Black Phosphorus Based Multicolor Light-Modulated Transparent Memristor with Enhanced Resistive Switching Performance

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ABSTRACT: Light-modulated transparent memristors combining photoresponse and data storage are promising as multifunctional devices. Herein, a multicolor light-modulated transparent memristor based on black phosphorous (BP) is designed, fabricated, and investigated. BP is a class of emerging two-dimensional (2D) materials with a natural direct band gap and a broad light absorption. Herein, BP nanosheets (BP@PS NSs) coated with polystyrene (PS) are prepared and serve as the resistive switching (RS) layer in the ITO/BP@PS/ITO memristor, which shows >75% transmittance between 350 and 1100 nm. With the aid of PS, the BP@PS-based memristor has excellent RS characteristics such as no initial preforming, low operating voltage, and long retention time. According to the energy band model, the RS mechanism of the high and low resistance states contributes to the transformation from ohmic contact to Schottky contact. During light illumination ranging from ultraviolet (380 nm) to near infrared (785 nm), the Schottky barrier height is elevated further so that the resetting voltages and power consumption decrease. Moreover, the ON/OFF ratios are improved and the maximum enhancement is demonstrated to be more than 10 times. BP is a promising RS material in light-modulated memristors, and the novel device configuration provides insights into the development of multifunctional microelectronic devices based on 2D materials.

KEYWORDS: black phosphorous, memristor, two-dimensional material, light-modulated, resistive switching

1. INTRODUCTION

Spurred by the rapid development of computation and communication technologies, memory devices with high speed and storage capability as well as multifunctional characteristics are essential.1–3 Since scaling of traditional silicon-based microelectronic devices is approaching the end of Moore’s law, new device design and materials are required for advanced memory technology.4,5 Recently, memristors have received widespread attention for the high storage capacity and synaptic-like behavior.6,7 By switching between the low resistance state (LRS) and the high resistance state (HRS) as a means to store data,8 memristors can deliver better performance such as smaller power consumption, expanded memory window, and stability.9–12 Among the various forms of external stimulation, light modulation is the most convenient way to discriminate between the different resistance states and achieve multilevel data storage capability.13 In addition, light-modulated memristors can expand the functions of microelectronic devices and simplify the circuitry in optical sensors.14 In fact, the broader the excitation light wavelength, the more diverse are the device functions.15 Transparency is also an emerging requirement for light-modulated memristors in wearable and portable devices,16–18 but multicolor light-modulated transparent memristors are still in the developmental stage.

Two-dimensional (2D) materials with atomic thickness and strong light–matter interactions have attracted enormous interests.19–21 The unique electrical characteristics of 2D materials such as a fast photoresponse and high mobility bode well for light-modulated memristors.22–27 Among the different types of 2D materials, black phosphorous (BP) is especially promising as a resistive switching (RS) layer in memristors due to the unique structure, natural direct band gap, broad light absorption range, and high carrier mobility.28–30 Recently, BP and BP-based hybrid systems such as ZnO/BP have been applied to memristors,31,32 but these devices are not transparent and the underlying mechanism of light-modulated memristors is still not well understood.

In this work, a transparent memristor (ITO/BP@PS/ITO) composed of BP nanosheets (BP@PS NSs) coated with polystyrene (PS) and indium tin oxide (ITO) electrodes is designed and fabricated. The RS behavior and optoelectronic response of the memristor is investigated both without light...
and upon illumination with light ranging from ultraviolet (UV) to near-infrared (NIR) regimes. The RS mechanism based on energy band bending and transport of carriers transport is proposed and discussed. This BP@PS-based memristor with excellent properties has large potential in transparent and wearable electronic devices.

2. RESULTS AND DISCUSSION

Surface modification of BP and fabrication of the transparent memristor are schematically illustrated in Figure 1a,b, respectively. The BP NSs are exfoliated with a liquid-phase probe ultrasonically and mixed with polystyrene (PS) to form the PS-coated BP NSs (BP@PS NSs). To fabricate the BP-based transparent memristor, the BP@PS NSs are spin-coated on the ITO/glass substrate to form a switching layer. The top ITO electrodes with a diameter of 200 μm are evaporated thermally through a shadow mask using a deposition current of 0.2 A·s⁻¹ for 50 min.

