

Research article

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Porous Ag/TiO₂-Schottky-diode based plasmonic hot-electron photodetector with high detectivity and fast response

<https://doi.org/10.1515/nanoph-2019-0094>

Received March 27, 2019; revised May 13, 2019; accepted May 15, 2019

Abstract: Due to the advantages of narrow energy distribution of plasmonic hot-electrons in Ag and the high density of states in the TiO₂ conduction band, an Ag/TiO₂ composite is considered to be an ideal combination to construct a plasmonic hot-electron photodetector with high detectivity and a high response speed. In this work, we fabricate a porous Ag/TiO₂-Schottky-diode based plasmonic hot-electron photodetector. This detector shows a high detectivity of 9.8×10^{10} cmHz^{1/2}/W and a fast response speed, with a rise and fall time of 112 μs and 24 μs, respectively, under 450 nm light illumination at zero bias voltage. In addition, the height of the Ag/TiO₂ Schottky barrier can be decreased by removing the chemisorbed oxygen from the surface of TiO₂ with ultraviolet light illumination, and as a result, the responsivity of the Ag/TiO₂ plasmonic hot-electron photodetector at 450 nm can increase from 3.4 mA/W to 7.4 mA/W.

Keywords: photodetector; plasmonic hot-electron; porous Ag/TiO₂; Schottky junction.

1 Introduction

Plasmonic hot-electrons are highly energetic electrons that are generated in metal in the decay of surface plasmons [1]. The combination of an appropriate plasmonic

metal and semiconductor to form a metal/semiconductor Schottky junction can transform light energy to other forms of energy via the plasmonic hot-electrons, and they have a wide application in photocatalysis [2], photoelectrochemical water splitting [3], photovoltaic conversion [4], photodetection [5–7] and so on. The plasmonic hot-electron photodetector composed of a metal/semiconductor Schottky junction is a new kind of photodetector [8–11] which has the advantages of enabling a response to the photons with energy below the bandgap of the semiconductor substrate and having a tunable spectral response peak by simply adjusting the metal nanostructure [7, 12], therefore attracting a great deal of attention. In the past several years, much effort has been focused on improving the performance of photovoltaic hot-electron photodetectors. With the evolution of the plasmonic metal materials from separated nanorods to integrated nanoporous membranes, the responsivity of the Au/Si photovoltaic hot-electron photodetectors has increased from 8 nA/mW to 8.2 μA/mW in the near-infrared region [7, 13–15]. However, the detectivity and response time of a photovoltaic hot-electron photodetector, which are of more importance than the responsivity in the applications of optical imaging and optical communication [16], have not improved much.

An Ag/TiO₂ Schottky junction is considered to be an ideal material for a plasmonic hot-electron photodetector. On the one hand, although most of the plasmonic hot-electron photodetectors developed recently are based on Au/semiconductor-Schottky-diodes [7, 13–15, 17–20], Ag is considered to be a better plasmonic material than Au due to the higher density of plasmon electric fields [21] and narrower energy distribution of generated hot-electrons in Ag [1], and as a result, it can lead to a higher photoelectric conversion efficiency. On the other hand, TiO₂ is by far the most frequently used electron-accepting material and the high density of states in the TiO₂ conduction band enables fast electron injection [22, 23]. Thus, the hot-electron photodetector based on a Ag/TiO₂ Schottky junction may have high detectivity and a fast response speed. However, the

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fabrication of a Ag/TiO₂ Schottky junction is full of challenges due to the fact that the work function of Ag is too low for Ag to form a Schottky contact with n-type TiO₂ [24], so that the Ag/TiO₂ based hot-electron photodetector has not yet been developed successfully. Recently, our work showed that the chemisorbed oxygen on the surface of TiO₂ can change the surface energy band of TiO₂, which enables the formation of Schottky contact between TiO₂ and Ag [24].

In this work, we synthesized a porous Ag/TiO₂-Schottky-diode based plasmonic hot-electron photodetector, and systematically studied its performance. This photodetector shows a fast response speed with a rise and fall time of 112 μs and 24 μs, respectively, and a high detectivity of 9.8×10^{10} cmHz^{1/2}/W under 450 nm light illumination at zero bias voltage; both of these values are substantially better than those previously reported. By decreasing the Schottky barrier through a long-hours ultraviolet light illumination process, the responsivity of the device at 450 nm increased from 3.4 mA/W to 7.4 mA/W.

