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Application of a Schottky barrier to dye-sensitized solar cells (DSSCs) with multilayer thin films of photoelectrodes

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ABSTRACT

This study combines Au nanoparticles with TiO_2 nanoparticles to form a Schottky barrier, and applies it to the photoelectrode thin film of dye-sensitized solar cells (DSSCs). First, commercial TiO_2 powder (Degussa P25) is put in the alkaline solution to prepare for TiO nanotubes (Tnt) by using hydrothermal treatment. Tnt are sintered at 550 °C to obtain Tnt-C550 particles. In addition, TiO_2 nanoparticles (H180) prepared by subjecting Tnt to two cycles of hydrothermal treatment. H180 served as the first layer, and Tnt-C550 as the second. The third layer adopts salt reduction method to prepare for Au nanoparticles. Experimental results show that the DSSCs prepared with three layers of photoelectrode thin films (H180/Tnt-C550/Au) enhanced the light-to-electricity efficiency of DSSCs by as high as 21% (6.34–7.65%).

1. Introduction

Dye-sensitized solar cells (DSSCs) have the advantages of simple fabrication, low cost and large areas. Recent research has indicated that the photoelectric conversion efficiency of DSSCs has exceeded previous levels by 10–11% [1,2]. The photolelectrodes of DSSCs are made from nano crystal porous TiO_2 film [3–5]. Photoelectrode is a very important substance for DSSCs to achieve high efficiency. TiO_2 nanotubes can serve as the material of photoelectrode because of their large surface area, their porous structure facilitates electrolyte diffusion. Therefore, a photoelectrode fabricated from TiO_2 nanotubes can smooth the transmission path for photoelectrons and reduce the possibility of the recombination of electrons and holes generated from photoelectrons with the electrolyte [6,7]. In addition, TiO_2 particles fabricated by different methods can increase the length of the path, along which photons pass through light-scattering properties if TiO_2 particles with good properties of optical transmittance and scattering properties are used [8,9]. With very high chemical energy, the Au nanoparticles exhibit resonance absorption when the incident light frequency approaches the surface plasmon frequency of Au nanoparticles, making the electrons of Au nanoparticles to move from the orbit *d* to the surface plasmon absorption band, and thus, easily produce chemical bonds with molecules. This phenomenon will directly affect optical properties and thus can be applied in DSSCs [10,11], increasing their optical effects. In addition, when TiO_2 thin film is coated with an Au thin film, with the Fermi level of TiO_2 and Au being −3.9 eV and −4.8 eV, respectively, since the Fermi level of Au is lower than TiO_2, Au and TiO_2 would form Schottky barrier [12,13]. It implies that after electrons have passed through LUMO energy gap of dye molecules and penetrated the conduction band of TiO_2 thin film, electrons cannot come back to the dye molecules or electrolyte because of the existence of Schottky barrier. Thus, the injection efficiency of electrons to photoanodes can be effectively improved [14,15].

To effectively enhance the photoelectric conversion efficiency and reduce the possibility of electrons being transmitted back from the photoelectrode to the dye and electrolytes, the study attempts to take two strategies. First of all, the study uses TiO_2 materials with two different morphologies for the two-layer thin film of photoelectrode of DSSCs. The excellent scattering, good transparency and compact arrangement between nanoparticles in the two-layer thin film can increase the interaction between photons and dye molecules, adsorb more dye, facilitate the diffusion of the electrolyte and the transfer of photoelectrons, assist photoelectrons to transmit electrode to the photoelectrode and reduce the occurrence of dark current. Secondly, the study coats Au nanoparticles on the TiO_2 thin film so as for forming Schottky barrier on TiO_2 thin film. Schottky barrier can reduce the possibility of electrons being trans-

