Positive and Negative Photoconductivity Conversion Induced by H$_2$O Molecule Adsorption in WO$_3$ Nanowire

Yahui Liu, Peng Fu, Yanling Yin, Yuehua Peng, Wenjun Yang, Gang Zhao, Weike Wang, Weichang Zhou and Dongsheng Tang *

Abstract

Negative photoconductivity effect has been observed in the Au/WO$_3$ nanowire/Au devices in a high humidity environment, which might be attributed to the accumulation of H$^+$ ions on the surface of WO$_3$ nanowire. Under illumination with violet light (445 nm), the photo-excited holes can oxidize the adsorbed H$_2$O molecules to produce H$^+$ ions and O$_2$, while the photo-excited electrons at the conduction band bottom do not have enough energy to reduce H$^+$ ions. These H$^+$ ions will accumulate on the surface of the hexagonal WO$_3$ nanowire. They will capture mobile electrons and then reduce the concentration of carriers, which will result in a significant increase in the height of interface barrier and then a significant decrease in the conductance of the Au/h-WO$_3$ nanowire/Au device. By adjusting the relative humidity, light intensity, or bias voltage, the concentration and distribution of H$^+$ ions and then the conversion between positive and negative photoconductivity, as well as resistive switching properties, can be well regulated in this kind of devices.

Keywords: Hexagonal WO$_3$ nanowire, Negative photoconductivity, Positive photoconductivity, Hydrogen ion, Schottky emission

Introduction

Tungsten oxide (WO$_3$) exhibits excellent photo-(electro-, gas-, thermo-)chromic properties and resistive switching behaviors [1–13], which might be attributed to its distinctive crystal and electronic band structures. WO$_3$ is constructed from WO$_6$ octahedra by sharing the equatorial oxygen atoms, which leaves more empty interstices in the oxygen sub-lattice. As a result, WO$_3$ can accommodate external species such as hydrogen ions and alkali metal ions into its solid framework to form stable nonstoichiometric intercalation compounds with the color from yellowish green to gold and the conductivity from insulator to metal. Meanwhile, the bottom of the conduction band of WO$_3$ lies below the hydrogen ion reduction level, while the top of the valence band lies above the level of H$_2$O molecular oxidation. Therefore, H$_2$O molecules adsorbed on the surface of WO$_3$ can be oxidized to produce hydrogen ions (H$^+$ ions) and O$_2$ by the excited or injected holes at the top of the valence band, while H$^+$ ions cannot be reduced by electrons at the bottom of the conduction band. Generally speaking, the coloring or resistive switching of WO$_3$ in atmospheric environment under external excitation such as illumination and bias voltage can be attributed to the H$^+$ ions embedded in the lattice [14, 15].

Therefore, it is possible to manipulate the optical and resistive switching properties of WO$_3$ by regulating the transport and distribution of H$^+$ ions in the lattice or on the surface of WO$_3$. Single crystalline hexagonal WO$_3$ nanowire (h-WO$_3$ NW) possessing large specific surface area and conductive channel might be an ideal platform for studying the effect of the H$^+$ ions produced by H$_2$O oxidation. In our previous work, the single-crystalline h-WO$_3$ NWs grown along the c direction do exhibit memristive effect or resistive switching phenomenon, which can be enhanced remarkably and even regulated by...
the H\(^+\) ions produced by the oxidation of the adsorbed H\(_2\)O molecules [16–19].

In this letter, we explored the photoconductivity of h-WO\(_3\) NW under different relative humidity and found that the positive photoconductivity (PPC) effect is always accompanied by negative photoconductivity (NPC) effect in a high relative humidity environment. By adjusting the relative humidity, light intensity, or bias voltage, it is possible to manipulate the creation, distribution, and annihilation of H\(^+\) ion on the surface of WO\(_3\) and then regulate the concentration of carriers in the WO\(_3\) nanowire and the height of the interface barrier.

