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Development of Titania Nanotubes Loaded with Au Nanoparticles and their Opto-electronic Response under UV Light

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Abstract: Au nanoparticles surface-modified titania nanotubes were produced by direct-current (DC) magnetic sputtering technology. The morphology of the nanotubes was characterized by X-ray diffractometry (XRD) and field emission scanning electron microscope (FESEM). Opto-electronic properties were tested under UV light. Comparing with original titania nanotubes, Au/TiO_2 nanotubes can generate the photocurrent with great improvements in constant potential and dynamic potential. At constant potential (1.0V) test under UV light, the photovoltaic current generated by Au/TiO_2 is 0.4mA, 1.8-fold of original nanotubes'. While at dynamic photocurrent (−1.5V to 1.5V) test, the photocurrent has reached 0.75mA, which is 3.75-fold of that for original nanobubes under the scan voltage of 1.5V.

Key words: titania nanotubes; DC magnetic sputtering; photocurrent

One-dimensional nanostructure materials with nanotubular symmetries are proved to be very efficient as physical and chemical nanodevices due to their valuable high surface area structure, and own great potential applications in the sensing, fuel cells and water photolysis[1]. Titania dioxide, a well-known oxide semiconductor material, has been extensively studied, owing to its high photocatalytic (PC) activity, chemical stability, nontoxicity and relatively low price[2-3]. Oxide materials are attractive because of their ability to withstand photocorrosion, wide-spread availability, and affordability; however, most of the stable oxides are photochemically active only in ultraviolet (UV) light without band-gap engineering[4-9]. The optical properties of anatase titania nano-materials have been intensively studied since the opto-electronic properties of titania play a key role in determining their performance in optical sensors, photovoltaic cells and in photocatalytic reactions[10-11].

Most of attentions and efforts have been focused on the titania particles in terms of characterization of their crystallographic structures and microscopic morphologies, while there is lack of attention given to the electronic modification of titania nanotubes[12-13]. Because of highly special surface area, ion-exchangeable ability and photocatalytic, titania nanotubes have been considered for extensive application. In order to improve the ability of photo-electronics of titania nanotube, loading metal particles on the surface is one of the most effective methods. Nishijima *et al*[14] have developed a titania nanotube loaded site-selectively with Pt particles by UV irradiation under ethanol atmosphere and the nanotubes exhibited a high photocatalytic activity for oxidation of acetaldehyde. Kang *et al*[15] have fabricated Gold-Platinum nanoparticle-decorated titania nanotubular electrode by electrochemically depositing Au and Pt nanoparticles onto a highly-oriented titania nanotube array. After modified the electrode with glucose oxidase (GO_x) the resultant glucose biosensor possesses high sensitivity to glucose in the range of 0 to 1.8mmol/L with a response time of 3s and detection limit of 0.1mmol/L.

In this article, Au nanoparticles are loaded by DC magnetic sputtering technology to make the electronic modification of titania nanotubes, the surface of Au-modified titania nanotubes is observed with a scanning electron microscope, the crystal structure is analyzed by the X-ray diffraction, photo-electronic effect is tested under UV light, positive results are obtained.

1 Experimental

1.1 Preparation of Au/TiO_2 nanotubes (TiNT)

Densely and highly ordered TiO_2 nanotubes are fabricated by anodic oxidation method. Au nanoparticles are prepared by DC magnetic sputtering technology, the vac-

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uum system consists of turbo molecular pump and mechanical pump ensuring a clean vacuum environment and the chamber base pressure is up to 3.1×10^{-4}Pa, sputtering is done in an ambient of inert gas Ar (purity > 99.99%), whose pressure values is 0.8Pa. The sputtering voltage is typically 386V, while the applied power is in the range from 50 to 150W. Planar magnetron sputtering source which can accommodate 50mm diameter targets, and can operate at the maximum input power level of 1kW (dc), though the average power level used was typically much smaller. The Au target with the purity of 99.999% is a 5mm thickness, 50.8mm in diameter. The distance between target and substrate is fixed at 5.5cm. Au nanoparticles have been successfully deposited on the surface of the anatase titania nanotubes for 60s.

1.2 Characterization of Au/TiO_2 nanotubes

The morphology of titania nanotube is investigated by using field emission scanning electron microscope (FESEM A Hitachi S4800) with an accelerating voltage of 30.0kV. The X-ray analyses of the nanotube were done on an XRD machine (PAN analytical) using monochromatic CuKα radiation.

1.3 Measurement of the opto-electronic properties

Photocurrent density is measured by corrtest CS300UA with titania nanotube arrays deposited with Au nanoparticles as photoanode and platinum foil as counter electrode in 0.01mol/L Na_2SO_4 electrolyte. The high-pressure mercury lamp is placed vertically outside the reactor as UV-light source. Constant potential test: bias potential applies on photoanode is 1.0V (*vs* SCE) under UV illumination with characteristic wavelength of 254nm for 600s, collecting data frequency of CS300UA is chosen as 5Hz. Dynamic potential test: the range of scan voltage is −1.5V to 1.5V, the scan rate sets at 5mV/s, and the frequency is 5Hz, all tests are implemented under room temperature.