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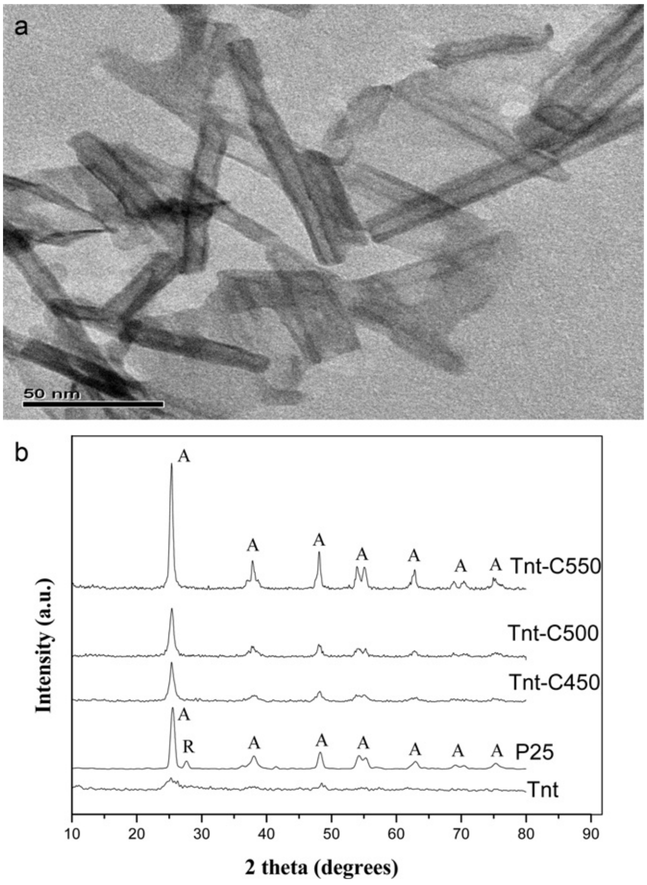

Fig. 1. (a) HRTEM images of the prepared titania nanotubes (Tnt). (b) XRD patterns of Degussa P25, Tnt, and Tnt sintered at 450 °C, 500 °C and 550 °C, respectively.

mitted back from the semiconductor to the dye and electrolytes, thus effectively enhancing the photoelectric conversion efficiency of DSSCs.

Thus, this study uses hydrothermal treatment to prepare for Tnt [16,17]. To increase the photoelectric conversion efficiency, this study adopts two different morphologies of TiO_2 materials and Au nanoparticles to prepare a three-layer photoelectrode with the structure of H180/Tnt-C550/Au. H180, Tnt-C550 and Au nanoparticles are fabricated into three-layer compound films of photoelectrodes and their photoelectric conversion efficiency is compared as well.

2. Experimental

After 20 g NaOH solids were put in the bottle made from perfluoroalkoxy (PFA), 50 ml of deionized water was added to fabricate 10 M NaOH solution. After NaOH solids dissolved, 1.5 g Degussa P25 TiO_2 powder was added and stirred for 30 min at room temperature to make TiO_2 powder disperse evenly to present white suspension liquid. 70 ml of suspension liquid was poured into teflon and enclosed with a stainless autoclave and put in an oven at 130 °C to react for 24 h. After reacting, a stainless autoclave was removed from an oven and teflon was drawn out to be added into the alkaline solution. And then, white sediment was removed by a teflon scrape spoon and added into 500 ml of deionized water. After being filtered, 0.1 M HNO_3 was added to repeatedly acid-wash to pH 1.5 and the mixed solution was put in an oven at 80 °C to be dried until the next day. Finally, white sediment was ground into powder in an agate bowl to obtain TiO nanotubes (Tnt), as shown in Fig. 1(a).

The most popular commercial TiO_2, called Degussa P25 TiO_2 (P-TiO_2), containing approximately 85% anatase and 15% rutile, usually exhibits high photocatalytic activity. To prepare Tnt, 20 g of sodium hydroxide was placed in perfluoroalkoxy and 50 ml of deionized water to prepare for a 10 M NaOH solution. Then, 1.5 g of Degussa P25 powder was added to the 10 M sodium hydroxide solution. The solution was stirred at room temperature for 30 min, and then placed in an autoclave. After the autoclave was placed in an oven at 130 °C for 24 h, to complete the reaction of this mixed solution, it was removed and allowed to cool to room temperature. Then, the white sediment in the autoclave was extracted and added to 500 ml of deionized water, and the fluid was stirred and dispersed. After filtration, the sediment was washed repeatedly with 0.1 M of HNO_3 until it had a pH value of 1.5.

