

# Ultraviolet photodetector based on Au doped TiO<sub>2</sub> nanowires array with low dark current\*

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Au nanoparticles doped TiO<sub>2</sub> nanowires (NWs) arrays with an average diameter of 100 nm were synthesized through a facile solvothermal method. Thereafter, metal/semiconductor/metal (MSM) structured detectors with Ag electrodes were fabricated on these NWs. The ultraviolet (UV) sensing characteristics of pure TiO<sub>2</sub> and Au-doped ones (Au-TiO<sub>2</sub>) were investigated. Compared with pure TiO<sub>2</sub>, the Au-TiO<sub>2</sub> NWs based device shows a much lower dark current of 1.5 nA at 3 V bias. The low dark current mechanism might be due to the promoted directional transmission of carriers induced by Au doping. The photoresponse is nearly one order of magnitude under 360 nm monochromatic illumination. The Au-TiO<sub>2</sub> NWs detector with simple fabrication process, low noise and good overall performance provides a broad way in fabricating UV imaging arrays.

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Ultraviolet (UV) detectors have drawn much attention due to civil and military applications, including UV communication, smart wears, meteorological monitoring, and medical fields<sup>[1-3]</sup>. Compared with visible and infrared detectors, UV detectors have remarkable tolerability towards bad environments, and are more sensitive due to the low atmospheric background noise of UV radiation. The sensing substrate for UV detectors covers many wide bandgap semiconductors, such as GaN, ZnO, TiO<sub>2</sub> and some perovskite structured compounds<sup>[4-6]</sup>. UV detectors based on these materials have advantages of stable structure, low power dissipation and high photoelectric conversion efficiency.

Among various semiconductor materials, TiO<sub>2</sub> with a direct wide bandgap (3.2 eV for anatase and 3.0 eV for rutile type) is commonly used in photocatalyst, solar cells and chemical sensors due to its excellent physico-chemical stability and optical properties<sup>[7-9]</sup>. Zhang et al previously reported the UV detector based on TiO<sub>2</sub> nanowires (NWs), with a high photoresponse of two orders of magnitude, but also accompanied with a large dark current<sup>[10]</sup>. Low dark current would benefit a lot to the good linearity and sensitivity of instruments. Besides, low dark current is important for fabricating detectors with a small noise dissipation.

It is known that the photoresponse of UV detectors can be affected by the grain size and surface defects in crystalline. Some researches have been devoted to develop high performance semiconducting detectors by adding

various dopants or decorating noble metal (such as Au, Pt, Ag)<sup>[11,12]</sup>. The latter provides an effective and facile way to modify the electronic, chemical and morphological properties of a sensitive film.

One-dimensional (1D) nanostructures are usually considered as promising substrate choice for detectors, since they don't readily agglomerate and have high length-to-diameter ratio<sup>[13]</sup>. In addition, 1D NWs have low recombination probability between photo-generated carriers, thus the carrier's lifetime is prolonged. The NWs also show reduced dimensionality and straight electron conduction pathways, which are beneficial in producing detectors with high sensitivity and fast response speed. The adopted metal/semiconductor/metal (MSM) structure usually endows a detector with low dark current and large photosensitive area, when compared with other device structures.

In this paper, pure and Au doped TiO<sub>2</sub> NWs (Au-TiO<sub>2</sub> NWs) were successfully prepared. The UV sensing properties of samples were studied and the results indicate that Au-TiO<sub>2</sub> NWs exhibit evident improvement in the dark current. Additionally, mechanisms about the sensing performance of the Au-TiO<sub>2</sub> NWs were discussed in detail.