2 Results and discussion

2.1 FESEM

The morphology of the titania nanotube loaded Au nanoparticles by DC magnetic sputtering technology is studied by SEM (Fig. 1(a) and (b)). It shows clearly that the titania nanotube arrays grow orderly on the surface of titanium sheets and they have an average length of 500nm, inner diameter 90nm and wall thickness 10nm. The gold nanoparticles are loaded and well dispersive on the surface of the titania nanotube walls compared with original titania nanotubes (Fig. 1(c) and (d)). The particles do not cover the whole nanotubes, so the light can illuminate directly on the titania nanotube, and do not impede the reaction of the titania nanotubes with the light and reduce the response area. The dimension of Au particles is about 4nm, all particles' sizes are almost equal and distributed uniformly.

2.2 XRD pattern

The XRD pattern of Au nanoparticles surface-modified titania nanotubes prepared by DC magnetic sputtering technology is given in Fig. 2. The high-intensity peak is generated by the titanium substrate. The peak of titania appeared in many different places (the anatase phase represent as A). Among them, the strongest peak is at the position $2\theta=25.3°$ corresponding to the (101) crystal face of anatase TiO_2. The crystal particle size is 26nm calculated by Scherrer's formula. The characteristic peak of Au were not detected because of the low content of gold and few sputtering time.

2.3 The opto-electronic properties of the Au/TiO_2 nanotubes

The Photo-electronic effect testing is carried out in 0.01mol/L Na_2SO_4 electrolyte solution by using Au nanoparticles surface-modified titania nanotubes as an anode and Pt foil as a cathode under UV illumination with

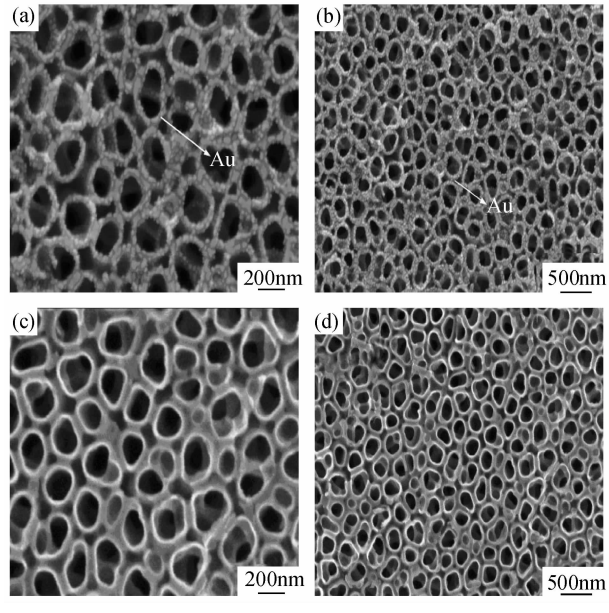

Fig. 1 The SEM images of the titania nanotubes deposited with Au nanoparticles ((a) and (b)) and original titania nanotubes ((c) and (d))

characteristic wavelength of 254nm for 600s. The photocurrent and photoelectrochemical current response are measured by an electrochemical workstation (CS300UA). The results are shown in Fig. 3. As shown in Fig. 3, Curve B stands for original titania nanotube calcined at 450℃ in muffle furnace for 2h, the photovoltaic current is about 0.22mA. Curve A represents titania nanotube arrays deposited with Au nanoparticles after annealing. The photovoltaic current generated by Au nanoparticles surface-modified titania nanotubes photovoltaic current is 0.4mA. Comparing with original titania nanotube, the generated-photocurrent of Au/TiO_2 is 1.8-fold of that for original titania nanotubes. The phenomenon can be interpreted as follows. Firstly, loaded on the surface of the titanium dioxide nanotubes, Au nano-particles prevent the photogenerated electron-hole pairs from recombination effectively, and prolong the time of their combination. In the 0.01mol/L Na_2SO_4 electrolyte solution adding a certain voltage (1.0V), the photo-induced-electrons rapidly move along with a certain direction so as to effectively avoid the occurrence of recombination with photo-induced-holes. Secondly, when Au particles contact with the semiconductor of titanium dioxide, the surface of them will form a Schottky barrier. Electrons will transfer from the material with low work function to the material with high work function. The work function of Au is 5.1eV is higher than that of TiO_2 (4.2eV)[16]. So photo-induced-electrons move from titanium dioxide nanotubes to Au nanoparticles and Au nanoparticles become the electron capture center. Therefore, Au nanoparticles greatly reduce the chance of recombination to the photogenerated electron-hole pairs.