**Methods**

**WO\(_3\) Nanowire Synthesis**

The h-WO\(_3\) nanowires used in this investigation were synthesized using a simple hydrothermal method as previously reported [20, 21]. In a typical synthesis, 8.25 g sodium tungstate (Na\(_2\)WO\(_4\)*2H\(_2\)O) was dissolved in 250 mL deionized water. Hydrochloric acid (HCl, 3 M) was used to adjust the pH value of the Na\(_2\)WO\(_4\) solution to 1.2. After being filtered, the precipitate was washed sequentially with deionized water and ethanol to remove contaminant ions and then dispersed in 200 mL citric acid (C\(_6\)H\(_8\)O\(_7\), 0.1 M) to form a translucent homogeneous and stable WO\(_3\) sol. A 45-mL volume of WO\(_3\) sol was transferred into a 50-mL autoclave, and then 1.3 g potassium sulfate (K\(_2\)SO\(_4\)) was added to the sol. The autoclave was sealed and maintained at 240 °C for 32 h, and then cooled down to room temperature. The precipitates in the solution were filtered, washed sequentially with deionized water and ethanol to remove possible remnant ions, and then dried at 60 °C.

**Device Fabrication**

The individual h-WO\(_3\) nanowire-based devices were fabricated on heavily n-doped Si substrate covered with a 100 nm thick thermally grown SiO\(_2\) layer. Electrodes were

![Fig. 1 Typical I-T curves (V\(_{ds}\) = 3 V) of an Au/h-WO\(_3\) NW/Au device recorded repeatedly with laser (445 nm, 500 mW) on and off under 40%RH (a), 50% RH (b), 60% RH (c), and 70% RH (d). The lower inset of a: SEM image of an Au/h-WO\(_3\) NW/Au device, the nanowire between two electrodes with a diameter of about 300 nm, and a length of about 4 μm.](image-url)
defined on the Si substrate with WO₃ nanowires by using a standard photo-lithography technique (ABM, Inc., San Jose, CA (405)) and formed by metal deposition (100-nm-thick Au) and a lift-off process.

**Electrical Measurement**

Electrical transport measurements were conducted on a probe station at room temperature by using semiconductor characterization systems (Keithley 2602). The probe station is placed in a homemade vacuum chamber, which is firstly vacuumized to a base pressure less than 10⁻¹ Pa by a mechanical pump. The relative humidity (RH) in the environment was adjusted by evaporation of deionized H₂O and a dehumidifier. The accuracy of the humidity sensor used in our experiments was about ± 1%.

**Results and Discussion**

Figure 1 shows the typical current-time (I-T) curves of an Au/h-WO₃ NW/Au device recorded with laser (445 nm, 500 mW) on and off under different RH levels. When the RH is 40% (Fig. 1a), the current rises slightly under illumination, which is the normal PPC due to the inter-band transition [22, 23]. As the RH increases to 50% (Fig. 1b), the current rises slightly when the laser is turned on. And then, after about 10 s, the photocurrent drops significantly, namely the intriguing NPC effect. With increasing the RH gradually, the device exhibits the more excellent and stable NPC as shown in Fig. 1c, d. The NPC effect has been reported in some nanomaterials [24–26], but never been observed in WO₃. Preliminarily, the NPC effect of WO₃ nanowire might be attributed to the adsorbed H₂O molecules on the surface. After all, H₂O molecule adsorption and photo-desorption have been proved to play an important role in determining the photoelectric properties and lead to NPC effect in nanoscale materials [27–29]. It means that the conductance of these nanoscale materials depend sensitively on the amount of adsorbed H₂O molecules. However, unlike the photocurrents, the dark currents recorded under the different RH levels are almost the same (80 nA) as shown in the Fig. 1, which proves that the changes in the photocurrents under different RH levels cannot simply be attributed to photo-induced desorption H₂O molecules. Therefore, there is a new physical mechanism answering for the NPC effect of the h-WO₃ NW. In addition, the dark current in Fig. 1d is slightly larger than 80 nA. When the RH is very high, more H₂O molecules are adsorbed on the WO₃ NW and can form the H₂O film on the surface of WO₃. And this layer of water molecule can increase the conductance of the device based on the Grothuss mechanism [30]. Therefore, the dark current in Fig. 1d increases slightly.