2 Experiments

2.1 Device fabrication

The TiO₂ nanoporous membrane was fabricated by electrochemical anodization of Ti foil (Tianmai Titanium Industry Ltd., Baoji, Shaanxi, China) in electrolyte [25]. Before anodization, the Ti foil was degreased by sonication in acetone (Sinopsin Group Chemical Reagent Ltd., Shanghai, China) and ethanol (Sinopsin Group Chemical Reagent Ltd., Shanghai, China) sequentially, and then dried in air. Afterwards, pre-anodization of the Ti foil was carried out in ethylene glycol solutions containing 0.3 wt% NH₄F and 2 vol% H₂O at a constant voltage of 60 V for 2 h at 20°C, and then the formed TiO₂ membrane on the Ti foil was removed by sonication in deionized water, leaving ordered concaves on the Ti foil. Subsequently, the Ti foil with ordered concaves on the surface was anodized again in ethylene glycol solutions containing 0.3 wt% NH₄F (Sinopsin Group Chemical Reagent Ltd., Shanghai, China) and 6 vol% H₂O at a constant voltage of 60 V for 1 min to obtain a thin TiO₂ nanoporous membrane on the Ti foil. After rinsing in ethanol, the TiO₂/Ti foil was annealed at 400°C in air for 3 h to obtain anatase TiO₂ membrane. Finally, the annealed TiO₂/Ti foil was covered with a mask, and then an Ag layer with thickness of about 30 nm was sputtered on it by the sputter coater (Emitech K550x) in a vacuum of 10 Pa at a current of 40 mA for 3 min. Peeling off the mask, a photodetector device with a working area of 28 mm² was obtained.

2.2 Device characterization

The current–voltage (I–V) curves and photocurrent response of the sample were measured by a Keithley semiconductor parameter analyser (4200-SCS, Keithley Instruments Inc., Cleveland, OH, USA) model 4200-SMU with the sample placed in a probe station (TTPX, Lake Shore Cryotronics Inc., Westerville, OH, USA) under a vacuum environment of 6×10^{-4} Pa. A 500 W xenon lamp (GLORIA-X500A, Zolix Inc., Beijing, China) equipped with a monochromator (iHR320, Horiba Inc., Piscataway, NJ, USA) was used as the tunable light source for spectral photoresponse characterization, while tunable power lasers (RD450-1000F3, RD660-1000F3, and RD980-1000F3, Richeng Science & Technology Inc., Xi'an, Shaanxi, China) were used as 450 nm, 660 nm, and 980 nm light sources, respectively, and an LED light (XPE-365nm, Cree Inc., Durham, NC, USA) with a central wavelength of 365 nm was used as the light source for ultraviolet light illumination. An electronic timer (GCI-73, Daheng Science & Technology Inc., Beijing, China) was used to control the switch of the light path to generate the low-frequency (<1 Hz) pulsed light. High-frequency (>1 Hz) pulsed 450 nm light was provided by a pulsed laser (RD450-1000G3, Richeng Science & Technology Inc., Xi'an, Shaanxi, China). The time response of the device to the high-frequency pulsed light was measured by a Keithley semiconductor parameter analyser (Keithley 4200-SCS) model 4200-PMU.

The surface morphology of the sample was characterized by field-emission scanning electron microscopy (SU8020, Hitachi, Ltd., Tokyo, Japan). The crystal structure of the sample was identified by X-ray diffraction using a X-ray diffractometer (Philips X'Pert Pro MPD, PANalytical B.V., Almelo, The Netherlands) equipped with a Cu Kα1 ($\lambda = 0.15406$ nm) radiation source. The optical transmittance was measured using a UV-vis dual-beam spectrophotometer (CARY-5E, Varian Australia Pty Ltd., Mulgrave, Victoria, Australia).