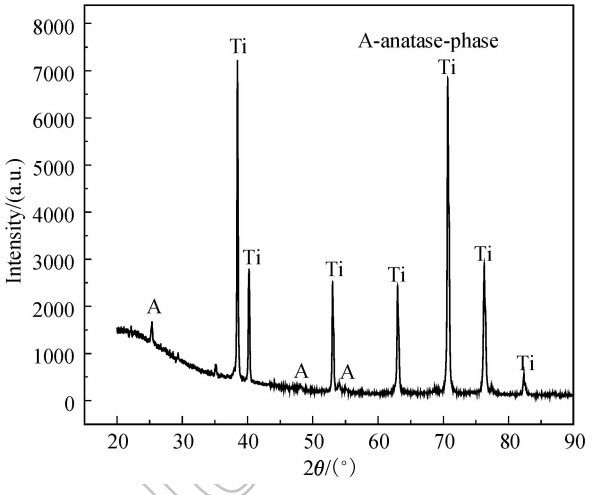

Fig. 2　XRD pattern of the titania nanotubes deposited with Au nanoparticles

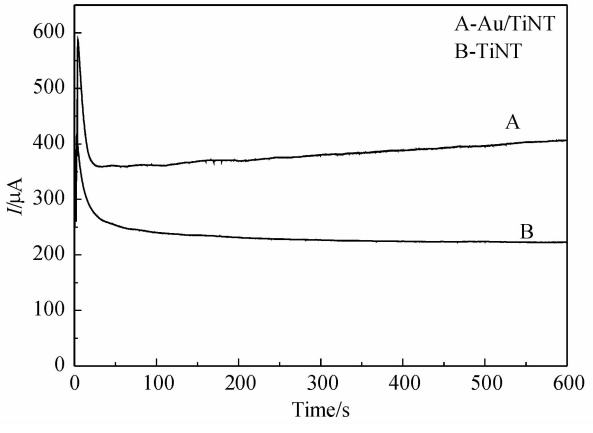

Fig. 3　*I* – *t* curves of titania nanotubes under UV light by constant potential test

Au nanoparticles surface-modified titania nanotubes analyse the change of photocurrent at dynamic potentia circumstance (the scan voltage range of – 1.5V to 1.5V). Figure 4 shows titania nanotubes under UV light by dynamic potential test. The generated-photocurrent of the modified nanotubes is increasing rapidly with the increasing potential. As scan voltage is 1.5V, the photocurrent has reached 0.75mA. While the photocurrent generated by original titania nanotubes is tend to a constant value about 0.2mA with increasing in potential. Therefore, the current density of Au nanoparticles surface-modified titania nanotubes is much greater than the unmodified titania nanotubes.

3　Conclusions

The method of DC magnetic sputtering technology is an effective way to deposit Au nanoparticles on the surface of titania nanotube arrays. The nanoparticles uniformly distribute on the nanotube arrays. At constant potential circumstance, the photovoltaic current generated by Au nanoparticles surface-modified titania nanotubes is 0.4mA under UV-light. The photocurrent efficiencies are 1.8 times comparing with original titania nanotubes.

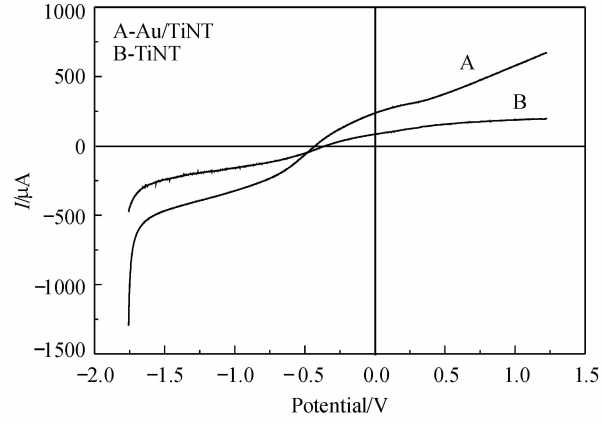

Fig. 4　*I-P* curves of titania nanotube under UV light by dynamic potential test

At dynamic potential circumstance, the photocurrent generated by modified nanotubes increase rapidly with the increase of potential. It reaches 0.75mA when scan voltage is 1.5V.

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TiO_2 纳米管负载纳米金的制备及其在紫外光下的光电性能

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摘 要: 利用直流磁控溅射法制备纳米金颗粒表面改性 TiO_2 纳米管,并通过 XRD,FESEM 对其结构进行表征. 在紫外光下测试其光电效应,结果发现在定电位和动电位下,纳米金改性后的 TiO_2 纳米管产生的光电流都要比未改性的 TiO_2 纳米管大. 在定电位下(1.0V),Au/TiO_2 纳米管产生的光电流为0.4mA,是 TiO_2 纳米管的1.8倍. 在动电位下(−1.5~1.5V),当电位达1.5V时,Au/TiO_2 纳米管产生的光电流为0.75mA,是 TiO_2 纳米管的3.75倍.

关 键 词: TiO_2 纳米管; 直流磁控溅射; 光电流

中图分类号: O644 **文献标识码**: A