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Enhanced Photoelectrocatalytic and Photoelectrochemical Properties by High-Reactive $TiO_2/SrTiO_3$ Hetero-Structured Nanotubes with dominant {001} Facet of Anatase TiO_2

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ABSTRACT

High-reactive TiO_2 crystals with controllable facets have been widely investigated in photocatalysis, photoelectrocatalysis, solar energy conversion and other related fields due to their unique structure-dependent properties. In this work, high-reactive $TiO_2/SrTiO_3$ (TSr) hetero-structured nanotubes with dominant TiO_2 {001} facet are fabricated in a $Sr(OH)_2$ solution by varying the hydrothermal time, utilizing anodizing TiO_2 nanotubes on a Ti substrate as both a “structure-directed” template and an initial reagent to obtain these hetero-structured composites. Based on XRD, FE-SEM with EDS, FE-TEM, XPS and Raman characterization, the high-reactive TSr hetero-structured nanotubes with dominant {001} facet of anatase TiO_2 are definitely synthesized and well-dispersed, crystallized $SrTiO_3$ are acquired on the surface of TiO_2 nanotubes after the hydrothermal treatment. Compared with the reference TiO_2 nanotubes, transient photocurrent (*I-t*) and open circuit voltage (*V-t*) measurements indicate that the photoelectrochemical properties of these resulting composites are distinctly enhanced by controlling the hydrothermal time to regulate $SrTiO_3$ coverage on the surface of nanotubes. In particular, photoelectrocatalytic (PEC) degradation of “target molecules” MB are further implemented to evaluate their PEC activities, and these data reveal the significant improvement of their corresponding activities over the reference TNT2, and this $TiO_2/SrTiO_3$ composite with the hydrothermal time of 30 min (TSr3) possesses the highest PEC rate of 99.93% for MB after the degradation of 20 min. These above results are attributed to the high-reactive TiO_2 {001} facet of $TiO_2/SrTiO_3$ interior and the hetero-structured interfaces by $SrTiO_3$ generated on TiO_2 nanotubes in a hydrothermal process. In addition, the mechanism of PEC degradation is also simply discussed in comparison to the relevant photocatalytic (PC) and electrocatalytic (EC) reaction. This work demonstrates that a synergetic mechanism between high-reactive {001} facet of anatase TiO_2 and hetero-structured characteristics contributes to enhancing their PEC activities and according photoelectrochemical properties, which can be extended to other binary compounds with high-reactive facets.

1. Introduction

Since the endeavor of Fujishima and Honda on the TiO_2 photocatalyst in 1972 [1], nano-structured TiO_2 electrode, as the one of the promising photocatalytic (PC) materials, has extensively investigated due to its exceptional advantages, such as low cost, chemical stability, environmental friendship and outstanding oxidization ability. During the last decades, the electrode design, based on nano-engineering technology, was rapidly developed to improvement the reactive efficiency of photoelectrochemical cell, and these relevant works made great efforts in increasing the reactive sites, intensifying the charge transfer/transport and reducing the electron/hole combination. TiO_2 physicochemical activities are mostly affected by intrinsic electronic structures and their size, shape, organization, and surface properties, such as reactive crystal facets. During the crystal growth processes of equilibrium conditions, the high-active facets of TiO_2 crystals are prone to diminish quickly and spontaneously evolve into specific shape with exposed low-active {101} facets ($0.44\,J/m^2$ for {101} $< 0.53\,J/m^2$ for {100} = {010} $< 0.90\,J/m^2$ for {001}) to minimize the

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total surface free energy. Thereupon, the controllable fabrication of anatase TiO_2 crystals with exposed high-active facets is becoming an urgent challenging, followed by exploiting their improved surface properties for photoelectrocatalytic (PEC) and related applications. In 2008, Yang et al. elaborately designed anatase TiO_2 single crystal with 47% {001} facet [2], and the following endeavor highlighted anatase TiO_2 with exposed {001} facet-based fabrication and applied research in photocatalysis, solar cells and lithium ion batteries [3–6]. These results implied that the high activities of {001} facet are primarily described to dissociatively adsorb water to form hydrogen peroxide and peroxide radicals. Recently, TiO_2 nanotube (TNT) arrays with dominant high-reactive {001} facet of anatase TiO_2, grown on a Ti substrate by anodization, revealed the prominent photoeletrochemical properties because the characteristic architectures afforded unidirectional electric channels for the transport of photo-generated electrons. The improved transport properties prolonged the electron diffusion length and retarded the charges combination [5,6].

The positive coupling effect of the hetero-structured composites, combining TiO_2 and other PC semiconductors is always considered as one of the effective approaches to promote TiO_2 reactive properties. The structures directionally migrate the photo-generated charge carriers transfer at the hetero-structured interface to retard their recombination, and, thus, heighten the photoelectrochemical properties in comparison to reference TiO_2 [7]. Among them, $SrTiO_3$, a well-known perovskite semiconductor with the band gap of 3.2 eV is widely investigated in photocatalysis, dye-sensitized solar cells and other applications. In contrast to TiO_2, $SrTiO_3$ has the similar electronic structure and band gap, and $SrTiO_3$ has good PC degradation ability for organic pollutants. More importantly, the conduct band (CB) of $SrTiO_3$ is 200 mV more positive than that of TiO_2, inducing the shift in the Fermi level to a more negative potential. The hetero-structured configuration provides a favorable energy of photocatalysis and sequentially contributes to the improvement of photo-generated charges separation [7–16]. Several groups have already reported that the hetero-structured $TiO_2/SrTiO_3$ (TSr) nanotubes under UV irradiation exhibited the strengthened PC and photoelectrochemical performance since the resulting hetero-structured interface can stimulate the orienting transfer of charge carriers and further reinforce their separation [15,17,18]. Furthermore, three-dimensional nanostructures, which provide an efficient current path, is becoming a fascinating path to advance their PEC and photoelectrochemical performance [8,13,15].

