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Revelation of rutile phase by Raman scattering for enhanced photoelectrochemical performance of hydrothermally-grown anatase TiO$_2$ film

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ABSTRACT

Photoelectrochemical (PEC) performances of the anatase TiO$_2$ films hydrothermally grown on the seeded fluorine-doped tin oxide (FTO) substrates are examined in this work. Structural characterizations of the TiO$_2$ films were conducted using Raman scattering spectroscopy. Although there is no obvious rutile peak appearing, an asymmetrical peak centered at ~399 cm^{-1} was observed in the Raman spectra of the TiO$_2$ films deposited either on the low-temperature-formed seed layers or with low concentrations of Ti precursor. The asymmetrical Raman shift can be deconvoluted into the B$_{1g}$ mode of anatase and E$_g$ mode of rutile TiO$_2$ peaks centered at ~399 cm^{-1} and ~447 cm^{-1}, respectively. Therefore, a minute quantity of rutile phase was inspected in the anatase film using Raman scattering spectroscopy. With the same light harvesting ability, we found that the PEC performance of the anatase TiO$_2$ film was significantly enhanced as the minute quantity of rutile phase existing in the film. It is ascribed to the formation of the anatase/rutile heterojunction which is beneficial to the charge separation in the photoanode.

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1. Introduction

The development of clean and renewable energy sources has been the focus of considerable attention recently due to the issues of global warming and increasing demand for energy. The direct conversion of solar energy, which is the most abundant renewable energy source, to electrical power is realized by photovoltaic devices [1]. Alternatively, conversion of solar energy into chemical fuel through photocatalytic water-splitting for hydrogen production offers an additional promising way for clean, low-cost and environmentally friendly production of green energy with no reliance on fossil fuels and no emission of carbon dioxide [2–4].

In 1972, Honda and Fujishima successfully demonstrated the splitting of H$_2$O into O$_2$ and H$_2$ in a photoelectrochemical (PEC) cell composed of a TiO$_2$ photoanode and a Pt counter electrode under uv irradiation [5]. Afterwards, scientific and engineering interests in TiO$_2$ photocatalysis have developed significantly because of its low-cost, stability, and nontoxicity [6–8]. TiO$_2$ exists in three different polymorphs-namely rutile, anatase, and brookite [9]. Among them, rutile is the most stable phase whereas anatase exhibits the highest overall photocatalytic activity [8,9]. The optimization of photocatalytic properties of hydrothermal TiO$_2$ particles by the

control of phase composition and particle morphology has been widely investigated [10]. Hydrothermal growth of TiO$_2$ directly on transparent conductive oxide substrate such as fluorine-doped tin oxide (FTO) has also attracted research attention for the PEC water splitting [11–14]. It has been demonstrated that the oriented rutile phase TiO$_2$ nanostructures can be easily grown on FTO substrates due to the tetragonal rutile structure of FTO and the small lattice mismatch between tetragonal FTO and rutile TiO$_2$ [15]. In contrast, formation of pure anatase phase TiO$_2$ on FTO substrates is restricted that an appropriate seed layer on FTO substrate is required [14,16].

In this work, TiO$_2$ films were deposited on the seeded FTO substrates using hydrothermal method. Nondestructively structural characterizations of the TiO$_2$ films were conducted using Raman scattering spectroscopy [17,18]. Although there is no obvious rutile peak appearing, an asymmetrical peak centered at ~399 cm^{-1} was observed in the Raman spectra of the TiO$_2$ films either deposited with low concentrations of Ti precursor or deposited on the low-temperature-annealed seed layers. A minute quantity of rutile phase in the anatase film was therefore identified by further inspecting the asymmetrical Raman shift peak, which consists of B$_{1g}$ mode of anatase and E$_g$ mode of rutile TiO$_2$ centered at ~399 cm^{-1} and ~450 cm^{-1}, respectively. Transmission electron microscopy (TEM) characterizations confirmed the existence of rutile TiO$_2$ nanoparticles in the grain boundary regions of the anatase

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TiO_2 film. Moreover, we found that the PEC performance of the anatase TiO_2 film was significantly enhanced as a minute quantity of rutile phase existing in the film. It is attributed to the formation of staggered (type-II) anatase/rutile heterojunctions which facilitates the charge separation in the photoanode. The revelation of a minute quantity of rutile phase, using nondestructive Raman scattering characterization, successfully explained the enhanced photoelectrochemical performances of hydrothermally-grown anatase TiO_2 films. This result addresses a critical concern that the crystal phase should be carefully examined for the investigation of photocatalytic properties of the TiO_2 films on FTO substrates.