To elucidate the origins of the NPC, the involving conductive mechanism needs to be determined firstly. As shown in the inset of Fig. 2a, the typical current-voltage (I-V) curve is recorded with the bias voltage scanning and the laser on and off under the 70% RH, which indicates NPC effect as well as resistive switching. For the purpose of making an obvious contrast, the I-V curves were...
converted to the $I$-$T$ curves as displayed in Fig. 2a and replotted based on the Schottky law ($\ln I \propto V^{1/2}$) [31]. For both photocurrent and dark current, $\ln I$ is linear with $V^{1/2}$ under high bias voltage. The conduction mechanisms for both cases are Schottky emission and barrier height which can be obtained from the intercept of the Schottky plot. The Schottky barrier under light illumination is much higher than that in dark environment as indicated by the green intercepts in Fig. 2b. Therefore, the NPC effect of the h-WO$_3$ NW might be attributed to the increase of the Schottky barrier height induced by violet light illumination. As previously reported [15], the resistive switching properties this kind of devices has can be enhanced remarkably by adsorbed H$_2$O molecules. In that situation, the holes injected from the positively charged electrode oxidize the adsorbed H$_2$O molecules producing H$^+$ ions and O$_2$, while the electrons injected from the negatively charged electrode under small bias voltage do not have enough energy to reduce H$^+$ ions because of the peculiar electronic band structure of WO$_3$. The H$^+$ ions produced by H$_2$O oxidation will accumulate gradually on the surface under continuous bias scanning, which will deplete all mobile electrons in the WO$_3$ nanowire. Therefore, under illumination with violet light (445 nm), the photo-excited holes can also oxidize the adsorbed H$_2$O molecules to produce H$^+$ ions. The only difference is that the H$^+$ ions are produced and accumulated faster, which prevents H$^+$ ions from entering the lattice of WO$_3$ NW more easily to transform it into a metallic state. They will capture mobile electrons to form the electric double-layer and then reduce the concentration of carriers as shown in Fig. 2c, which will result in a significant increase in the height of interface barrier and then a significant decrease in the conductance of the Au/h-WO$_3$ NW/Au device. If the RH level is low (less than 50%), there are less than two H$_2$O molecular layers on the surface, and the amount of H$^+$ ions produced by water oxidation is relatively small. Furthermore, H$^+$ ions cannot move freely in the discontinuous layers of H$_2$O molecules to accumulate near the negatively charged electrode. Accordingly the ability of

![Typical $I$-$T$ curves ($V_{ds}=3\,\text{V}$) of an Au/h-WO$_3$ NW/Au device recorded repeatedly with laser (445 nm, 200 mW (a), 400 mW (b), 500 mW (c), and 600 mW (d)) on and off at 70% RH. The right inset of (a): the $I$-$T$ curves of 300 mW. The four schematic insets showing the effect of H$^+$ ions under different laser powers](image-url)
localizing mobile electrons is weak or even negligible, and then the device exhibits the PPC effect (Fig. 1a).

To further investigate the origin of the NPC effect and confirm the reasonableness of the above mechanism, the power-dependent $I-T$ measurements were carried out systematically as shown in the Fig. 3. When the power of the laser is set at 200 mW, the device exhibits stable PPC effect under illumination (Fig. 3a). As the power increases to 300 mW, some traces of NPC can be clearly observed (the right inset of Fig. 3a). With further increasing laser power from 300 to 400 mW and 500 mW, the current rises quickly at first seconds under illumination exhibiting the PPC effect, and then drops suddenly exhibiting the NPC effect (Fig. 3b, c). Upon switching off the light source, the current does not change significantly until it increases to initial value rapidly after more than 20s. It is clear that the current increases more significantly and drops more quickly with the light intensity increasing, which might be attributed to the rate of hydrogen ion production and aggregation proportional to the light intensity. When the light intensity is weak (less than 200 mW), the efficiency of inter-band transition is very low, and then the generated H$^+$ ions are negligible or reduced by hot electrons. When the light intensity is strong, the concentration of carriers (electrons and holes) increases abruptly upon illumination, and then there is the generation and aggregation of hydrogen ions. The conversion from PPC to NPC can be well explained by the process of H$^+$ ion accumulation on the surface. When the laser power further increases to 600 mW (Fig. 3d), the photocurrent fluctuates drastically, which might be attributed to the competition between the production and reduction of H$^+$ ions. The efficiency of the inter-band transition is so high that the adsorbed H$_2$O molecules are consumed fast and cannot be supplied just in time. After all, it takes a certain time for the H$_2$O molecules in atmosphere to relax onto the h-WO$_3$ NW surface. From the above analysis, we concluded that the productivity of H$^+$ ions is dependent on the efficiency of inter-band transition. When the power of laser is low, the efficiency of inter-band transition is relatively low, and it will take more time to produce enough H$^+$ ions to achieve the conversion from PPC to NPC.