Tnt were added into 50 ml of 0.1 M HNO_3 and put into an oven to be processed two times with hydrothermal treatment and the hydrothermal temperature was set at 180 °C. After reacting for 13 h, the mixed solution was centrifugated for 30 min at 6000 rpm, acid solution was added, the white sediment was withdrawn by and a teflon scrape and was put in the oven at 80 °C to dry until the next day to obtain the product – H180. To fabricate H180, Tnt prepared earlier was added to 0.1 M HNO_3. The solution was placed in an oven at 180 °C for 12 h to undergo hydrothermal treatment. It was then centrifuged at 6000 rpm for 30 min, and the white sediment was extracted, which was then dried in an oven at 80 °C until TiO_2 nanoparticles were obtained. Nanoparticles formed by the hydrothermal treatment at 180 °C are referred to as H180.

H180 particles, sintered by two hydrothermal treatments, were added into 0.67 ml 0.1 M HNO_3 and stirred violently at room temperature for 60 min. The solution was then vibrated by an ultrasonic machine for 30 min. Then, the mixed solution was added into polyethylene glycol (PEG) (MW = 20,000), heated and stirred until completely dissolved and vibrated by an ultrasonic machine for 30 min to fabricate translucent sol, which served as the paste spread by the doctor blade as the first layer. TiO_2 particles prepared by hydrothermal treatment were sintered at 550 °C and added into 0.67 ml deionized water and vibrated at room temperature for 60 min and by an ultrasonic machine for 30 min. Then, the mixed solution was added into 0.04 g PEG (MW = 20,000), heated and stirred until dissolved and vibrated by an ultrasonic machine for 30 min to fabricate white colloidal dispersion, which acted as the paste spread the by doctor blade to prepare for the second layer.

The third layer was fabricated by salt reduction to prepare for Au nanoparticles. The 100 ml 0.127 mM $HAuCl_4$ was heated back to the boiling point and 1 ml of 1 wt.% Trisodium citrate ($C_6H_5Na_3O_7$) solution was added to serve as reductant. After violent stirring, the color of the mixed solution changed from yellow to purple. Continuously stirred and heated for 1 h, the mixed solution was cooled down at room temperature. This study used the surface of TiO_2 electrode layers to modify Au nanoparticles by the self-assembly method. TiO_2 electrode layers were soaked and the mixed solution was combined with ammonia, hydrogen peroxide and water (NH_4OH:H_2O_2:H_2O = 1:1:5) [18] for 3 h to make its surface consist of negatively charged hydroxyl. Afterwards, ITO glass was soaked in 1 wt.% Mercapto-propyl-tri-methoxy-silane (MPTMS) for 24 h to make the second layer of TiO_2 film possess sulfur blends. Au nanoparticles and thiol form covalent bonds to make Au nanoparticles stick to the second layer, thus accomplishing the fabrication of the photoelectrodes of DSSCs.

Photoelectrodes were soaked in N719 dye for 24 h. After being soaked for 24 h, acetonitrile was used to cleanse the surface of the photoelectrodes to remove N719 dye without absorbing on the surface of the photoelectrodes and dried to obtain the photoelectrodes of DSSCs. Additionally, redox electrolyte I^-/I_3^- was poured into the gap of the counter electrodes coated with platinum (Pt). Photoelectrodes and counterelectrodes were integrated compactly and a fish tail clip was used to fix them to prevent the formation of bubbles and to form the sandwich structure of DSSCs. The test of the DSSCs adopts 150-W Xe light, combined with simulated sunlight (AM 1.5) and Keithley 2400 to form an *I–V* curve analyzer. Before testing, the distance between the light and the specimen was adjusted and the density of light was set at 100 mW/cm^2. The results showed the *I–V* curve and the data of V_{OC} (V), J_{SC} (mA/cm^2), FF and η%.

3. Results and discussion

Fig. 1(b) shows the XRD spectra of Tnt, TiO_2 powder (Degussa P25), and Tnt sintered at 450 °C, 500 °C and 550 °C, respectively. The results show that Tnt fabricated by this study was baked at 80 °C without any calcination. Therefore, Tnt has no clear anatase and rutile structure and belongs to amorphous $H_2Ti_2O_7$, which is not beneficial to serve as electrode materials. Accordingly, Tnt requires sintering to make its phase transform amorphous to anatase. It can be seen from Fig. 1(b) that with the rise of sintering temperature, the intensity of the diffraction peak of anatase is reinforced.

