Study on Preparation and Photocurrent Response Properties of In/In$_2$O$_3$/TiO$_2$ Nanotubes Arrays Compound Heterojunction Semiconductor

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Abstract. TNTs were prepared in ethylene glycol with 0.5wt%NH$_4$F and 1.5Vol%H$_2$O by the anode potential of 60V. In/In$_2$O$_3$/TiO$_2$ nanotube arrays (TNTs) heterojunction semiconductor was prepared by two electrochemical steps of reduction and oxidation in 0.01 mol/L InCl$_3$ ethanol solution. The element In and In$_2$O$_3$ nanofibers were distributed in and on the TNTs by SEM figures. By the photocurrent results, TNTs photocurrent response was reinforced by In$_2$O$_3$ and In modification in UV and visible light region. The monochromatic incident photon-to-electron conversion efficiency (IPCE) reached to 58% under the 350nm light radiation and was nearly 5 times that of TNTs. Two oxidation phases were got from the photocurrent data (the energy band gap $E_g=3.08eV$ and $E_g=2.2 eV$), which was propitious to the absorption light red shift and response under the visible light. The flat band potentials shifted to electric positive direction for In/TNTs prepared by one step of reduction or In/In$_2$O$_3$/TNTs prepared by two steps of reduction and oxidation according to the Mott-Schottky curve. The donor density (ND) of the In/In$_2$O$_3$/TNTs was slightly higher than TNTs and the ND of In/TNTs was the highest for 14.6 times that of TNTs. The results show that heterojunction is formed between In$_2$O$_3$ and TNTs to promote visible light absorption and carrier separation. A great deal of element In makes the photo generated electrons and holes recombination to reduce the photocurrent response, but a small amount of element In can reduce the $E_g$ of semiconductor and promote the absorption light to red shift for TNTs. The transfer mechanism of In and In$_2$O$_3$ modified by TNTs was discussed.

As a highly efficient photocatalyst, TiO$_2$ has received extensive attention, but its wide bandgap ($E_g=3.2eV$) limits the use of sunlight. Therefore, the modification research is widely carried out at present, and the modification mainly from two aspects. On the one hand, morphology modification of TiO$_2$ itself, and to form nano-particles, nano-wires, nano-clusters, nano-tubes, etc., increase its specific surface area and aspect ratio to increase photocatalytic efficiency, the TiO$_2$ nanotube array has become a research hotspot due to its neat tubular structure and a large specific surface area[1, 2]on the other hand, it is doped or added with other substances on TiO$_2$, such as deposition of metal elements or doped metal ions (Pt, Au, Cu, Pd, etc.) [3-6], doped non-metallic substances (C, N, etc.) [7,8], formation of heterojunctions with semiconductors such as metal oxides or sulfides[9-12], combined with organics [13] and other modification methods to improve the efficiency of light carrier separation or reduce the semiconductor band gap, enhance the utilization of visible light. In recent years, researchers have organically combined varieties of modification methods to prepare composite semiconductor catalysts [13-20], which can effectively promote the separation of photogenerated electrons and holes in TiO$_2$, and can also make the absorption light red-shift. Researchers composite semiconductor catalysts in order to effectively use the sun and play very good results.
In$_2$O$_3$ is a new n-type semiconductor functional material, with a bandgap width of $E_g=2.8eV$, a small resistivity, and a high catalytic activity, and has been widely used in the fields of optoelectronics, gas sensors, and photocatalysts [21]. The In$_2$O$_3$ particle size up to the nano level also has the surface effects of nanomaterials, quantum size effects, small size effects and macroscopic quantum tunneling effects in addition to the above functions. As an oxide semiconductor photocatalyst, In$_2$O$_3$ has similar photocatalytic properties as TiO$_2$, but its narrower band gap can also promote the absorption of light from the UV region to the visible region [22]. Liu et al.[23] prepared In$_2$O$_3$ nanorods/Ti-Ni-O nanomaterials Heterojunction photocatalyst can efficiently Photoelectrocatalytic pyrolysis of water.