3 Results and discussion

3.1 Porous Ag/TiO₂-Schottky-diode and plasmonic photoelectric response

The porous Ag/TiO₂ photodetector consists of a porous Ag layer, an anatase porous TiO₂ membrane (Figure S1) and a Ti substrate electrode (the inset of Figure 1A). The porous Ag layer can absorb light to generate plasmonic hot-electrons, and the porous TiO₂ membrane is used as

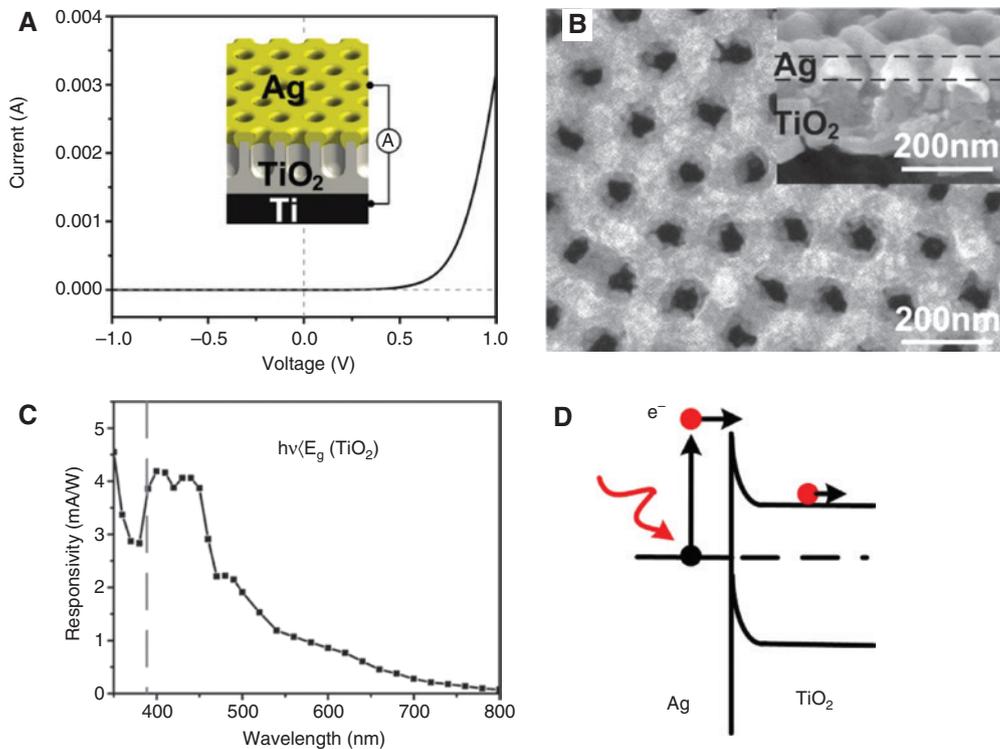


Figure 1: Photodetector structure and plasmonic hot-electron participated photoresponse. (A) Schottky I–V curve of porous Ag/TiO₂ composite film measured in vacuum. (B) Scanning electron microscopy images of the porous Ag/TiO₂ membrane. (C) Spectral responses of the porous Ag/TiO₂ photodetector. (D) Band diagram for the generation of plasmonic hot-electrons photocurrent.

electron-accepting material. The I–V curve of the device exhibited a typical rectifying behavior, proving that the fabricated Ag/TiO₂ heterojunction is a Schottky junction (Figure 1A). The Schottky barrier height was calculated to be 0.83 eV (detailed calculation process refers to Supplementary note and Figure S2). Figure 1B shows scanning electron microscopy images of the porous Ag/TiO₂ membrane; the ordered pores showed a period of 120 nm. In addition, it is clear to see that the thickness of the Ag layer and the TiO₂ membrane were approximately 50 nm and 150 nm, respectively. Due to the low vacuum sputtering condition, the sputtering silver atoms have low collimation, resulting in the sputtering silver atoms mainly reaching the surface of the pores and forming a cap shape coverage.

Such a porous Ag/TiO₂-Schottky-diode is a self-powered plasmonic hot-electron photodetector that can work under zero voltage. The response spectrum of the photodetector ranged from visible to near-infrared with a responsivity peak of 4 mA/W at 440 nm (Figure 1C). Because the energy of the visible light (1.6–3.1 eV for 400–780 nm photons) was lower than the bandgap of anatase TiO₂ (3.17 eV) [24, 26, 27], the photoresponse shown in Figure 1C is

believed to be a plasmon-participating photoresponse, which can be proved by the agreement in wavelength between the photocurrent responsivity peak and surface plasmon resonance peak of the porous Ag/TiO₂ membrane (Figure S3) [14, 24, 28]. Figure 1D illustrates the energy band diagram for the plasmon-participating photoresponse, where incident light excites surface plasmons on the porous Ag layer and some of the plasmons then decay into hot-electrons and holes [29]. The hot-electrons with enough energy will jump across the Schottky barrier at the Ag/TiO₂ interface and then contribute to a detectable photocurrent.

