Cr₂O₃ Nanoparticles Modified TiO₂ Nanotubes for Enhancing Visible Photoelectrochemical Performance

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TiO₂ nanotube arrays modified by nanoparticles Cr₂O₃ with high sensibility in the visible spectrum were prepared by annealing the anodic TiO₂ nanotube arrays pre-loaded with Cr(NO₃)₃ solution which was uniformly clung to the TiO₂ nanotube arrays. The influence of the dipping time on the microstructure of the Cr₂O₃/TiO₂-nanotubes was investigated. The microstructure and the elemental analysis were characterized by scanning electron microscope (SEM) and Energy dispersive X-ray (EDX). The photoelectrochemical performances of the as-prepared composite nanotubes were determined by measuring the photogenerated current and voltage under illumination of ultraviolet-visible (UV-vis)/visible light. The TiO₂ nanotube arrays modified by Cr₂O₃ showed higher photocurrent values than those of unmodified TiO₂ nanotube arrays. The enhanced photoelectrochemical behaviors can be attributed to the modified Cr₂O₃ which increases the probability of charge-carrier separation and extends the range of the TiO₂ photoresponse from UV to visible region due to the low band gap of 2.3 eV of Cr₂O₃.

Keywords: TiO₂ Nanotubes, Anodization, Cr₂O₃, Photoelectrochemistry, Visible Light.

1. INTRODUCTION

Since the synthesis of unique, highly ordered TiO₂ nanotube arrays film was reported in 2001,¹ it has been attracting considerable attention over the past several years in photocatalytic degradation of pollutants,^{2–5} solar cell,^{6–8} gas sensor,^{9–11} and photolysis water applications.^{12,13} However, the relatively large bandgap of TiO₂ (3.2 eV) limits the efficiency of photocatalytic reactions due to the high recombination rate of photogenerated electrons and holes formed in photocatalytic process and the low absorption capability for visible light. Many studies have been devoted to the improvement of photocatalytic and photoelectrochemical properties of TiO₂ nanotube arrays, such as doping metal ions,^{4,5,14} non-metal,^{15–17} and semiconductor nanoparticle modification.^{18,19}

Comparatively, modified TiO₂ with transition metal cations is an effective strategy to reduce electron-hole recombination rate and increase photoelectrochemical properties. In particular, Cr₂O₃ is considered to be an interesting dopant of TiO₂ in terms of its semi-full electronic

configuration. Many efforts concerning Cr³⁺ doped TiO₂ focus on the topic of nanoparticle powders or nanoparticle films, including preparation, characterization, dynamics of charge transfer, trapping and recombination, photocatalytic behavior, etc. Hiroshi Irie adopted impregnation method to graft Cr³⁺ onto TiO₂ powder to improve the photocatalytic property under visible light irradiation.²⁰ Lee researched the Cr-doped TiO₂ thin films prepared by RF-sputtering, and demonstrated that such species as-prepared possessed different band gaps on the basis of the difference of the RF-sputtering process parameter.²¹ Wang synthesized Co-doped and Cr-doped mixed crystal TiO₂ powders by sol-gel method and compared their sonocatalytic activities of azo, and they found that both Cr-doped and Co-doped mixed crystal TiO₂ powders exhibit the higher sonocatalytic activity than that of undoped TiO₂ powder.²² Zhang investigated the synergistic effects of C-Cr codoping in TiO₂ and found the sonocatalytic activity was enhanced under ultrasonic irradiation.²³ Awate synthesized Cr containing Ti/MCM-41 and SiO₂-TiO₂ catalysts and found the aqueous eosin can be photo catalytic degraded effectively.²⁴ You found the S/Cr doped mesoporous TiO₂

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obtained via a solid state reaction route possessed high active degradation property under visible light.²⁵ More recently, Wang synthesized natural zeolite supported Cr-doped TiO₂ photocatalysts to improve the recovery and photocatalytic efficiency of TiO₂. They found that the photocatalytic activities of the doped samples strongly depend on the concentration of chromium ions and the calcination temperature.²⁶ All the above experimental results proved that the Cr species can be adopted to enhance the photocatalytic activity.