In this paper, In/In$_2$O$_3$/TiO$_2$ nanotube array heterojunction composite semiconductor catalysts were prepared by electrochemical method. The photoelectrocatalytic performance of TiO$_2$ nanotube arrays is improved by the combination of metal In and oxide semiconductor In$_2$O$_3$.

1. Experiment

1.1. Preparation of TiO$_2$ Nanotube Arrays
Titanium foil (10×10×0.2 mm) was ultrasonically cleaned with anhydrous ethanol and deionized water for 20 minutes respectively, then polished for 5 seconds with chemical polishing solution which the composition is V (HF): V (HNO$_3$): V (H$_2$O) = 1:4:5, at last the treated sample was rinsed and dried with deionized water. Two-electrode anodization was used in the experiment, the titanium foil was an anode and platinum was a cathode. The ethylene glycol was added 0.5 wt% of NH$_4$F and 1.5 Vol% of H$_2$O as the electrolyte and magnetic stirring. Using phased voltage, the first stage uses a linear voltage, from 0V to 60V, for 60 seconds, the second stage is to maintain a constant voltage of 60V, and maintain the oxidation for 3600 seconds. Then it is annealed at 450°C for 2 hours, stored in a desiccator after natural cooling, prepared samples are referred to as TNTs.

1.2. Preparation of In/In$_2$O$_3$/TiO$_2$ Nanotube Array Heterojunction Semiconductors
A certain amount of InCl$_3$ was dissolved in an absolute ethanol solution, and a solution with an In$^{3+}$ concentration of $1\times10^{-2}$ mol/L was configured. The TiO$_2$ nanotube array was placed in a sample holder, and the surface of the sample was sealed with an organic tape and leave 0.2826cm$^2$ of exposed area in contact with the solution. The sealed sample was placed in the holder and immersed in above solution, static adsorption 30min. Then, the TiO$_2$ nanotube array was used as the working electrode, the saturated calomel electrode (SCE) with capillary was used as the reference electrode, Pt was the negative electrode for indium deposition. The applied voltage was -6V and the electricity reached 0.01C. This sample was recorded as TNTs-In. Subsequently TNTs-In was oxidized with an oxidation potential 1 V and oxidized charge of 0.001 C. The prepared samples were recorded as TNTs-InOx.

1.3. Morphologies Analysis
Characterize the morphologies of TiO$_2$ nanotube arrays and their modified catalysts. Cold field emission scanning electron microscope (JSM-4800F) was used to characterize the composition of the sample. X-ray photoelectron spectroscopy (XPS, MT-500, Microtech) was used. Using the Al detector (C1s located at 284.8eV).

1.4. Photoelectric Response Performance and Mott-Schottky Test
Photoelectric response performance test using 450W xenon lamp and CT110 monochromator, PARSTAT2273 potentiostat optocoupler test system, in a three-electrode electrolytic cell with a quartz window, the modified TiO$_2$ nanotube array electrode prepared above as a working electrode, the platinum film is an auxiliary electrode. The saturated calomel electrode connected by salt bridge is a reference electrode. Under the open circuit potential, a 0.1 mol/L $\text{Na}_2\text{SO}_4$ solution is used as the supporting electrolyte; the tests are performed at room temperature.
2. Results and Discussion

2.1. Characterization

Figure 1 shows the TiO$_2$ nanotube array and the modified sample surface topography. It can be seen from Figure 1a that the TiO$_2$ nanotube array is well-arranged, the tube diameter is about 100 nm, and the tube wall thickness is about 10 nm. Figure 1b is the morphology of TNTs-In surface which after the reduced indium modification. It can be seen that the modified materials are distributed in the form of nanofibers on the surface of the TiO$_2$ nanotube array and in the TiO$_2$ tube. Figure 1c shows the surface morphology of indium-modified TNTs-InO$_x$. Compared with Figure 1b, it can be seen that the modified substances are also distributed on the surface of the TiO$_2$ nanotube array and in the TiO$_2$ tube after oxidation, but the nanofibers are shortened and contact status is not obvious. Figure 1d shows the lateral morphology of the damaged TNTs-InO$_x$ membranes. The film thickness is approximately 7-8 μm. The top of the membrane to the bottom of the membrane is in the form of a tube.