3.2 High detectivity and fast response

Figure 2A shows the photoresponse of the Ag/TiO₂ photodetector to the light with a wavelength of 450 nm at zero bias voltage, where the on-off interval of the light was 30 s. Our device clearly displayed a rapid and stable response to the pulsed light. Furthermore, the photocurrent of the device almost kept a linear relationship with the incident light power (Figure 2B).

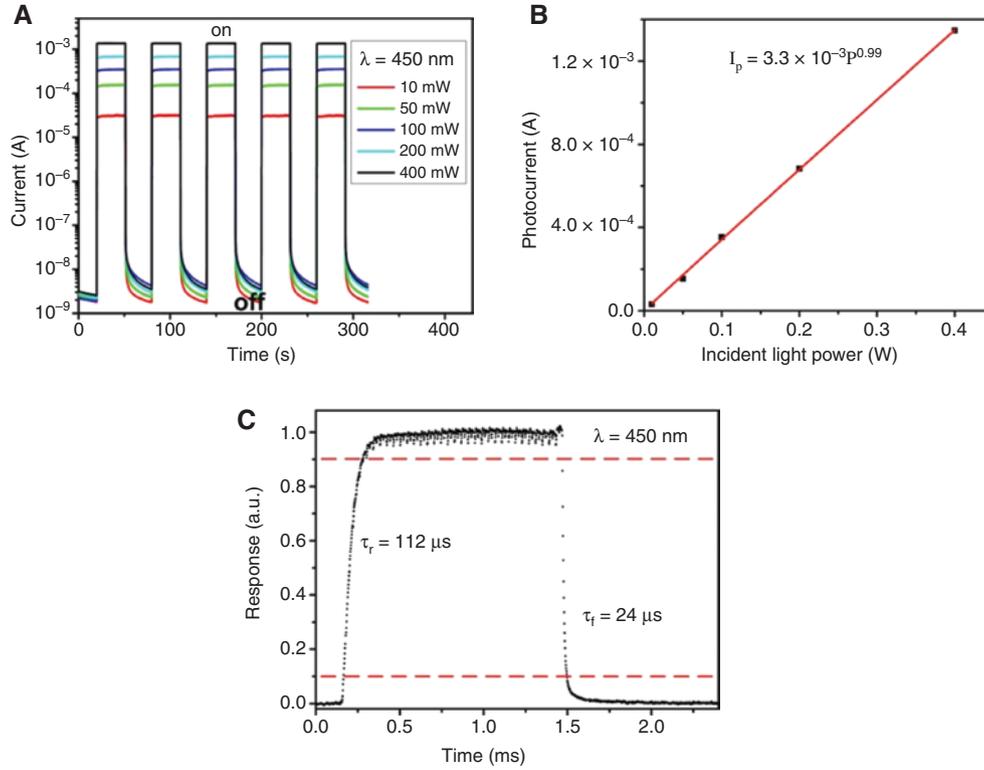


Figure 2: Photocurrent response under 450 nm light illumination.

(A) Response under pulsed light illumination with different power at zero bias voltage. (B) Fitting curve of the relationship between the photocurrent and light power. (C) A single normalized cycle of the photocurrent response.

To quantify the performance of the porous Ag/TiO₂ photodetector, three key metrics, viz., responsivity (R), external quantum efficiency (η) and detectivity (D^*), were calculated by using the following equations [30]:

$$R = I_p / P \quad (1)$$

$$\eta = (I_p / e) / (P / h\nu) = (hc / \lambda e) (I_p / P) \quad (2)$$

$$D^* = S^{1/2} R / (2eI_d)^{1/2} \quad (3)$$

where I_p , P , h , c , λ , e , S and I_d are the photocurrent, incident light power, Planck's constant, speed of light, light wavelength, unit of elementary charge, working area of the photodetector and dark current, respectively. Using the data presented in Figure 2A, we calculated the responsivity R and the external quantum efficiency η to be 3.3 mA/W and 0.91%, respectively; these values are comparable to the results reported for the Si-based hot-electron near-infrared photodetector with R of 3.5 mA/W and η of 0.35% [14]. On the basis of the S value of 28 mm² and the I_d value of 1 nA, the detectivity D^* was estimated to be 9.8×10^{10} cmHz^{1/2}/W.