Advanced photoelectrochemical oxidation has been proposed as an alternative method to eliminate environmental organic pollutants and toxic compounds, and the PEC degradation, combining PC and electrocatalytic (EC) processes, is referred to as electrochemically assisted PC degradation via an applied external potential, resulting in the photo-generated electrons continuously extracted from the anode by the external circuit and, thereby, intensifying the photo-generated electron/hole separation [19]. One crucial factor of PEC process is to assemble an electrode material which possesses remarkable optical and electrical catalytic properties simultaneously. TiO_2, which can undertake the double features in PEC degradation, had also been definitely demonstrated in these PEC applications [20–24]. In particular, high-reactive anatase TiO_2 with dominant {001} facet [3,4,25–30] and hetero-structured TSr composites [7,8,13–15] can significantly promote their PC activity and photoelectrochemical properties. Besides, a TNTs/Ti electrode, whose films are coated on a Ti substrate, indicates a better PEC activity due to the less impedance between TNT arrays and a Ti substrate [31]. As a consequence, the affirmative cooperation, derived from the high-active {001} facet of anatase TiO_2 and the coupling composites of TiO_2 and $SrTiO_3$, is expected to realize the enhanced PEC and photoelectrochemical properties by using the high-reactive TSr composites.

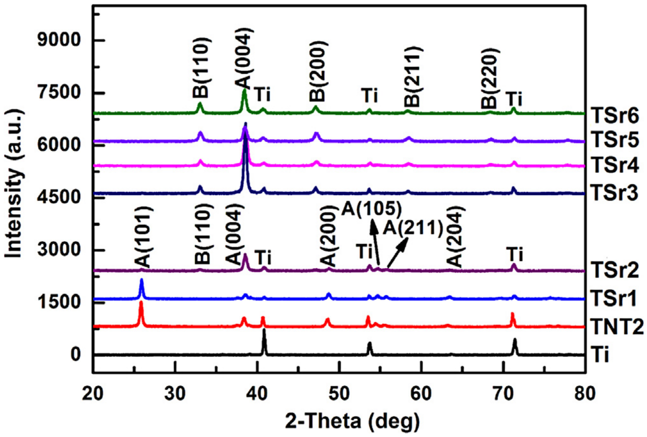

Fig. 1. XRD patterns of the hetero-structured composites and reference TNT2, Ti substrate; A, B signifies anatase TiO_2 and perovsikte $SrTiO_3$, respectively.

Herein, according to the optimizing synthesis condition of our previous work [32], the hetero-structured TSr nanotubes with high-reactive {001} facet of anatase TiO_2 were fabricated via a conventional anodization and a hydrothermal treatment with the time from 0 min to 60 min, followed by annealing at 450 °C. Based on XRD, FE-TEM, FE-SEM with EDS, XPS and Raman characterizations, this work highlighted the fabricating mechanism of the high-reactive TSr nanotubes and the effect of hydrothermal time on their according PEC and photoelectrochemical properties by transient photocurrent (*I*-*t*), open circuit voltage (*V*-*t*) measurement, and PEC degradation of MB. These above results indicate that their outstanding PEC properties are attributed to the synergetic effect of high-reactive {001} of anatase TiO_2 and the positive coupling of TiO_2 and $SrTiO_3$ in comparison to reference TiO_2 nanotubes.

2. Experimental Section

2.1. Fabrication of hetero-structured $TiO_2/SrTiO_3$ nanotubes with high-reactive {001} facet of anatase TiO_2

Well-aligned TiO_2 nanotube arrays on a Ti substrate was fabricated via traditional anodizing method according to our published report [33]. Prior to anodization, a Ti substrate was ultrasonically treated in anhydrous ethanol, isopropanol, and distilled water for 10 min, respectively, and the subsequent anodization at a direct current of 60 V was executed in a two-electrode electrochemical system with a Ti substrate (0.5 mm, 1.0 cm × 4.0 cm, 99.7%) as the anode and a Pt silk (99.7%) as the cathode. The whole process was divided into the pre-treatment and re-anodizing parts, a Ti substrate was firstly anodized 30 min and then removed the as-formed thin film from the substrate in an ultrasonic cleaner, and the pre-treated substrate with similar "hexagon" patterns, which is used as the template, was re-anodized in this electrochemical system for 2 h, and the resulting TNT arrays were marked as TNT2.

The resulting TNT2 with a Ti substrate is used as a "structure-directed" template and an initial reactant to fabricate the hetero-structured TSr nanotubes in a typical hydrothermal solution. The above anodizing Ti substrate was vertically fixed in a 50 mL of Teflon-lined stainless steel autoclave with 40 mL of 0.025 M $Sr(OH)_2$ hydrothermal solution, and the autoclave was kept at 200 °C for 0 min, 10 min, 20 min, 30 min, 40 min, 50 min, and 60 min, respectively. After this process, the resulting