![SEM images of the samples](image)

**Figure 1.** SEM images of the samples (a) TNTs (b) TNTs-In and (c) TNTs-InO$_x$, (d) cross-section of TNTs-InO$_x$.

Figure 2 shows XPS spectra of the surface composition of the TNTs-InO$_x$ samples. Figure 2a clearly shows that TNTs-InO$_x$ contains characteristic peaks for C1s, In3d, Ti2p, and O1s, and Figure 2b shows Ti2p3/2 and Ti2p1/2 characteristic peaks at 458.9 eV and 464.6 eV, respectively, these peaks show that Ti exists as a typical TiO$_2$ form [24]. Figure 2c shows the In3d5/2 characteristic peak. Obviously, this peak has a tailing phenomenon. Therefore, according to the literature fit the peak [23], the In3d5/2 binding energy of elemental In is 444.2 eV and the In3d5/2 binding energy of In$_2$O$_3$ is 445.1 eV. Oxide-state indium modified substances containing two kinds of matters that are In and In$_2$O$_3$. The elemental In and In$_2$O$_3$ accounts for 9.4% and 90.6% respectively, based on the fitted peak area. Figure 2d is a fitting plot of the O1s map. Fitting peak 1 at 529.9 eV is the characteristic peak of lattice oxygen. Fitting peak 2 at 531.3 eV is the characteristic peak of adsorbed oxygen. This adsorbed oxygen may come from the air adsorbed on the sample surface like O$_2$ and H$_2$O [25, 26].
2.2. Photoelectric Response Performance Analysis

Figure 3 shows the photocurrent spectrum of the modified TiO₂ nanotube array (λ= 250-600 nm), first in the ultraviolet (UV) part (λ= 250-400 nm), comparing the samples TNTx, the reducing In modified TNTs-In sample photocurrent response is weakened, but after the sample is oxidized, the photocurrent response of the TNTs-InOₓ in the UV part is significantly enhanced, and the wavelength of the highest photocurrent response is red-shifted. Figure 3 shows the photocurrent response spectrum of the visible part (λ= 400-600 nm). It can be seen from the figure that, compared with the TiO₂ nanotube array, the photocurrent response of the reduced indium modified TNTs-In is also not strengthened, but the photocurrent response has been enhanced after oxidation like the sample TNTs-InOₓ, this phenomenon indicates that the oxidized sample TNTs-InOₓ can effectively use visible light.

Figure 2. XPS spectra of (a) whole spectra (b) Ti2p (c) In3d and (d) O1s
According to Figure 3, the monochromatic incident photon-to-electron conversion efficiency (IPCE) of the indium-modified TiO$_2$ nanotube array at each wavelength is converted. As shown in Figure 4, it can be seen that the TiO$_2$ nanotube array has the highest light quantum conversion efficiency of 11.7% at the wavelength of 340 nm. The TiO$_2$ nanotube array composite catalyst modified by In and In$_2$O$_3$ can achieve a photon conversion efficiency of up to 58% at a wavelength of 350 nm and five times that of a TiO$_2$ nanotube array. The photocatalyst conversion efficiency of this catalyst in the visible light region is also significantly enhanced.

