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Structure, chemical state and photocatalytic activity of TiO_{2-x} nanostructured thin films by glancing angle deposition technique

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ABSTRACT

Nonstoichiometric titanium dioxide nanostructured thin film (TNF) has attracted a range of interest in the green energy field. In this paper, we introduce the glancing angle deposition (GLAD) technique to produce the amorphous TNFs with discrete nanoscale columnar structures. In order to improve the crystallinity and/or gain the Ti^{3+} doped states, amorphous TNFs were annealed at 400 °C in air or H_2. XRD, SEM, AFM, XPS and PL were used to characterize the crystallization structure morphology, chemical state, PL properties of the TNFs with different annealing conditions. Photocatalytic activities of the samples were reflected by decolorization experiments of methylene blue (MB) solution irradiated by the simulated sunlight light of AM 1.5 G. The photocatalytic activity of amorphous TNF is higher than that of conventional TiO_2 thin film, indicating the prominent properties of nanostructures. Compared with annealing in air, the photocatalytic activity of TiO_{2-x} nanostructures annealed in hydrogen is further increased and higher. The results demonstrated that Ti^{3+} and oxygen vacancies were beneficial and played the dominant role for the enhancement of photocatalytic activity.

1. Introduction

Due to the large surface-to-volume ratio, availability, low cost, non-toxicity and high chemical stability, titanium dioxide nanostructured thin film (TNF) has motivated more and more researchers to active in photo-catalytic performance [1]. For producing the TiO_2 nanostructured materials, a wide variety of fabricating methods, including the sol–gel approach [2], hydrothermal [3,4], electrospinning methods [5], atomic layer deposition [6,7], and anodization [8] etc. have been reported. Taking full advantage of chemical synthesis methods, one can obtain the relatively budget and facile one-pot routes to quickly produce titanium oxide nanostructures. Nevertheless, these chemical synthesis routes could cause TiO_2 nanostructures with the defects of low-purity [4], large mechanical instability [9] and low crystal quality [10]. The physical vapor deposition technique is beneficial for the fine adhesive force and high crystallinity of the TiO_2 nanostructures.

As a miscellaneous nanostructured thin film preparation technique based on the self-shadowing effect, the glancing angle deposition (GLAD) technique could produce the unique characteristics including topological sculptured thin film, hetero-nanostructure design and constituent adjustment [11]. The inclined incident particles will lead to nanostructured films with titled, zigzag and helical nanorods structures [12–15]. The height, diameter and the length of nanorods can be tailored by the substrate rotation speed and the deposition rate. These outstanding technical properties of GLAD can more accurately control the morphology of the nanostructure than the chemical synthesis methods. Motofumi Suzuki et al. [16] demonstrated the optimum morphology for photocatalytic activity of TiO_2 sculptured thin film could be available at the deposition angle $\varphi = 70°$, irrespective to shape of columns such as zigzag, cylinder and helix. Wilson Smith et al. [17,18] studied the photocatalytic activities of WO_3/TiO_2 and Cr: TiO_2 nanorods fabricated by the GLAD technique.

Recently, self-doped (Ti^{3+} and/or oxygen vacanies) TiO_{2-x}

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[19–21] has been reported as an effective material to extend the light absorption [22] due to localized oxygen vacany states from 0.75eV to 1.18eV below the conduction band [20]. Diffenence from the conventional doping methods (incorporating metal ions, nonmetal or rare earth elements) [23,24], oxygen vacanies (or Ti^{3+} ions) as the self-doping style introduce none impurity elements [25]. It is very advantageous to maintain the intrinsic TiO_2 phase and reduce the recombination of electron-hole pairs. Several techniques have been adopted to produce TiO_{2-x} including heating TiO_2 under vacuum or reducing conditions (H_2, CO etc.), high energy particle (laser, electron, or r-ray etc.) bombardment [26]. The high energy particle irradiation methods are much restricted and unsuitable for large-scale production because of the high cost and complicated procedures. Fan Zuo et al. [20] fabricated partially reduced TiO_2 powder by the reducing gas and studied its enhanced hydrogen production activity. Xiaobo Chen et al. [21] demonstrated a conceptually different approach to enhancing solar absorption by introducing disorder and Ti^{3+} vacanies in TiO_2 nanocrystals surface through hydrogenation. Alberto Naldoni et al. [27] studied the effect of nature and location of defects on bandgap narrowing in black TiO_2 nanoparticles obtained through one-step reduction process i.e. annelaing treatment in H_2 stream. In aggregate, annealing in reducing atmosphere is a practical and available technique. All of these papers cited study the TiO_2 powders, however, a post-filtration procedure must be required for recovering the powder dispersion from the reacted water [28]. In addition, the unclear detailed structure, chemical state comparison after hydrogenation as well as the machanism of high photoactivity are still not clear. Therefore, studing the structure, chemical states and photocatalytic activity of self-doped TiO_{2-x} nanostructured thin films deposited by GLAD is necessary and meaningful.