The minimum detectable light intensity (E_{\min}) is another important metric, which is defined as the incident light intensity when the generated photocurrent (I_p) is equal to the dark current (I_d). As $R = I_p / P$ and $P = E \cdot A$, so $E = I_p / (R \cdot A)$, where I_p , R , P , E , and A are the photocurrent, responsivity, incident light power, incident light intensity, and working area of the photodetector, respectively. When $I_p = I_d$, E_{\min} can be obtained by the equation $E_{\min} = I_p / (R \cdot A) = J_d / R$, where I_d and J_d are the dark current and dark current intensity, respectively. Owing to the current-limiting effect of the Schottky barrier at the Ag/TiO₂ interface, the dark current intensity (J_d) was only 3.6 nA/cm², which contributed to a low E_{\min} of only 1.1×10^{-6} W/cm² that was more superior than other reported photovoltaic plasmonic hot-electron photodetectors [7, 15, 20].

In addition to the aforementioned metrics, the response speed is also a key parameter for practical applications of a photodetector in optical communications and optical switches, which is often evaluated by the rise time (τ_r) and the fall time (τ_f) of its response to a pulsed signal [16, 30, 31], where τ_r and τ_f are always defined as the time intervals required for the photocurrent to rise from 10% to 90% of its peak value (τ_r) and for the response to decay from 90% to 10% of its peak value (τ_f) [30]. As shown in

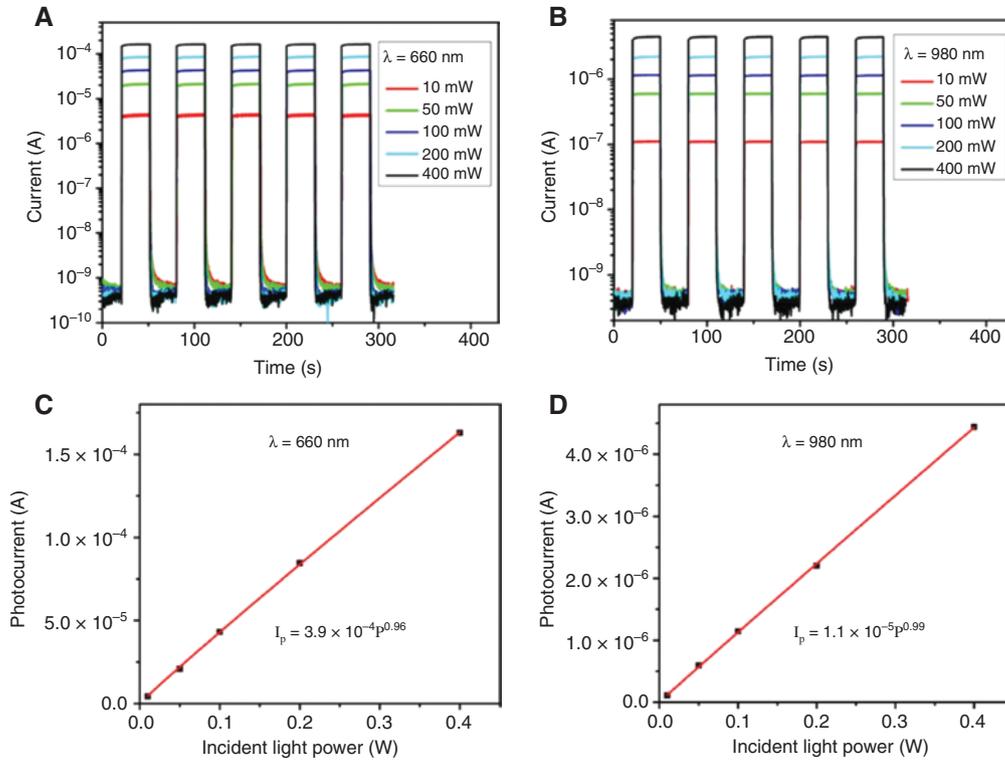


Figure 3: Photoresponse under 660 nm and 980 nm light illumination.

(A) Photocurrent response under 660 nm light illumination. (B) Photocurrent response under 980 nm light illumination. (C) I_p - P curves under 660 nm light illumination. (D) I_p - P curves under 980 nm light illumination.

Table 1: Comparison of the device performance of the present porous Ag/TiO₂ photodetector with other plasmonic hot-electron photodetectors.