However, to date, there are little reports on modifying Cr₂O₃ into the highly ordered, self-organized TiO₂ nanotube array films. Specific modified TiO₂ nanotube arrays film nanostructuring is crucial for photolysis or photocatalytic applications, where both optimal material and suitable architecture are required to limit the recombination of photoinduced carriers.²⁷

In this work, we demonstrated for the first time a simple and facile dip-annealing method to modify TiO₂ nanotube arrays film. The TiO₂ nanotube arrays films with different amounts of Cr₂O₃ were obtained by controlling the dip-coating time in the modification process. The effect of Cr₂O₃ on the morphology and photoelectrochemical property of the Cr₂O₃/TiO₂-NTs were systematically investigated.

2. EXPERIMENTAL DETAILS

2.1. Preparation of TiO₂ Nanotube Arrays

The TiO₂ nanotube arrays film on Ti substrate were prepared by using an electrochemical anodic oxidation process reported previously.²⁸ In a typical preparation procedure, Ti foils (99.5% purity, thickness of 250 μm, Alfa-Aesar) were polished and chemically cleaned following with acetone, anhydrous ethanol, and deionized water in an ultrasonic bath and dried in air. Subsequently, Ti foils were anodized at 20 V for 8 h in glycerol/water (75:25 vol.%) containing 0.5 wt.% NH₄F using a platinum foil counter electrode in an electrochemical cell at room temperature.

2.2. Preparation of Cr₂O₃ Modified TiO₂ Nanotube Arrays

Totally, Cr₂O₃ modified TiO₂ nanotube arrays (denoted as Cr₂O₃/TiO₂-NTs) were prepared by using a dip-coating method. In a brief, the amorphous anodic TiO₂ nanotube arrays with Ti substrates were held vertically in 1 M Cr(NO₃)₃ solution added 4 vol.% ethylene glycol, 6 vol.% acetone agitated with an ultrasonic wave. The dipped duration were kept at 60 s, 90 s, 120 s, respectively. In order to obtain uniform mixed solution, Cr(NO₃)₃ solution was oscillated using an ultrasonic bath before the dipping process. The aim of adding some ethylene glycol and acetone to the dipping solution mentioned above is to keep a appropriate viscosity of the solution used. All the as-prepared samples were subsequently calcinated at 450 °C

in air ambient for 3 h with heating rate of 5 °C/min to induce crystallization.

2.3. Characterization of Catalysts

The morphologies of the nanotube arrays film were observed using a field emission scanning electron microscope (FESEM, JEOL-JSM-6700, Japan). Energy dispersive X-ray (EDX) spectrometers attached to the electron microscopes were used for elemental analysis. The UV-vis absorption spectra of the species were recorded using a UV-vis spectrometer (Hewlett-Packard 8453).

2.4. Photoelectrochemical Measurements

Photoelectrochemical studies were carried out using a CHI(900B) analyzer in a three electrode configuration with the Cr₂O₃/TiO₂-NTs electrodes as working electrode with 0.2 cm² geometrical area exposure to electrolyte solution, a platinum gauze counter electrode and a Ag/AgCl reference electrode. 1 M KOH solution was used as the electrolyte. Light irradiation was performed through the electrolyte solution using a 150 W Xe lamp with an incident light intensity of about 100 mW/cm². A UV cutoff filter (> 420 nm) was used for visible light irradiation.

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization

Figure 1(a) shows a representative SEM image of the as-synthesized TiO₂ nanotube arrays. It is clear that the average pore diameter as calculated from SEM images is approximately 120 nm with a standard deviation of 8 nm, wall thickness of around 30 nm with a standard deviation of 5 nm. Figures 1(b)–(d) show the SEM images of Cr₂O₃/TiO₂-NTs films prepared by dipping the as-prepared TiO₂ nanotube arrays films in the 1 M Cr(NO₃)₃ solution electrolyte containing 4 vol.% ethylene glycol, 6 vol.% acetone with 60 s, 90 s, 120 s, respectively. As can be seen, Cr₂O₃ were efficiently deposited onto the top surface of the TiO₂ nanotube arrays. From Figures 1(b), (c), the morphology of the modified sample are still with the nanostructure of nanotube arrays. As observed, when the dipping time of 60 s was used in the modification process, the loaded Cr₂O₃ nanoparticles are rare and only covered small part of the TiO₂ nanotubes, and a small amount of Cr₂O₃ nanoparticles was deposited into the inner of the TiO₂ nanotubes without clogging the channels (Fig. 1(b)). It is noteworthy, when the dipping time reaches 90 s (Fig. 1(c)), the amount of the loaded Cr₂O₃ nanoparticles increased a lot, covering much part of the TiO₂ nanotubes, and a greater amount of loaded Cr₂O₃ nanoparticles entered into the interior of the TiO₂ nanotubes. With the dipping time increased to 120 s, as seen in Figure 1(d), the vast majority of TiO₂ nanotubes has been covered by the loaded Cr₂O₃ nanoparticles. The loaded Cr₂O₃ on the surface of the TiO₂ nanotube arrays forms the flower-like crystals of about 50 nm in