In this paper, amorphous TNFs were deposited by the GLAD system. Amorphous TNFs were annealed at 400 °C in air and H_2 to improve the crystallization and gain the Ti^{3+} doped states. TNF annealed in H_2 shows excellent stability with the faint yellow color storage in ambient for one year. The changes of morphology, crystallization structure, Ti/O chemical state, PL properties and surface modification of TNFs with different annealing treatments have been characterized and discussed. Photocatalytic activity of TNFs has been reflected by decolorization of methylene blue (MB) solution irradiated by full solar irradiation at AM 1.5 G. The MB decolorization rate of amorphous TNF is higher than that of conventional TiO_2 thin film with 0° deposition. TiO_{2-x} nanostructured thin films annealed in H_2 exhibit higher photocatalytic activity than that annealed in air, which indicated the ratio of Ti^{4+}/Ti^{3+} in samples controls the photocatalytic efficiency. In this paper, we give a comprehensive understanding of TNFs annealed under different thermal treatment conditions and highlight the designing novel TiO_{2-x} nanostructured thin film.

2. Experimental section

2.1. Preparation of TNFs

Amorphous TNFs were fabricated with the GLAD system based on the electron beam deposition technique, which could be interpreted in the literature [11,15,29]. During the deposition process of GLAD, the inclined substrate controlled by two step-motors results in a self-shadowing effect, resulting in the orientation growth of the protrusion towards the incident vapor. Prior to deposition, the prepared fused silica glass substrates were ultrasonically cleaned in acetone and ethanol for 30 min. The deposition angle φ i.e. the angle between the incident particle flux and the substrate normal was fixed to be 70°. With the 1.5×10^{-5} Torr background pressure of the vacuum chamber, the pure oxygen with a 200 sccm gas flow rate was filled in the vacuum chamber for achieving the 2 mTorr working pressure. Without the substrates rotation and heating, the granular TiO_2 material (purity 99.99%) completely premelted was evaporated to the substrate surface with the 27 cm evaporation distance. Amorphous TNFs as-deposited were annealed to improve crystallization in the muffle furnace. In view of our previous the results [15,29], the annealing conditions are set to 400 °C for 2 h in air or H_2. The samples are labeled TNF as-grown, TNF 400 °C and TNF 400 °C H_2, respectively.

2.2. Characterizations

The morphologies of samples were characterized by the Hitachi S-4700, Auriga, Carl Zeiss field emission scanning electron microscopy and Veeco Dimension 3100 atomic force microscope. The X-ray diffraction (XRD) structures of TNFs were characterized with Empyrean PANalytical X-ray diffractometer (Rigaku D/MAX-2550 with Cu Kα, λ = 1.5408 Å) within 20°–80° range. Raman spectra were measured using a Renishaw Invia Raman Spectrometer with a 532 nm wavelength laser for exciting samples. The optical properties of TNFs were measured by the Lambda 900 spectrophotometer within the range from 300 nm to 800 nm. The K-Alpha Thermo Scientific X-ray photoelectron spectroscopy (XPS) with the Al Kα emission at 1486.6 eV was performed to characterize the Ti ions chemical binding energy of samples. PL measurements were obtained using a 350 nm excitation light of 4 mW Kr ion laser. The scattered light was reduced with a long-pass filter, and the emission spectra were probed with a single monochromator and CCD detection using backscattering geometry.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the samples are reflected by decolorization of methylene blue (MB) aqueous solutions at ambient temperature under illumination of AM 1.5 G at 200 mm from the reactor. The initial concerntration of MB solution was 10 mg/L MB. Prior to irradiation, the MB solution were magnetically stirred in the dark for 120 min to ensure the adsorption/desorption equilibrium of MB on the photocatalyst. The solution samples were collected from the reactor at once every 30 min intervals, and analyzed to determine the amounts of residual MB after photo-irradiation.

3. Results and discussion

3.1. Structure analysis

XRD diffraction patterns of TNFs are shown in Fig. 1. Amorphous films as-deposited can be achieved with the noncrystalline and unheated fused silica glass substrates. The amorphous TiO_2 films annealed at around 350 °C in air transformed into the anatase phase. In view of our previous results [15,29], TNF was annealed under 400 °C in air for 2 h to achieve the best crystalline and morphology structure. The average crystallite sizes of samples could be calculated by the Scherrer's formula according to $D = K\lambda/B\cos\theta$, where the B is the peak width at half maximum of the XRD peak, K is the constant equal to 0.89, λ is equal to 1.54059 Å, and θ is the reflection angle. The average crystallite sizes of TNF 400 °C is 103 Å. However, the XRD pattern of TNF 400 °C H_2 exhibits the very weak and broad anatase A(105) peak and another undefined peak, which is contributed to the lack of oxygen. Therefore, different atmospheres could affect the cooperative atom diffusion, causing the different crystal qualities.

Raman spectroscopy as a local probe is a sensitive spectrum technology to measure molecular vibration, which could detect the