According to the following formula (1) and the incident light intensity obtained by the Si photoelectrode, Figure 3 converts the relationship between the photocurrent response and the photon energy, as shown in Figure 5.

\[
\frac{I_{ph}}{I_0} = A (hv - E_g)\]

(1)

Where $hv$ is the photon energy, $I_0$ is the light intensity of the incident light, and $n$ is determined by the transition form of electrons between the valence band and the conduction band, for amorphous semiconductors, when the incident light photon energy is greater than its bandgap, the value is same as the indirect transition of the crystalline semiconductor, that is $n=2$, $A$ is a constant, and $E_g$ is the bandgap width of the characteristic oxide phase. From the figure, it can be seen that TNTs and TNTs-In have only one oxidation phase energy band width. This is 3.18 eV, which corresponds to the band width of the anatase TiO$_2$, but after oxidation, the sample shows two oxidized phases of about 3.08 eV and 2.20 eV respectively.

**Figure 3.** The photocurrent responses plots of TiO$_2$ nanotubes modified by In and its oxide

**Figure 4.** IPCE spectra of TiO$_2$NTs modified by In and its oxide
2.3. Analysis and Discussion

The preparation process of the catalyst is shown in figure 6(a). A TiO$_2$ nanotube array film was prepared by electrochemical anodic oxidation. After annealing, In and In$_2$O$_3$ nanofibers were deposited in the film and on the surface and were formed In/In$_2$O$_3$/TiO$_2$ nanotube array heterojunction composite semiconductor catalyst.

Through the above experimental data analysis, the prepared reducibility In modified materials can not promote the photocurrent response of TiO$_2$ nanotube arrays, but instead reduce their photocurrent response. This may be because excessive elemental In has become a recombination center of photoelectrons and holes. The recombination center reduces the efficiency of photocarrier separation, resulting in a decrease in photoresponse. At the same time, these single In materials do not change the energy band gap width of TiO$_2$ nanotube arrays. However, after the oxidation, the photo-response is enhanced in both the UV and visible regions. On the one hand is due to semiconductor band theory; surface modification can form an additional energy level [27] in the original bandgap of TiO$_2$. The conduction band of TiO$_2$ is close to In doping level [28], and the electron transfer reaction mechanism is shown in figure 6(b). Through the above experimental data, it can be seen that the width of the semiconductor band after modification is reduced from 3.18 eV to 3.08 eV. It can be known from the XPS data that after the modified material is oxidized, the content of elemental In is smaller (9.4%), the introduction of a small amount of elemental In energy level in the band gap of TiO$_2$ enables photons with lower energy to excite electrons and holes which are trapped at the impurity level, causing red shifting of the absorption band edge of TiO$_2$, thereby broadening the absorption range of light by the semiconductor and at the same time the separation efficiency of photogenerated carriers is promoted, improve the utilization of photons; On the other hand, the reason is that oxidation generates In$_2$O$_3$ semiconductors (theoretical $E_g$=2.8 eV) can absorb visible light. The new energy band width is obtained from figure 4, which can calculate as $E_g$=2.2 eV. This may also be due to the effect of a small amount of elemental In on the In$_2$O$_3$ energy band, the In$_2$O$_3$ energy band width is reduced, and the absorbed light is further red shifted, and the sample is oxidized to form a heterojunction composite structure semiconductor catalyst In/In$_2$O$_3$/TNTs, which further improves the utilization of visible light and promotes photogenerated carrier separation.
Figure 6(a). A schematic illustration of the synthesis process and structure of the catalyst and (b) a reaction mechanism diagramed for charge transfer in the In/In$_2$O$_3$/TNTs photoanode.

3. Conclusion
Based on the above analysis, the TiO$_2$ nanotube array modified by reducing element In, although the carrier concentration is the highest, the single indium becomes the recombination center of photoelectrons and holes, it makes the photocurrent weakened; the TiO$_2$ nanotube arrays modified by the oxidation state of indium, form a heterojunction composite catalyst with TiO$_2$ nanotube arrays under the combined action of In$_2$O$_3$ and a small amount of elemental In, resulting in a reduction in the band width of the semiconductor catalyst and the photocurrent response enhancement in both the ultraviolet and visible regions. The modified material is conducive to light carrier separation and absorption of visible light. However, the modified materials make the flat band potential of the semiconducting catalyst become positive and reduce the reducibility of the photoelectron transition to the conduction band.

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