Figure 1. Surface-view SEM images of: (a) unmodified TiO₂ nanotubes, (b)–(d) Cr₂O₃/TiO₂-NTs prepared with dipping time of 60 s, 90 s, 120 s, respectively.

size. Efforts to extend the amount of deposited material by prolonging the dipping time for 120 s resulted in a noticeably denser coverage of the surface. The nanotubes morphology of the modified sample here are not typical nanotubular compared to Figures 1(b) and (c).

It is worth noting that, in these modified process, the Cr₂O₃/TiO₂-NTs are still with orientation characteristics without losing their architectures after the annealing process. There are no obvious breakage and collapse in the nanotubes with the modified samples. Besides, the nanotubes wall gets thicker after annealing due to the crystallization and crystal growth (Figs. 1(b)–(d)). The inset in Figure 1(d) is the image at a lower magnification. As can be seen, there are still some part of nanotubes which are not covered by the Cr₂O₃ coating.

The incorporation of Cr in/on TiO₂ nanotube arrays was further demonstrated by EDX which exhibited the

Figure 2. EDX spectrum of Cr₂O₃/TiO₂-NTs sample with a dipping time of 90 s.

presence of Cr element in the bulk of the TiO₂ nanotube arrays besides Ti and O (Fig. 2).

3.2. UV-Vis Absorption Spectra Analysis

The effect of Cr incorporating on the light absorption characteristic of TiO₂ nanotube arrays is shown in Figure 3. The onset of the absorption for TiO₂ nanotubes is at ca. 390 nm, which is consistent with the intrinsic bandgap absorption of anatase TiO₂. It is apparent that for Cr₂O₃/TiO₂-NTs samples, the bandgap edges were shifted toward more the visible light region (red shift) and the

Figure 3. UV-vis absorption spectra of the TiO₂ nanotube arrays before (a) and after Cr₂O₃ loaded with different dipping time, (b) 60 s, (c) 90 s, (d) 120 s.

absorption in the visible light region was significantly enhanced with the increase of the dipping time due to the low band gap of Cr₂O₃ (2.3 eV). The origin of visible light sensitivity in Cr₂O₃/TiO₂-NTs samples can be ascribed to the appearance of additional energy levels such as Cr 2p level and oxygen vacancies within the band gap of TiO₂ due to the existence of Cr₂O₃. The red shift of the absorption edge and enhanced visible light absorption can also be attributed to a sub-band-gap transition between the 3d electrons of Cr³⁺ → Ti⁴⁺ or ⁴A_{2g} → ⁴T_{1g} of Cr³⁺ and ⁴A_{2g} → ⁴T_{2g} *d-d* transitions of Cr³⁺ giving rise to a band center at about 700 nm.^{29,30}

3.3. Photoelectrochemistry of Unmodified TiO₂ versus Cr₂O₃/TiO₂-NTs

The photoelectrochemical properties of the unmodified TiO₂ versus Cr₂O₃/TiO₂-NTs were studied by means of linear sweep voltammetry. Figure 4 shows the photocurrent density versus applied electrode potential curves under the visible light irradiation. The potential was increased gradually (5 mV/s) from the open circuit condition until 1.0 V. The electrolyte used in this photoelectrochemical study was 1 M KOH solution. As can be seen from Figure 4, the photocurrent density of the unmodified TiO₂ nanotube sample under visible light irradiation is very small (-6.80×10^{-4} mA/cm² at 0 V) and can be ignored compared to the Cr₂O₃/TiO₂-NTs samples which indicated that TiO₂ possessed little activity under the visible light irradiation, consistent with the intrinsic high bandgap absorption of TiO₂.

