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Preparation and photocatalytic activities of Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays via an ion exchange adsorption method

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ABSTRACT

A novel photocatalyst, which is composed of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays, was synthesized by combining an anodization method with an ion exchange adsorption method. Resultant products were characterized by X-ray diffraction analysis, scanning electron microscopy and UV–vis absorption spectroscopy. Results indicate that the Sb_2S_3 thin film layer can be well deposited on inside surface of the TiO_2 nanotubes to form the coaxial heterogeneous structure arrays and there is an obvious absorption band peaked at 650 nm with a deposition of the Sb_2S_3 film layer. Furthermore, the photocatalytic activities of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays were also evaluated to exhibit a photodegradation for the methyl orange aqueous solution under UV–visible irradiation, which is mainly attributed to a formation of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays.

1. Introduction

In recent decades, water problem has attracted considerable attention since it has an influence on human lives directly [1–3]. Thus, some conventional techniques, such as physical methods, biological methods, chemical methods, have been extensively studied for water treatment [4–7]. These methods are helpful in the water treatment, but they are high cost, time-consuming, energy-consuming and easily bringing about a secondary pollutant. In order to overcome these tough problems, photocatalysis becomes one of the popular research subjects in the field of water treatment and protection [8–11]. Titanium dioxide (TiO_2) as one of the most important photocatalysts has been widely used for a purification of a wide variety of aqueous organic contaminants due to its high activity, chemical stability, low toxicity and low cost [10–13]. TiO_2 nanotube arrays as a promising photocatalyst are the most investigated nanotube structures. Especially, superior properties of the TiO_2 nanotube arrays, such as good photon-induced properties and facilitating the separation of the photoexcited charges, have been widely applied in photocatalysis [14–16], sensing [17], solar cells [18,19] and electrodes [20]. However, one of the critical drawbacks of TiO_2 is its wide band gap of 3.2 eV, that is, only ultraviolet (UV) ($\lambda \leqslant 390$ nm) light can be absorbed by pure TiO_2. To improve the photocatalytic efficiency, many efforts including coupling with narrow band gap semiconductors, such as PbS [21], CdTe [22], CdS [23–26], and CdSe [26,27], have been carried out to extend the optical absorption into visible-light region. Among them, the coupling of the TiO_2 nanotube arrays (TNAs) with the CdS has been considered to be an important and attractive method because the CdS has a narrow band gap and its conduction band level is higher than that of TiO_2, which usually acts as a visible-light sensitizer and is also responsible for an effective charge separation to suppress a recombination process in the nanojunction [23,24].

Actually, antimony trisulfide (Sb_2S_3) has also received some attention as a potential candidate in solar energy conversion, since its band gap (about 1.78–2.5 eV) covers the maximum span (almost the visible and near infrared range) of the solar spectrum [28–30]. As compared with some other narrow band gap semiconductors such as CdS, Sb_2S_3 has a smaller band gap and a bigger light absorption coefficient. Sb_2S_3 as a novel photocatalyst was synthesized and showed a degradation of Methyl Orange (MO) under visible light irradiation, which has a higher conversion ratio of MO (up to 97%) than that of CdS [31]. Recently, Weller reported that a post-preparative surface treatment can enhance the photostability of the electrodes by using the Sb_2S_3 particles as sensitizers for various nanoporous wide band gap semiconductors [32], and Hodes also successfully obtained the Sb_2S_3 sensitized nanoporous TiO_2 solar cells [33].

Herein, a novel photocatalyst, which consists of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays, was synthesized by an anodization method and an ion exchange adsorption method. The Sb_2S_3 film layer was deposited into inside surface of the

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TiO_2 nanotube to form a coaxial heterogeneous structure. It should be mentioned here that the coaxial heterogeneous structure is such a structure that consists of a matter with a basically coaxial structure, such as tubular and linear structure, and is then deposited with other heterogeneous matter. The as-synthesized specimens were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV–vis absorption spectroscopy. Results indicate that the resultant photocatalysts exhibit a photodegradation activity for Methyl Orange (MO) aqueous solution under UV–visible irradiation. Effects of the Sb_2S_3 content on the photocatalytic activity of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays photocatalysts were also evaluated. Present study is expected to be helpful for overcoming the difficulty of recycling photocatalyst as compared to that of the powder form.