Device	R (A/W)	D* (cmHz ^{1/2} /W)	τ_r/τ_f	E_{min} (W/cm ²)	Ref.
Porous Ag/TiO ₂	3.3×10^{-3}	9.8×10^{10}	112/24 μ s	1.1×10^{-6}	This work
Porous Au/Si	3.5×10^{-3}	–	–	–	[14]
Au nanorods/Si	1×10^{-5}	–	–	2.5×10^{-6}	[7]
Au/Pyramid-Si	8.2×10^{-3}	1.8×10^{10}	–	1.5×10^{-3}	[15]
Au/SrTiO ₃ /Si	3.7×10^{-4}	–	~1 ms	1.6×10^{-2}	[20]

Figure 2C, our device shows a fast response speed with τ_r of 112 μ s and τ_f of 24 μ s.

Moreover, the porous Ag/TiO₂ photodetector can also show a good photoresponse in the visible to near-infrared light region far away from the surface plasmon resonance wavelength. The responsivity values of the photodetector at 660 nm and 980 nm were 0.39 mA/W and 11 μ A/W, respectively, and the detectivity values at 660 nm and 980 nm were 1.7×10^{10} cmHz^{1/2}/W and 4.6×10^8 cmHz^{1/2}/W, respectively (Figure 3A and B). These results show that, although the responsivity of the detector decreases sharply with increasing light wavelength, a relatively high detectivity is still maintained owing to the low dark current. In addition, both in the visible light region and in the near-infrared region, the photocurrent of the device increases almost linearly with the light power, and the

linear relationship keeps in a broad light power range (Figure 3C and D).

Table 1 summarizes the key metrics of our device and those of other reported photovoltaic plasmonic hot-electron photodetectors. In previous literature, most attention was focused on the responsivity (R) of the photodetectors, while other key metrics of the hot-electron photodetectors such as detectivity (D*) and response time (τ_r/τ_f) have remained largely unexplored. Our porous Ag/TiO₂ hot-electron photodetector shows a high responsivity that is comparable to the highest responsivity of photovoltaic hot-electron photodetectors [14, 15]. Furthermore, the response speed of our device is much faster than the previously reported values [20], and the detectivity and minimum detectable light intensity are also comparatively superior [15].

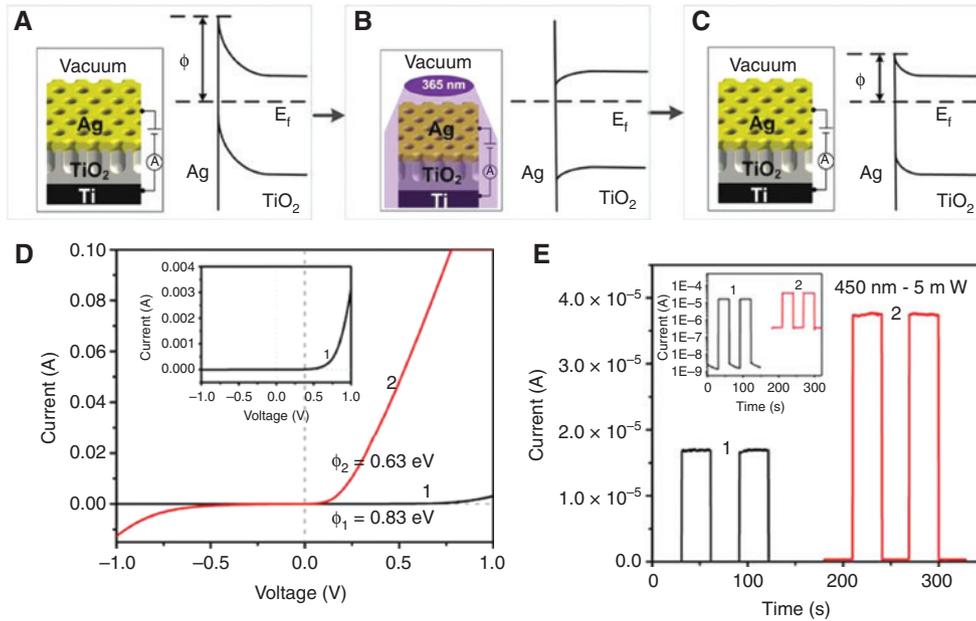


Figure 4: Responsivity improvement by decreasing Schottky barrier height.