Fig. 2 shows the FE-SEM images and XRD pattern of H180 nanoparticles processed by two hydrothermal treatments. It can be observed that the morophlogy of nanoparticles sample H180 is the same, with the size of about 20–35 nm. According to XRD patterns, it is found that H180 nanoparticles possess the anatase phase. The crystallinity of crystal has the decisive influence on the photoelectric conversion efficiency of DSSCs.

Fig. 3(a) shows the TEM images of Au nanoparticles, displaying that the morphology of Au nanoparticles is round, with the average size of 27 nm. Au nanoparticles are examined by XRD tests and the results from Fig. 3(b) show clear an Au peak. The above-mentioned tests prove that Au nanoparticles can be well fabricated.

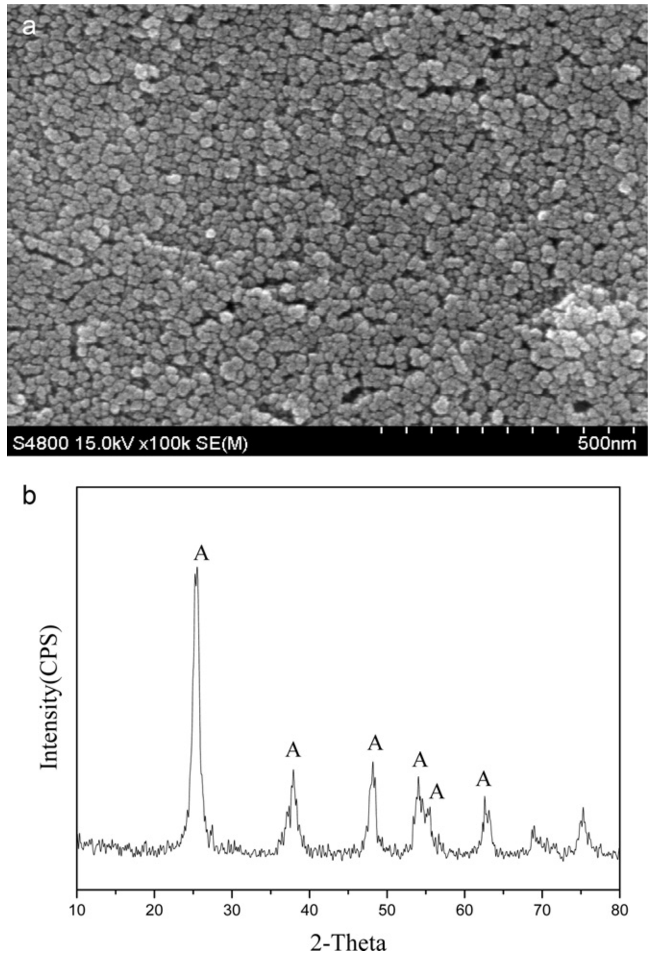

Fig. 2. (a) FE-SEM images and (b) XRD pattern of H180 particles processed by two hydrothermal treatments.