Transmission electron microscopy (TEM) is employed to examine the morphology of the BP@PS NSs. As shown in Figure 2a,b, the lateral size of the BP@PS NSs ranges from 200 to 500 nm similar to that of the uncoated BP NSs (Figure S1). The high-resolution TEM (HR-TEM) image inset in Figure 2b shows a lattice spacing of 0.190 nm corresponding to the (040) plane of BP. The atomic force microscopy (AFM) graph is conducted to characterize the thickness of BP NSs. As shown in Figure S2, the thickness of BP NSs ranges from 10 to 20 nm. The X-ray diffraction (XRD) spectrum of the BP@PS NSs (Figure 2c) reveals the (020), (040), and (060) planes of BP as well as the (210) and (220) planes of PS. The results corroborate successful combination of BP NSs and PS. The Raman spectroscopy (Figure S3) shows that no new peaks appear after adding PS to BP NSs. Considering that polystyrene (PS) has a long and stable chain, we assume that only simple physical adsorption interaction exists between BP and PS. As the memristor array has a ITO/BP@PS/ITO architecture, the transmission spectrum is acquired from an area of 1 × 2 cm². Owing to the thin structure of BP@PS NSs, the device exhibits nearly 75% transmission in the UV region and 80% transmission in the visible and NIR regimes (Figure 2d). The inset photograph in Figure 2d corroborates successful preparation of the BP@PS-based transparent memristor.

The electrical transport curves of the BP@PS-based transparent memristor are acquired to evaluate the electronically controlled RS characteristics. As shown in the direct current (DC)−voltage (I−V) curves in Figure 3a, a stable bipolar RS behavior is observed and there is no initial preforming process, which is different from traditional memristors. In the setting process, a passive voltage is applied and the device is switched from the high-resistance state (HRS) to the low-resistance state (LRS) at −0.5 V. In the resetting process at a voltage of 2 V, the device returns to HRS, showing an abruptly reduced current. After repeating RS switching 100 times, no obvious attenuation is observed from the BP@PS memristor. In contrast, the device consisting of unmodified BP shows poor stability, as shown in Figure 3b. The maximum ON/OFF ratio of the BP device without PS is 20, and the performance degrades with the increase in switching cycles. The electrical signals degrade obviously with switching cycles due to the ambient instability of bare BP NSs. The ON/OFF ratio of the BP@PS device is nearly 100,
which is five times larger than that of the pure BP device; the BP@PS device also can maintain this performance for a much longer time. Moreover, different BP/PS ratios are also taken, including 1:2, 2:1, etc. As shown in Figure S4a, when the ratio is 1:2, the ON/OFF ratio is lower than 10 and the memristors cannot be repeated many times. When the ratio is 2:1 (Figure S4b), the stability of the device is poor. Therefore, the most suitable ratio is 1:1, which indicates that overfull or less PS admixture will reduce the device performance. These comparisons disclose that PS modification enhances the stability of the BP NSs RS layer. Considering that ITO/PS/ITO has almost no RS ability (Figure S6), the main function of the PS coating is to prevent the oxidation of the BP NSs and adjust the subsequent resistance. In comparison, a double-layer structure is designed by directly spinning a PS layer on a BP layer, but the final film is not uniform (insert graph in Figure S7) and exhibits almost no performance enhancement. These results suggest that the PS needs to be first coated on BP nanosheets, and a suitable PS not only provides protection but can also allows the conductive nanosheets, and a suitable PS not only provides protection but also contributes to the high ON/OFF ratio and good RS ability, the ON/OFF ratio and switching voltage need improvement. As shown in Figure 4a, light illumination modulates the RS characteristics of the BP@PS memristor.