In the experiment, the Au-TiO<sub>2</sub> NWs array was prepared through a low temperature and simplified solvothermal method. A certain amount of toluene was chosen as the solvent to provide a liquid environment for the reaction. Subsequently, 1 mL of tetrabutyl titanate

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and 0.2 mL of titanium tetrachloride were added. Thereafter, 1 mL mixture of hydrochloric acid (0.9 mL) and Au-nanoparticles (AuNPs) aqueous solution (0.1 mL) was dropped slowly. The whole mixture solution was transferred into a 23 mL Teflon-lined stainless-steel autoclave. A piece of FTO substrate was treated by UV ozone to improve the adhesion of films in the growth. The above FTO cleaned after acetone, ethanol, and deionized water was placed into the autoclave. The conductive surface of FTO should be put downward. The NWs array was obtained after a reaction at 150 °C for 6 h. The AuNPs with an average diameter about 30 nm were synthesized by a citrate reduction method, which is similar to the method reported in Ref.[14]. 20 mL of 0.5 mmol/L HAuCl<sub>4</sub> solution was heated above 90 °C under magnetic stirring. Then 20 mL of 0.25 mmol/L sodium citrate solution was quickly added to the boiling solution. The solution changed colors from faintly gray to claret-red under heating. The solution was finally removed from the heat and cooled down to room temperature naturally, which should be kept in cold storage for later use.

The detector was fabricated by depositing Ag circle electrodes directly on NWs, with an active area of about 1 mm<sup>2</sup>. The final UV detector structure was shown in Fig.1. X-ray photoelectron spectroscopy (XPS) experiments were carried out by Thermo ESCALAB 250XI. field emission scanning electron microscopy (FESEM, Hitachi SU8010) and energy dispersive spectroscopy (EDS) was used to investigate the morphology and analysis elements. The FETEM was performed on JEM-2100. The absorption spectra were tested by a PerkinElmer UV/Vis spectrometer (Lambda 650S). Current-voltage (*I-V*) characteristics of detectors were measured using a Keithley 2601 source meter together with a UV power meter. A 30 W deuterium lamp was used as the light source and the monochromatic light was provided by a monochromator. The response time was recorded via a controlled intensity modulated photocurrent spectrometer 70 (CIMPS-2, ZAHNER) system. The test was conducted in a conventional two-electrode configuration.

Fig.1 illustrates the diagram of the final detector with a symmetry MSM structure. No matter positive or reverse bias is applied, one Schottky junction is always positively biased, and the other one is reversely biased. Hence the dark current and noise of such a structured device are low. In the photoelectric properties measurement, the UV light was illuminated from the back side of FTO.

To further confirm the formation of compound NWs, XPS and EDS measurements were adopted as shown in Fig.2. The peaks from Ti2p and O1s are clearly observed, indicating that high quality films were obtained. Additionally, the O1s spectrum is asymmetric and exhibits a main peak at 529.7 eV with an evident shoulder in the higher binding energy (BE) range. The high BE shoulder of sample was indicated as O<sup>chem</sup>, owing to the oxygen atoms chemisorbed at the surface<sup>[15,16]</sup>. As the low doping con-

centration, the peak from Au in EDS spectra behaves weak.