(A–C) Schematic for the long-hours ultraviolet illumination treatment: the high Schottky barrier of the initial fabricated sample (A) can be eliminated by long-hours illumination under 365 nm light of 0.4 mW/cm² for 8 h (B), then a lower Schottky barrier will recover after turning off the 365 nm light. (D, E) I–V characteristics (D) and photocurrent response (E) of the porous Ag/TiO₂ heterojunction before (line 1) and after (line 2) long-hours ultraviolet illumination. The incident 450 nm light power in (E) is 5 mW, the inset is the same diagram with the Y-axis on the log 10 scale.

3.3 Improvement of the responsivity by decreasing Schottky barrier

Due to certain energy distribution of the hot-electrons [1], a lower Schottky barrier can enable more hot-electrons to cross over it and contribute to a higher responsivity. In our previous work, the Ag/TiO₂ Schottky barrier was proved to result from the chemisorbed oxygen on the surface of porous TiO₂, and the height of the Schottky barrier can be decreased by ultraviolet light illumination through a process of oxygen desorption, however, the decreased Schottky barrier will turn back to a high value as the ultraviolet light is turned off [24]. In order to obtain a permanent decreased Schottky barrier, we propose a method of long-hours ultraviolet light illumination in vacuum (Figure 4A–C). As shown in Figure 4A, the initial fabricated sample had a high Schottky barrier in vacuum due to the high doping of chemisorbed oxygen on the surface of TiO₂, and then a process of long-hours ultraviolet light illumination was carried out to remove the chemisorbed oxygen until the Schottky barrier was eliminated (Figure 4B). When the ultraviolet light is turned off, the Schottky barrier will recover gradually with re-chemisorption of the surrounding oxygen; but owing to the vacuum environment that cannot provide sufficient oxygen, only a lower Schottky barrier is eventually formed (Figure 4C).

After long-hours ultraviolet illumination, the I–V curves of the sample showed a weaker rectification characteristic (line 2 in Figure 4D) than the sample before ultraviolet illumination (line 1 in Figure 4D), and the barrier heights of the Ag/TiO₂ heterojunction before (ϕ_1) and after (ϕ_2) 365 nm light illumination were estimated to be 0.83 eV and 0.63 eV, respectively, based on the I–V curves (Figure S2 and Supplementary note), where line 1 is the same I–V curve as in Figure 1A. Figure 4E shows the photoresponse of the samples to the 450 nm light illumination with a power of 5 mW. As can be seen, the Ag/TiO₂ heterojunction after ultraviolet light illumination treatment showed a higher photocurrent (line 2 in Figure 4E), corresponding to a higher responsivity of 7.4 mA/W, however, the dark current also increased (line 2 in the inset of Figure 4E), which led to a lower detectivity of 1.2×10^{10} cmHz^{1/2}/W. It can be concluded that while the low Schottky barrier is advantageous for obtaining high responsivity, it is simultaneously disadvantageous for detectivity.

4 Conclusions

In conclusion, we used thin porous TiO₂ to construct an Ag/TiO₂-Schottky-diode based hot-electron photodetector,

which had a broad response spectrum from visible to near-infrared. The responsivity, external quantum efficiency, detectivity, I_p/I_d ratio, and response rise and fall time of the porous Ag/TiO₂ photodetector at 450 nm were calculated to be 3.3 mA/W, 0.91%, 9.8×10^{10} cmHz^{1/2}/W, 1×10^6 , 112 μs and 24 μs, respectively. The responsivity of our device was comparable to the highest responsivity value of the previously reported photovoltaic hot-electron photodetectors. At the same time, the high detectivity and fast response speed of the porous Ag/TiO₂ photodetector were much better than the previously reported hot-electron photodetectors. In addition, we further increased the responsivity of the photodetector from 3.4 mA/W to 7.4 mA/W by decreasing the barrier height of the Ag/TiO₂ Schottky junction.

This work provides inspiration for the performance improvement of the hot-electron photodetectors and material design of the metal/oxide-semiconductor based devices. With performance of microsecond-responses and high detectivity, the porous Ag/TiO₂ hot-electron photodetector will have a promising potential for a variety of imaging, optical communications and optical switches applications.

Supplementary material: X-ray diffraction pattern of the TiO₂/Ti, LnJ-V characteristics, calculation of the height of the Schottky barrier and transmission spectrum of the porous Ag/TiO₂ membrane.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Nos. 51701207, 51471162, 51502294, and 51671183), the CAS/SAFEA International Partnership Program for Creative Research Teams.

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2019-0094>).