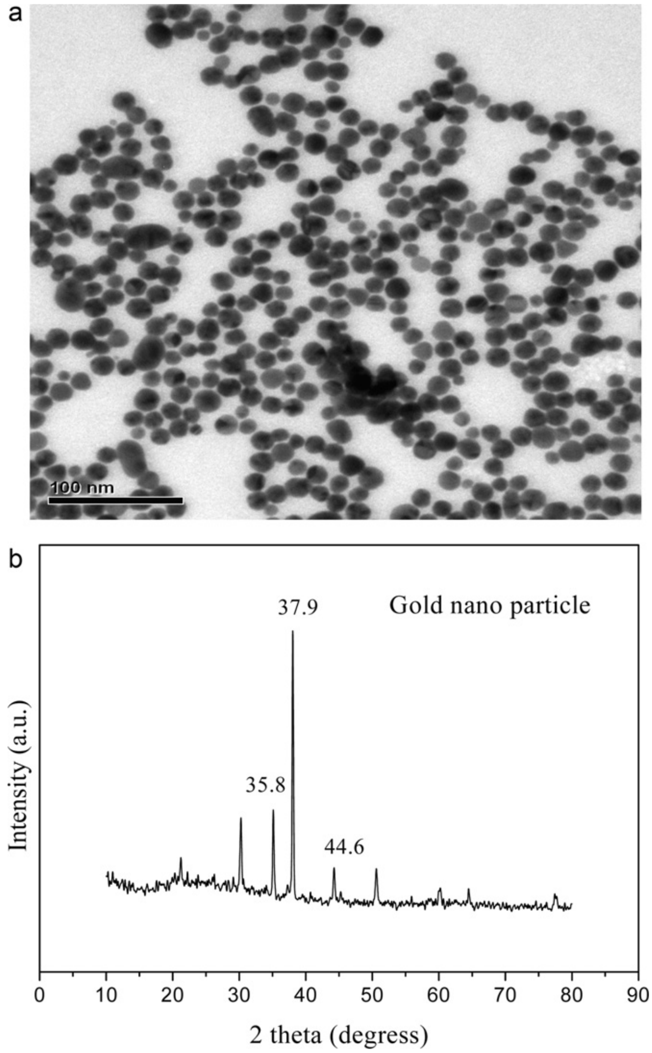

Fig. 3. (a) TEM images and (b) XRD patterns of Au nanoparticles.

The H180 was fabricated into translucent paste in this study through two hydrothermal treatments adopting a doctor blade to spread the first translucent and dense layer. Adding a dense layer leads to the occurrence of a dark current for DSSCs and a spreading translucent layer can slightly enhance resistance and block the loss of dark current occurrence by elevating resistance, and thus, increasing photoelectric conversion efficiency. This dense layer is formed by TiO_2 and has fewer errors with the energy levels of the second-layer film – Tnt-C550.

Fig. 4(a) is FE-SEM image of the cross-section of the three layers of films spread on photoelectrodes, showing the thickness of all the films of photoelectrode is 14 μm. Take the logarithm of current density measured from the dark field, and then draw a relational diagram between it and voltage. If linear results are shown in the diagram, it refers that the interface phenomenon of Schottky barriers exists. If the relational diagram appears to be more linear, it is closer to the ideal Schottky interface electrical response. Therefore, linear regression is done for the relational curve between voltage and current density, and relative coefficient can be calculated. If the relative coefficient is close to 1, it shows that the interface electrical properties tend to be a Schottky barrier [19]. The results from Fig. 4(b) show that when the voltage is less than 0.3 V, the linear relationship does not exist in the relationship between the current logarithm and voltage. Thus, electrical phenomenon does not correspond to Schottky barrier. When the voltage is greater than 0.3 V, the Schottky barrier of the photoelectrode thin film with Au nanoparticles is more apparent, and the relational curve between current logarithm and voltage is approaching linear. After linear regression analysis is made for the data of Fig. 4(b), it is found that the relative coefficient of TiO_2 thin film without coating of Au nanoparticles is 0.68, and that of TiO_2 thin film with coating of Au nanoparticles is 0.83. As observed from the above results, there is a significant difference of electrical properties between TiO_2 thin films with and without coating of Au nanoparticles. This is because if the relative coefficient is close to 1, Schottky barrier interface is more obvious. Therefore, the photoelectrode of TiO_2 thin film with coating of Au nanoparticles tends to be a Schottky barrier interface. Furthermore, when TiO_2 thin film with coating of Au thin film, the Fermi level of Au is lower than TiO_2; hence, Au and TiO_2 would form Schottky barrier. With the existence of Schottky barrier, electrons pass through the Au thin film and inject into the conduction band of TiO_2 thin film, thus enormously reducing the possibility of electrons being transmitted back to the dye or electrolytes. In this way, the photoelectric conversion efficiency of DSSCs can be effectively enhanced.

In this study, three layers of film serve as the photoelectrodes of DSSCs. The thickness of the film is controlled at 13–15 μm and the photovoltaic performances of each photoelectrode are summarized in Table 1 and the results are shown in Fig. 4(c). The results from Table 1 show that the photoelectric conversion efficiency of single layer – H180 is 5.92%. Adding Tnt-C550 to prepare for films of double-layer photoelectrodes (H180/Tnt-C550), the open circuit voltage increases from 0.735 V to 0.745 V, the short-circuit cur-