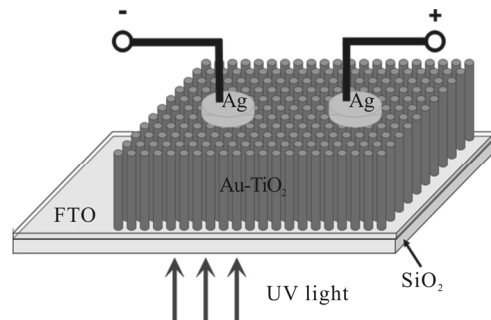


Fig.1 The diagram of the final detector

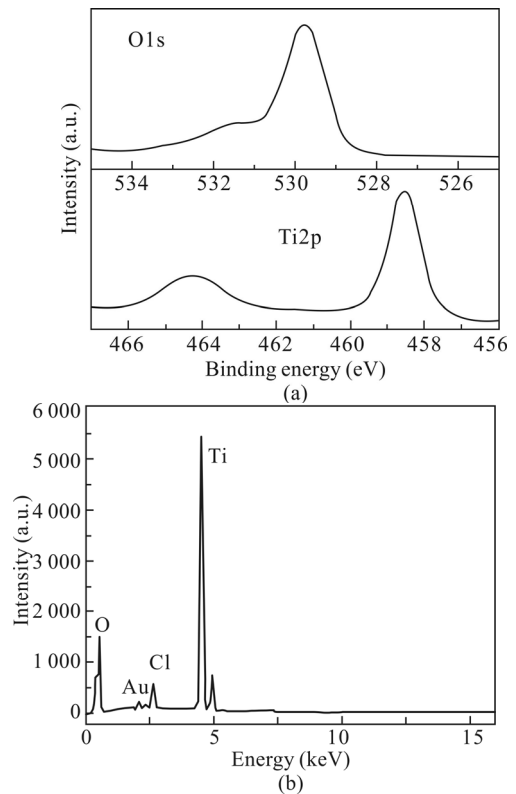


Fig.2 (a) XPS and (b) EDS spectra of compound NWs

Fig.3 displays the top-view scanning electron microscopy (SEM) image of Au-doped TiO<sub>2</sub> NWs arrays, which reveals the formation of 1D nanostructure. These NWs formed clusters, and the nanoclusters grew perpendicular to the substrate with a diameter of about 100 nm. The TEM image in Fig.3(b) confirms the well dispersed Au nanoparticles with dimension of around 30 nm.

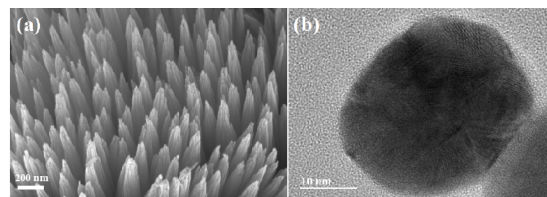
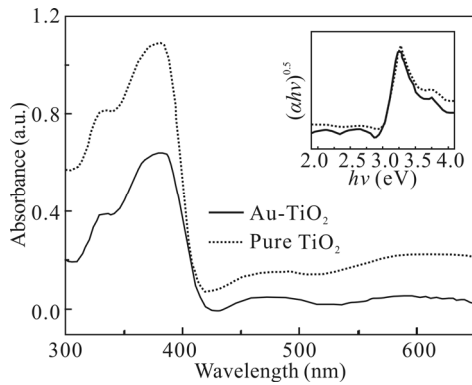


Fig.3 (a) The SEM image of Au-TiO<sub>2</sub> NWs and (b) TEM image of Au NPs

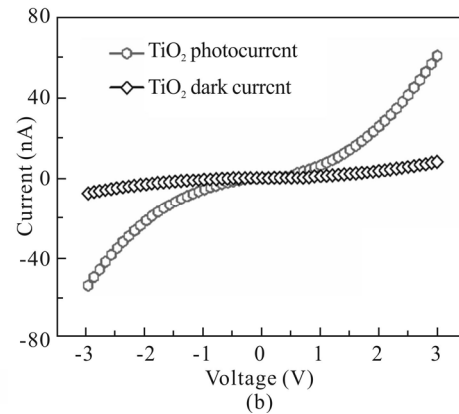
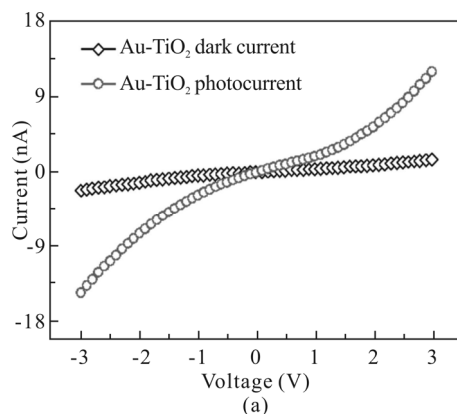
Fig.4 illustrates the UV-visible absorption spectra of pure TiO<sub>2</sub> and Au-TiO<sub>2</sub> NWs arrays. The pure TiO<sub>2</sub> NWs exhibit a higher absorption towards UV light, but the Au-TiO<sub>2</sub> NWs show lower response to visible light. The absorption edge of doped sample is around 414 nm.