2. Experimental

2.1. Chemicals and materials

Titanium foils (99.5% purity, 0.2 mm in thick) were purchased from General Research Institute for Nonferrous Metals, China. Before the anodization process, they were mechanically cut into small regular pieces (5 × 1.6 cm in area), and then the obtained small pieces of Ti foils were carefully cleaned by foamless eradicator and then degreased by sonication in acetone, ethanol, and distilled water, respectively. Followed the Ti foils were dried in oven at 80 °C for further use.

2.2. Synthesis procedure

2.2.1. Preparation of TiO_2 nanotube arrays

TiO_2 nanotube arrays (TNAs) were synthesized by the anodization method from the electrolyte containing fluorine ions. Two pieces of Ti foils were used in the anodization process, one as the working electrode and the other as the counter electrode. Then, the two electrodes were immersed into the electrolyte, which is composed of 0.5 wt.% NH_4F and 3 vol.% of H_2O in ethylene glycol. The anodic oxidation was carried out at room temperature by applying a voltage of 55 V for 3 h using a DC power supply (Model GPS-3303c, GW Instrument Co., Ltd., Taiwan). Throughout the reaction process, vigorously magnetic stirring was carrying out to ensure a uniform electrolyte solution. After the anodization process, the obtained pale yellow TNAs were first rinsed with the anhydrous ethanol and then soaked them in ethanol for more than 8 h, followed by drying them in oven at 80 °C for another 8 h and calcined at 450 °C in the muffle furnace for 2 h under air atmosphere, thus, the TNAs were prepared and would be used in the next step with further treatment.

2.2.2. Preparation of Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays photocatalysts

The Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays were prepared by the ion exchange adsorption method. 0.005 M of Sb^{3+} solution was obtained by dissolving 0.2852 g antimony chloride ($SbCl_3$) in 250 ml ethanol, and 0.005 M S^{2-} solution was obtained by dissolving 0.3002 g sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) in 250 ml methyl alcohol, both solutions with a vigorous stirring for about 30 min. Then the as-prepared TiO_2 nanotube arrays were successively immersed into the following different solutions for 30 s each, which includes 0.005 M of Sb^{3+} solution, pure ethanol, 0.005 M of S^{2-} solution, and pure methanol, respectively. Then the nanotube arrays film was rinsed with pure ethanol for 30 s or longer to remove excess precursor before the next deposition. Above process was considered as one cycle and different circles were repeated according to the requirement of the thickness of the Sb_2S_3 film layer. Under present experimental conditions, five samples with different circles were prepared and named as 3-Sb_2S_3/TNAs, 8-Sb_2S_3/TNAs, 10-Sb_2S_3/TNAs, 15-Sb_2S_3/TNAs and 30-Sb_2S_3/TNAs, which represent the deposition cycles of 3, 8, 10, 15 and 30 times, respectively. Thus, the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays were obtained after calcined them at 330 °C in the tube furnace for 30 min under nitrogen atmosphere.

2.3. Characterization

Scanning electron microscopy (SEM) was employed to observe the morphological properties of the TiO_2 nanotube arrays and the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays. X-ray diffraction (XRD) analysis was employed to characterize the crystalline properties of the prepared samples, using a D/max-2400 X-ray diffraction spectrometer (Rigaku) with Cu Kα radiation and operated at 40 kV and 100 mA. The scanning speed was 15° min^{-1} at the step of 0.02°. The UV–vis absorption spectra of the resultant samples were obtained by a JASCO Model V-570 UV/VIS/NIR spectrometer with a wavelength range from 300 to 800 nm.