To investigate the light-modulated characteristics, three different light sources, namely, 380 nm (UV), 500 nm (green), and 785 nm (NIR), are employed separately to acquire the $I$–$V$ curves under simultaneous electrical and optical stimulations (Figure 4b). First, the device switches from LRS to HRS when the positive sweeping voltage reaches the resetting voltage. Second, the device returns to HRS when the negative voltage reaches the setting voltage. In the positive voltage sweep, the reset voltages decrease to 1.8, 1.6, and 1.26 V upon illumination with light with wavelengths of 785, 500, and 380 nm, respectively. The ON/OFF ratios also exhibit a similar enhancement trend (Figure 4b) and so the memory storage window can be expanded by light irradiation. The setting and resetting voltages depend on the wavelengths, as shown in Figure 4c. The setting voltages remain the same for different wavelengths, but the resetting voltages exhibit a positive correlation with the wavelengths with the average resetting voltages reduced to 1.7 V (785 nm), 1.45 V (500 nm), and 1.17 V (380 nm), respectively. The power consumption during the operation of ITO/BP@PS/ITO can be reduced by 50% upon 380 nm UV illumination. All in all, UV light causes the biggest change in the resetting voltage and power consumption without degrading the active layer (Figure S8), whereas a longer wavelength introduces small effects. The wavelength dependence trend is consistent with the light absorption characteristics of BP.38–40 As shown in Figure 4d, the ON/OFF ratios increase to $1.66 \times 10^2$ (785 nm), $2.85 \times 10^2$ (500 nm), and $1.52 \times 10^3$ (380 nm) and the memory window is expanded obviously by decreasing the wavelength. The results demonstrate that light illumination modulates the resetting voltages, power consumption, and memory window simultaneously, but these improvements cannot be accomplished by electrical modulation directly. Besides, the white-light irradiation also has been tried to modulate the device performance. As shown in Figure S9, the $V_{\text{reset}}$ voltage shows obvious reduction and the ON/OFF radio also increases after applying the white light.

To elucidate the mechanism of light modulation, the $I$–$V$ curves are fitted and the temperature dependence is monitored. As shown in Figure 5a, there is a linear relationship between $\ln(I)$ and $\ln(V)$ in the $I$–$V$ curve of LRS with a slope of 1. It corresponds to ohmic conduction between the BP@PS and ITO electrode and is the predominant current conduction mechanism in the memristor for LRS.36 As shown by the $I$–$V$ curve of the memristor in the HRS mode in Figure 5b, a linear relationship between $\ln(I)$ and square root of the applied voltage ($V^1/2$) is observed and the slope is 3.1, indicating a Schottky emission conduction mechanism. This behavior is related to the energy barrier between the BP and ITO electrode

$$J = A_{\text{eff}} T^2 \exp \left(-\frac{\varphi_b - \sqrt{qE/4\pi\epsilon_r}}{kT}\right)$$

where $A_{\text{eff}}$ is the effective Richardson constant, $\varphi_b$ is the barrier height, and $\epsilon_r$ is the dielectric permittivity. By multiplying the above formula by the electrode area to get the current and taking the logarithms on both sides to get the relationship between current and voltage, we get

$$\ln\left(\frac{I}{T^2}\right) = \frac{q\sqrt{q/\pi\epsilon_r \alpha}}{kT} \sqrt{V} - \frac{q\varphi_b}{kT}$$

where $\alpha$ is the effective Richardson constant.
where \( \ln(I) \) is proportional to \( (V)^{1/2} \) at a certain temperature and the intercept is proportional to \( \phi_B \).

To further verify the Schottky emission conduction mechanism, experiments are performed to determine the temperature dependence. Figure S11 shows a linearly increasing tendency with temperature from 300 to 340 K, and Figure 5c reveals the linear relationship between \( \ln(I/T^2) \) and \( 1000/T \), consistent with the Schottky emission conduction mechanism.\(^{41}\) The \( I-V \) curves of the light-modulated HRS mode are fitted to further explore the conduction mechanism. As shown in Figure 5d–f, the conduction mechanism of light-modulated HRSs is also dominated by Schottky emission conduction. Moreover, the absolute value of the intercept increases with decreasing light wavelength, the shorter wavelength light causes BP to produce more photogenerated carriers and further cause greater band bending, resulting in a larger Schottky barrier.

