) Statistical distributions of the set voltages for ReS$_2$/WS$_2$-based and ReS$_2$-based planar memristors based on 100 and 30 consecutive switching cycles, respectively. (f) Comparison of both the LRS and HRS states between ReS$_2$/WS$_2$-based and ReS$_2$-based planar memristors from the statistics of 30 consecutive switching cycles. (g) Multiple resistance states achieved under various compliance current ($I_c$) for the ReS$_2$/WS$_2$-based planar memristor. (h and i) Statistical analysis of the HRS and LRS over 200 switching cycles, and the retention times recorded at the LRS and HRS states, respectively, for the ReS$_2$/WS$_2$-based planar memristor.
Figure 3

(a) Gate tunable $V_{\text{set}}$ of the ReS$_2$/WS$_2$-based planar memristor. (b) $I$-$V$ curves of the memristor at the gate voltages of 3 V, 4 V and 5 V. (c) Schematic diagrams of the resistive switching mechanism of the ReS$_2$/WS$_2$-based planar memristor.
Figure 4

Synaptic functions of the ReS$_2$/WS$_2$-based planar memristor. (a) Schematic demonstration of presynaptic and postsynaptic neuron-based synaptic functions. (b) The effect of pulse width and interval changing simultaneously on device conductance modulation. (c-e) Impact of different widths, intervals and amplitudes on device conductance modulation. (f) PPF ratio as a function of two sequential pulse interval. (g) Impact of different luminous powers on the $V_{\text{set}}$ of ReS$_2$/WS$_2$-based and ReS$_2$-based devices under 532 nm and 690 nm lasers, respectively. (h) Relationship between conductance and luminous power for ReS$_2$/WS$_2$-based device at 1 s pulse width and interval. (i) Time required for current stabilization under different luminous powers for ReS$_2$/WS$_2$-based device at 3 s pulse width and interval.
Figure 5

Schematic diagram and band structure evolution of the ReS$_2$/WS$_2$ heterostructure under different luminous.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryInformation.docx