For the three modified samples here, the photocurrent density reached almost a stable value at potentials more anodic than 0 V. After modified with a dipping time of 60 s, the photocurrent density became higher than that of the unmodified sample. When a dipping time of 90 s was adopted, the photocurrent density of the

Cr₂O₃/TiO₂-NTs sample increased a lot compared to the sample modified with 60 s, showing the maximum photocurrent density (e.g., -0.0738 mA/cm² at 0.2 V). The increase in the photocurrent density could be correlated to the photo induced open circuit potential (zero-current potential) which became more negative (-0.75 V) with the modification of Cr₂O₃. The open circuit potential for the as-prepared TiO₂ is -0.47 V. The photocurrent is from the photogenerated electrons in the conducting bands of Cr₂O₃ and TiO₂ with leaving holes in their valence bands under Xe-lamp irradiation. However, with a further dipping time of 120 s, the current profile showed a smaller photocurrent density in the entire range of applied potentials compared to that of the sample with a dipping time of 90 s.

Figure 5 shows the photocurrent density versus applied electrode potential curves under UV-vis light irradiation. As can be seen, the trend of the curves was similar to the curves tested under only the visible light irradiation. The Cr₂O₃/TiO₂-NTs samples possessed a much higher photocurrent than that of the unmodified TiO₂ nanotubes. The sample modified with a dipping time of 90 s showed the highest photocurrent. However, when the dipping time reaches 120 s, the photocurrent goes down, which agrees with the phenomenon in Figure 4, suggesting that 90 s duration is the optimal modifying time.

A proposed mechanism for the enhanced photoelectrochemical performances of the Cr₂O₃/TiO₂-NTs is shown schematically in Figure 6. Under UV-vis irradiation, electrons can be excited from the valance band (VB) to the conduction band (CB) of the anatase when a photo with higher energy is absorbed, which leaves behind an charge vacancy (hole) in the VB. In the absence of the Cr₂O₃, most of these charges quickly recombine without any valuable utilization. The band gap of Cr₂O₃ is 2.8 eV. When Cr₂O₃ nanoparticles are attached to the surface of the TiO₂ nanotubes, the relative position of the Cr₂O₃ CB edge

Figure 4. Variation of photocurrent density versus applied electrode potential in 1 M KOH under visible irradiation for the TiO₂ nanotube sample and the Cr₂O₃/TiO₂-NTs sample, with a dipping time of 60 s, 90 s, 120 s, respectively.

Figure 5. Variation of photocurrent density versus applied electrode potential in 1 M KOH under UV-vis irradiation for the TiO₂ nanotube sample and the Cr₂O₃/TiO₂-NTs sample, with a dipping time of 60 s, 90 s, 120 s, respectively.

Figure 6. Schematic diagram of a proposed model for Cr₂O₃ enhanced photoelectrochemical performances of the TiO₂ nanotubes.

permits the transfer of electrons from the TiO₂ surface, which allows a charge separation, stabilization, and therefore hinders recombination. Meanwhile, Cr₂O₃ can also absorb photons with lower energy and excite photoelectron from VB to CB. Those photoelectrons can be shuttled freely along the oriented TiO₂ nanotubes driven by the bias voltage, leading to the enhanced photoelectrochemical performances of the composites Cr₂O₃/TiO₂-NTs.

However, the probability of the photogenerated electron–hole recombination is also increased when Cr₂O₃ modifying amount exceeds a certain level, and the reason is that not all the photoelectrons on the nanoparticles can be scavenged in time by the bias voltage. Under this condition, Cr₂O₃ may act also as the recombination centers of the photogenerated electrons and holes, resulting in a decrease in photoactivity with high Cr₂O₃ content which is unfavorable to photoelectrochemical performances as shown in Figures 4 and 5. Therefore, the optimum modified process is with a dipping time of 90 s.

4. CONCLUSION

This work demonstrates for the first time an efficient Cr₂O₃ modified highly ordered TiO₂ nanotube array with a annealing method. The Cr₂O₃/TiO₂-NTs results in a negative shift of the zero-current potential from -0.47 V to -0.75 V under visible light irradiation, and a significant increase in the photocurrent. The maximum photocurrent is obtained with a dipping time of 90 s used. The increased photoelectrochemical behaviors can be attributed to the modified Cr₂O₃ which increases the probability of charge-carrier separation and extends the range of TiO₂ nanotube photoactivity from UV to visible region due to the low band gap of 2.3 eV of Cr₂O₃.

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