Since the BP and PS both are not phase-change materials and there is no metal material in the switching layer, the oxygen vacancy conductive filament model is speculated. During the liquid exfoliation, the BP adsorbs little oxygen (Figure S11). As a result, in the switching process, the oxygen ions migrate and form oxygen vacancy conductive filaments. Similar phenomena have also been reported in BP-based memristors.\(^{30,42}\) Because the oxygen vacancy plays a vital role, overfull oxygen vacancy will destroy the device performance and cause a complete failure. Afterward, an energy band model is proposed to explain the light-modulated RS properties of the BP@PS-based memristor. Owing to the different work functions of BP and ITO,\(^{35,44}\) electrons are transferred from the BP@PS active layer to the ITO electrode. As a result, the BP layer becomes positively charged and the ITO is negatively charged, consequently inducing an internal electric field between the BP@PS layer and the ITO electrode. It influences the surface potential of the BP@PS layer and bends the surface energy band upward. As shown in Figure 6a, in the LRS operation, the upward band leads to an ohmic contact between the p-type BP@PS and the ITO substrate consistent with the fitted results in Figure 5a. When a positive voltage is applied to the ITO electrode in the dark in the HRS operation, the external electric field changes the direction of the internal electrical field. As shown in Figure 6b, the energy band of the BP@PS bends downward and therefore a Schottky barrier is formed between the BP@PS layer and the ITO electrode. It is also in line with the fitted results in Figure 5b. When the memristor is exposed to light, the extrinsic trapping sites capture the photogenerated electrons and the surface potential increases. As shown in Figure 6c, the energy band of the BP@PS bends downward more extensively, while the Schottky barrier increases, thereby giving rise to a bigger ON/OFF ratio. Meanwhile, as the scattering centers are negatively charged by the captured photogenerated electrons, the internal electric field goes up. Then, the memristor can be switched off by a smaller external voltage and the resetting voltage decreases correspondingly. Using a shorter wavelength, a larger amount of photogenerated carriers is captured by the trapping sites and the Schottky barrier increases consequently, explaining the RS characteristics of the BP@PS memristor. It should be noted that if a resonant wavelength is applied, the performance may be better.\(^{45-47}\)

**Figure 5.** \( I-V \) curves of the BP@PS memristor: (a) fitted results of LRS in the dark; (b) fitted results of HRS in the dark; (c) linear relationship between \( \ln(I/T^2) \) and \( 1000/T \) of HRS in the dark; and fitted results of HRS upon illumination with (d) 785 nm, (e) 500 nm, and (f) 380 nm light.

**Figure 6.** Energy band model explaining the RS mechanism: (a) energy band diagram showing the ohmic contact for LRS; (b) energy band diagram of the Schottky contact for HRS in the dark; and (c) energy bands of the Schottky contact for HRS under light illumination.
3. CONCLUSIONS

A multicolor light-modulated transparent memristor composed of BP@PS NSs and ITO electrodes is designed, fabricated, and demonstrated. The virtues of the ITO/BP@PS/ITO device include no initial preforming, small operation voltage of ~0.5 V, and high ON/OFF ratio of ~10^4 as well as long retention time of ~10^4 s at an operating temperature of 85 °C. Conductive current from LRS to HRS is explained by the ohmic contact to the Schottky contact mechanism. The properties of the memristor is improved by light illumination ranging between UV (380 nm) and NIR (785 nm). Both the resetting voltage and the power consumption are reduced, and the ON/OFF ratio is increased by 10 times. The RS improvement stems from the fact that the capture of photogenerated electrons by trapping sites consequently increases the Schottky barrier height. The BP-based transparent memristor has excellent properties, and light modulation introduces a new strategy to improve the performance of devices under concerted electrical and optical stimulations.

4. EXPERIMENTAL SECTION

The experiments and methods are described in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c04493.

Experimental section; materials, methods, preparation of BP@PS nanosheets (BP@PS NSs), fabrication of transparent ITO/BP@PS/ITO memristor, characterization, and electronic and photoelectronic measurements; SEM/AFM images; Raman spectroscopy of BP NSs; and XPS core-level spectrum of P2p on the BP@PS (PDF)

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Author Contributions
Y.Z. and D.L. contributed equally.