**Fig. 4** Typical $I-T$ curves of a device recorded on different biases (2 V (a), 3 V (b), 4 V (c)) with laser (445 nm, 500 mW) on and off at 50% RH. d Schematic band structures of the Au/h-WO$_3$ NW/Au device under different bias voltages and the non-ballistic transport of the injected electrons.
effect. In contrast, when the power becomes larger, it will take shorter time to achieve this kind of conversion.

To further study the regulation of H⁺ ions and then the conversion between the PPC and NPC effect of the h-WO₃ NWs, the typical I-T curves of an Au/h-WO₃ NW/Au device were measured under different bias voltages as shown in Fig. 4. In this part, the RH level is set at 50%, because the amount of the adsorbed H₂O molecules is not so much that the effect of the bias voltages might be more obvious. When the bias voltage is 2 V, the NPC in the WO₃ nanowire is very stable under illumination (445 nm, 500 mW) as shown in Fig. 4a. However, with the bias voltage increasing, the I-T curves become more fluctuated as displayed in the Fig. 3b, c). Meanwhile, it also indicates that it takes less time to achieve the conversion from PPC to NPC effect under the small bias voltage. In addition, when the light was switched off, the current decreases a little at first because the photo-excited electrons and holes preferentially recombine as shown in Fig. 4, which is similar to the cases in InN thin film [32] and InAs nanowire [33]. To comprehend this phenomenon completely, the electronic band structure of the Au/h-WO₃ NW/Au device is shown in the Fig. 4d, which bends gradually with bias voltage increasing. Though the H⁺ ion reduction level lies slightly higher than the bottom of the conduction band of the WO₃ NW, the number of the hot electrons above the H⁺ ions reduction level injected from the negatively charged electrode based on Schottky emission might be large enough as long as the bias is large enough. These hot electrons exist only near the negatively charged electrode due to their non-ballistic transport behavior and will reduce the accumulated H⁺ ions quickly. As the H⁺ ions disappear, the height of the Schottky barrier decreases, and the voltage dropping on the barrier decreases accordingly. The number of the hot electrons above the H⁺ ion reduction level decreases correspondingly, which will lead to the accumulation of H⁺ ions again. Therefore, for the relatively long h-WO₃ NW, it is reasonable to consider that the H⁺ ions accumulate and are reduced by hot electrons alternatively, which results in current fluctuating as shown in Fig. 4c.

Conclusions
In summary, we have systematically investigated the photoelectric properties of the Au/h-WO₃ NW/Au devices. The experimental results indicate that the h-WO₃ NW presents excellent and stable NPC effect under high RH, moderate laser power, and small bias voltage. This is because the H⁺ ions produced by H₂O oxidation on the surface of h-WO₃ NW will capture mobile electrons and then reduce the concentration of carriers and will result in a significant increase in the height of interface barrier of the Au/h-WO₃ NW/Au device. By adjusting the relative humidity, light intensity, or bias voltage, the concentration and distribution of H⁺ ions and then the conversion between positive and negative photoconductivity can be well regulated in this kind of devices. This work might help to better understand the behavior of H⁺ ions and offer a new possibility to regulate the optical and resistive switching properties of WO₃.

Abbreviations
Au: Aurum; H⁺ ions: Hydrogen ions; h-WO₃: Hexagonal tungsten trioxide; I-T: Current-time; I-V: Current-voltage; NPC: Negative photoconductivity; NW: Nanowire; PPC: Positive photoconductivity; RH: Relative humidity

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Availability of Data and Materials
The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Authors’ Contributions
YHL and PF performed the experiments and drafted the manuscript with the help of YL, YHP, WI, GZ, WK, and WC. DS participated in the design of the study and helped to draft and revised the manuscript. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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