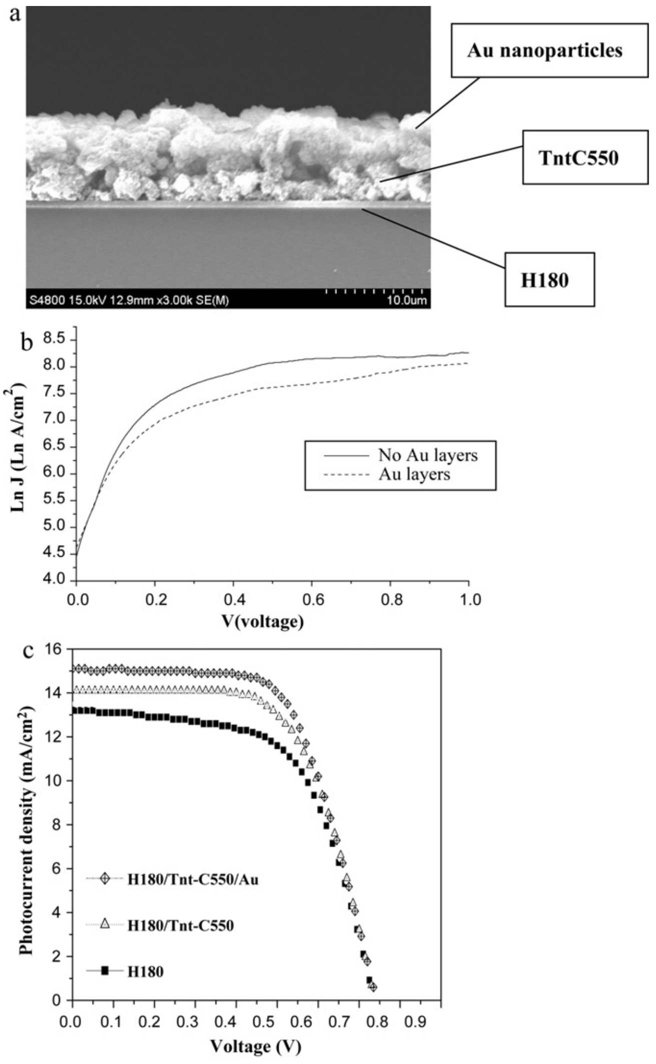

Fig. 4. (a) FE-SEM image of a cross-section of a three-layer thin-film photoelectrode (H180/Tnt-C550/Au nanoparticles). (b) *J–V* curve of Au loaded on a TiO_2 layer in the dark field for the DSSCs. (c) Photocurrent voltage characteristics of DSSCs with photoelectrodes of single-, two-, and three-layer thin films.

Table 1
Photoelectrochemical parameters of multilayer electrodes in DSSCs.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	η (%)	FF	Cell area (cm^2)
H180	0.735	13.31	5.92	0.59	0.25
H180–Tnt-C550	0.745	13.71	6.34	0.613	0.25
H180–Tnt-C550–Au	0.752	15.71	7.65	0.656	0.25

rent density increases from 13.31 mA/cm^2 to 13.71 mA/cm^2 and the photoelectric conversion efficiency increases from 5.92% to 6.34%. When adding Au nanoparticles to produce Schottky barriers (H180/Tnt-C550/Au), the photoelectric conversion efficiency elevates to 7.65%, the open circuit voltage elevates to 7.52 V, short-circuit current density elevates to 15.71 mA/cm^2, and the whole photoelectric conversion efficiency elevates 21% compared to when Au nanoparticles are not added. The results show that the three-layer structure of H180/Tnt-C550/Au enhances the conductivity of the TiO_2 electrode. Au nanoparticles are assembled on the surface of TiO_2 to act as Schottky barriers of DSSCs. Schottky barriers can reduce the possibility of electrons being transmitted back from the semiconductor to the dye and electrolytes, providing more efficient electron transfer, while also increasing short-circuit current density and photoelectric conversion efficiency.

4. Conclusions

From the abovementioned experimental results and discussion, the following conclusions can be drawn.

1. This study adopts chemical reduction to synthesize Au nanoparticles with an average size of 27 nm observed by HRTEM.
2. Tnt are sintered at high temperature and then processed at different temperatures of 450, 500 and 550 °C, respectively. The results show that the higher the sintering temperature, the stronger the diffraction peak of anatase.
3. For the current density logarithm and voltage diagram, if the relationship is linear, interface phenomena of the Schottky barriers exist. Experimental results show that Au nanoparticles produce Schottky barriers on the surface of TiO_2.
4. The photoelectric conversion efficiency of a single-layer photoelectrode increases from 5.92% to 6.34% for a double-layer photoelectrode. When adding Au nanoparticles to produce Schottky barriers, photoelectric conversion efficiency elevates to 7.65%.

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