Notes


Supporting Information

A Black Phosphorus Based Multi-Color Light-Modulated Transparent Memristor with Enhanced Resistive Switching Performance

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Experimental Section

1. Materials

The black phosphorus (BP) dispersion was obtained from Mophos (www.Mophos.cn) and stored in a dark Ar glove box. Acetone, ethanol, and polystyrene (PS) were acquired from Aladdin.

2. Methods

2.1 Preparation of BP@PS nanosheets (BP@PS NSs)

The purchased BP dispersion was centrifuged at 7,000 and 120,000 rpm for 10 min to collect the BP nanosheets (BP NSs). PS was dissolved in chloroform (1 mg/mL) and mixed with the BP NSs ultrasonically with a volume ratio of 1:1. The BP@PS NSs were then centrifuged and collected.
2.2 Fabrication of transparent ITO/BP@PS/ITO memristor

Indium tin oxide (ITO)/glass substrates with 200 nm thick ITO were used to fabricate the transparent memristors. The substrates were sequentially ultrasonicated in acetone, ethanol, and deionized water for 10 min each and exposed to UV/ozone for 15 min. The solution of BP@PS NSs was put on the substrates, spin-coated at 1,000 rpm for 40 s, and annealed at 60 °C in a glove box. The top ITO electrodes with a diameter of 200 µm and thickness of 60 nm were evaporated thermally on the BP@PS films through a shadow mask at a deposition rate at 0.2 A·s⁻¹ for 50 min.

2.3 Characterization

The high-resolution scanning electron microscopy (HR-SEM) images were acquired on the Zeiss Supra 55 and transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) spectra were obtained on the Tecnai G2 F20 S-Twin (FEI, America). Atomic Force Microscope (AFM) topography imaging was conducted on the Asylum Research Cypher S. X-ray diffraction (XRD) was performed on the Rigaku Smartlab 3 kW X-ray diffractometer. Raman scattering was performed on the Horiba Jobin-Yvon Lab Ram HR VIS high-resolution confocal Raman microscope. and the transmission spectra were acquired on the Shimazu UV-2450 spectrophotometer. The binding energies were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi XPS).
Electronic and photoelectronic measurements

The current-voltage (I-V) measurements were conducted with the Keysight B2912A digital source-meter and optoelectronic characteristics of the memristors were determined using the Agilent B1500A semiconductor parameter analyzer under ambient conditions. Considering the switching speed of same device usually is near a consistent, the power consumptions at different conditions are approximated by multiplying reset voltage \( V_{\text{reset}} \) and the corresponded current. The voltages were applied to the top ITO electrodes and the bottom ITO electrode was grounded.
Figure S1. SEM image of BP NSs.
Figure S2. (a) AFM image of BP NSs. (b) The height of BP NSs corresponding to Figure S2(a).
Figure S3. The Raman Spectroscopy of BP and BP@PS.
Figure S4. I-V curves of the ITO/BP@PS/ITO device with different ratio of BP and PS.

(a) BP:PS is 1:2. (b) BP:PS is 2:1.
**Figure S5.** I-V characteristics of the ITO/PS/ITO device.
Figure S6. The ITO/BP@PS/ITO device performance for different spinning times. (a) I-V curve. (b) Distributions of HRS and LRS.
Figure S7. I-V curves of the BP/PS double-layer memristor
Figure S8. (a) SEM image of active materials before UV light; (b) SEM image of active materials after UV light for 2 hours; (c) Raman spectroscopy of active materials before and
after UV light; (d) I-V curves of the BP@PS memristor after UV light for 2 hours.

The ITO/BP@PS/ITO memristors were manufactured to evaluate the effect of UV light on the degradation of the active materials (Figure S8). After conducted by UV light 2h, the ITO/BP@PS/ITO memristors conducted by UV light 2h shows unchanged Raman peak and SEM images. Moreover, the device performs no obvious degradation after applying UV light for 2 hours (control sample is corresponded to the I-V curve of UV light in Figure 4b). Above results exhibits that UV light would not accelerate the degradation of the active materials due to the complete PS coating on BP.
Figure S9.  I-V curves of the BP@PS memristor modulated by white light.
Figure S10.  HRS I-V curves at different temperature.
Figure S11. The XPS core-level spectrum of P2p on the BP@PS.