**Fig.4 Absorbance spectra and plot to determine the band-gap of pure and Au-TiO<sub>2</sub> NWs (Inset shows the optical bandgaps of both samples.)**

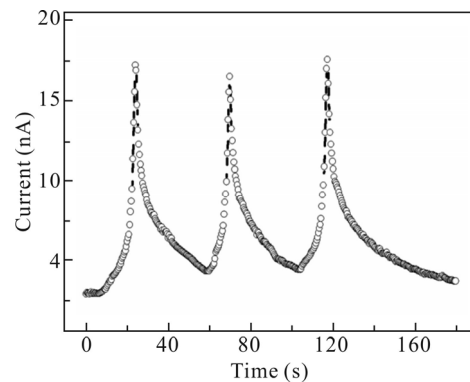
A slight absorption edge shift can be observed in Au-TiO<sub>2</sub> sample, which provides application prospects for an adjustable TiO<sub>2</sub> UV detector. The results reveal that the bandgap is approximately consistent with that of rutile TiO<sub>2</sub> (energy bandgap of 3.0 eV).

Fig.5 shows the *I-V* characteristics of detectors based on pure TiO<sub>2</sub> and Au-TiO<sub>2</sub> NWs in dark and under illumination. The curves exhibit nonlinear and unsaturated behavior of Schottky diode. No matter under forward or reverse bias, the photocurrent increases rapidly with voltage, and the light sensitivity is high. Thus the detector works in a wide voltage range. The dark current of Au-TiO<sub>2</sub> detector is as low as 1.5 nA at 3 V voltage, which is much smaller than that of 35 nA reported previously<sup>[10]</sup>. The photocurrent is 12 nA under the irradiation of 360 nm light. The sensitivity almost reaches one order of magnitude. The photocurrent and dark current of pure TiO<sub>2</sub> based detector are 61 nA and 7.9 nA at the same working voltage, respectively.



**Fig.5 The *I-V* characteristics of detectors based on (a) Au-TiO<sub>2</sub> NWs and (b) pure TiO<sub>2</sub> in dark and under illumination**

Response and recovery time are important parameters for an applied photodetector. Fig.6 is the time response of the Au-TiO<sub>2</sub> device. When the detector is exposed to light illumination, the photo-voltage will increase rapidly. While the voltage falls after removing the UV light. The average response and recovery time of Au-TiO<sub>2</sub> detector are about 14.4 s and 33.8 s, respectively. Moreover, it is found that the peak value and response speed change slightly during different testing cycles, indicating good reproducibility of Au-TiO<sub>2</sub> detector.



**Fig.6 Time response characteristics of the Au-TiO<sub>2</sub> detector**

The low dark current of detector may be ascribed to that Au NPs increase the conductivity of TiO<sub>2</sub>, thus promoting the directional transmission and reducing the random motion of carriers, benefiting a low power consumption and small noise. The photoresponse mechanism of detector should be due to the decrease of Schottky barrier height under UV light. The trapping states introduced by surface defects reduce the height of Schottky barrier under UV light irradiation. Thus more carriers get across the barrier and then the current is enhanced<sup>[17]</sup>. Another reason for the photoresponse in Au doped device could be the light adsorption efficiency by the Au nanoparticle-induced light scattering<sup>[18]</sup>. As an

active component, the catalytic effect of noble metals also helps to improve the device performance. Therefore, AuNPs play an important role in the good overall performance of Au-TiO<sub>2</sub> detector.

In conclusion, the synthesis and characterization of Au-TiO<sub>2</sub> NWs array were investigated. Thereafter MSM structured UV detectors based on pure TiO<sub>2</sub> and Au-TiO<sub>2</sub> were fabricated. The Au-TiO<sub>2</sub> detector exhibits a high performance, including a sensitivity nearly one order of magnitude, and a low dark current of 1.5 nA at 3 V bias. There's still much room for the improvement in response speed. The bandgap of pure TiO<sub>2</sub> can be slightly influenced by the addition of AuNPs, offering unique physicochemical and electronic properties for sensors. Furthermore, the introduce of Au NPs decreases the dark current, thus good sensing properties are obtained in the doped detector.

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