2.4. Photocatalytic activity measurement

The photocatalytic activities of the Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays photocatalysts were evaluated by observing the photodegradation of the MO aqueous solution, using a 500 W high-pressure xenon lamp as the light source. The Sb_2S_3/TiO_2 nanotube coaxial heterogeneous structure arrays samples cut into 1.6 × 2 cm in area were placed in the quartz tubes, with their surface facing toward the emitting light source. No filters were used and thus the continuous UV–visible light was obtained to irradiate the photocatalysts. The MO aqueous solution with a concentration of 20 mg/L was placed in the testing quartz tubes, 10 mL of solution for each. Firstly, the suspension was stirred in dark for 2 h to reach the adsorption–desertion equilibrium. During the illumination process, magnetic stirring was continuously carried out. A 500 W high-pressure xenon lamp, which was placed 10 cm away from the reaction vessels, was then turned on. The system temperature was controlled by a cooling fan. Every 30 min during irradiation, 5 mL of reaction liquid was withdrawn for testing and the solution was measured by the UV–vis spectrophotometer at 465 nm, which is the maximum absorption wavelength (λ_{max}) of Methyl Orange. After the test, the solution was then put back into original container to ensure the invariability of the volume of the reaction liquid.

3. Results and discussion

It is well known that TiO_2 mainly exists in anatase, brookite and rutile phases. Among them, anatase phase has been found to have the best photocatalytic activity. X-ray diffraction was employed to characterize the samples. Fig. 1 shows the XRD pattern of the TNAs calcined at 450 °C for 1 h under air atmosphere. It can be seen that the as-prepared TNAs are well crystallized after the heat treatment and these characteristic peaks match well with the refection planes of the anatase phase, which include (101), (004), (200) and (105) plans. Fig. 2 shows the XRD patterns of the Sb_2S_3 film deposited on glasses. The two curves represent the XRD patterns of the samples obtained after (Fig. 2a) and before (Fig. 2b) the annealing treatment, respectively. The annealing treatment was carried out at 330 °C for 30 min under Ar atmosphere. As shown in Fig. 2b, no obvious diffraction peak is observed before the annealing treatment, indicating that the Sb_2S_3 film has an amorphous phase property. However, the Sb_2S_3 film can be well crystallized after the annealing treatment and the single phase of the Sb_2S_3 film (JCPDS No. 42-1393) can be obtained, which corresponds to the stibnite crystal phase. Based on the above results, it can be concluded that the Sb_2S_3 film can well crystallize at 330 °C for 30 min. The well-organized crystallization of the Sb_2S_3 film is expected to be beneficial to the photocatalytic activity of the samples.

Morphological properties of the as-prepared nanotube arrays attached on the Ti metal plate, which include the surface and the side face, were observed by SEM. Fig. 3 shows the SEM images of the samples and reveals the well aligned nanotube arrays with a diameter of about 125 nm (Fig. 3a) and a length of approximately 16 μm (Fig. 3b) can be successfully obtained via the conventional electrochemistry anodization process. It is worthy to note here that the diameter and length of the TiO_2 nanotube can be controlled by the anodization conditions, such as applied potential, oxidation time, oxidation temperature and electrolyte. By comparing Fig. 3a and c, it can be seen that the Sb_2S_3 film layer can be effectively deposited to inside surface of the TiO_2 nanotube arrays by the ion exchange adsorption method with a deposition circle of 8. Especially, the top of the nanotubes is still open, indicating that well-ordered pore structure can be maintained. The inset of Fig. 3c, which is the partial enlarged SEM image of Fig. 3c, shows the morphology of the Sb_2S_3-deposited TiO_2 nanotube arrays. By comparing its tube inner diameter and wall thickness with Fig. 3a, it shows a very thin deposition layer grown on the tube wall surface. These results suggest that the deposition process with a suitable deposition circle of the Sb^{3+} and S^{2-} does not damage the ordered TiO_2 nanotube arrays structure and prove that our obtained samples have the coaxial heterogeneous structure. However, when the deposition circle is increased up to 30, the top of the nanotubes is almost covered by the Sb_2S_3 film layer as shown in Fig. 3d, thus,