2. Material and methods

The precursor solution composed of 0.5 mL of titanium (IV) tert-n-butoxide (TnBT) and 0.2 mL of HCl (37%) in 60 mL of ethanol was prepared for the formation of seed layers. It was spin-coated onto the FTO substrate followed by heat treatment at 90 °C for 3 min. The procedure was repeated twice. The substrates were then annealed at temperatures of 300–500 °C. TiO_2 films were grown on the seeded FTO substrates using hydrothermal method in the solution consisting of 0.6–1 mL of TnBT, 15.8 mL of HCl, 0.77 mL of H_2SO_4 and 20 mL of deionized water at 160–180 °C for 3 h. Afterwards, the TiO_2 films were annealed at 450 °C for 30 min.

The structures of the TiO_2 films were examined nondestructively using Raman scattering spectroscopy at an excitation length of 532 nm. Structural characterizations of the TiO_2 film were also conducted using TEM (JEOL 2100F). Optical absorptions of the photoanodes were measured using a UV–vis-IR spectrophotometer (JASCO V-670). PEC performances of the TiO_2 films were characterized in a three-electrode system with the electrolyte of 1 M KOH solution under AM 1.5G simulated sunlight at 100 mW cm^{-2} (100 W, Model 94011A, Oriel). The TiO_2 photoanodes with a well-defined area of 0.44 cm^2, a Pt foil, and a nonaqueous Hg/HgO electrode were employed as the working, counter, and reference electrodes, respectively.

3. Results and discussion

In this work, a seed layer was formed on the FTO substrate prior to the hydrothermal process for TiO_2 film deposition. The precursor solution for the formation of seed layers, which was composed of TnBT and HCl in ethanol, was spin-coated onto the FTO substrate. Three seed layers were separately prepared by further annealing the spin-coated layers at 300 °C, 400 °C, and 500 °C, for 1 h. For simplicity, they are named as SL-300, SL-400, and SL-500 hereafter. Fig. 1 shows the SEM images of the TiO_2 films grown on the three seeded FTO substrates using identical deposition process. It was carried out in a hydrothermal solution consisting of TnBT, HCl, and H_2SO_4 in deionized water at 180 °C for 3 h. Afterwards, the TiO_2 films were annealed at 450 °C for 30 min. As shown in the top-view SEM images of Fig. 1(a), (c), and (e), with identical hydrothermal condition for the film growth, the crystal size of the film slightly decreases as the formation temperature of seed layer is increased from 300 °C to 500 °C. Moreover, columnar growth of the TiO_2 films is revealed in the cross-sectional SEM images of Fig. 1(b), (d), and (f). The thicknesses of the TiO_2 films on different seeded substrates are ∼800 nm, indicating that the growth rate of the film is not significantly influenced by the formation temperature of seed layer.

To characterize the crystal structure of the TiO_2 film, X-ray diffraction and Raman scattering are the commonly used nondestructive methods [11–16]. As demonstrated in Fig. S1, compared to X-ray diffraction, the Raman scattering is more sensitive for the characterization of rutile phase in the mixed TiO_2 films prepared on FTO substrates. Therefore, structural characterizations of the TiO_2 films were conducted using Raman scattering spectroscopy in this work. Fig. 2(a)–(c) show that almost identical Raman spectra are acquired from the three TiO_2 films deposited on different seed layers. The Raman scattering peaks at 144 cm^{-1}, 197 cm^{-1}, 399 cm^{-1}, 519 cm^{-1}, and 639 cm^{-1} are pertaining to E_g, E_g, B_{1g}, A_{1g}, and E_g active vibrations of anatase TiO_2, respectively [17,18]. No obvious Raman scattering peak of rutile TiO_2 phase presents in the three Raman spectra. However, as respectively shown in the insets of Fig. 2(a) and (b), asymmetrical Raman scattering peaks at 399 cm^{-1} are observed in the spectra of TiO_2 films deposited on SL-300 and SL-400. The asymmetrical peaks can be deconvoluted to two peaks at 399 cm^{-1} and ∼447 cm^{-1}. The latter corresponds to the E_g mode of rutile TiO_2 [17,18]. The small rutile characteristic peak appearing in the Raman spectra indicates the existence of a minute quantity of rutile phase in the anatase TiO_2 films. On the other hand, a symmetrical peak at 399 cm^{-1} is obtained in the Raman spectrum of the TiO_2 film grown on SL-500, as shown in the inset of Fig. 2(c). It reveals that a rather pure anatase TiO_2 film was formed on the SL-500/FTO compared to those formed on the seed layers annealed at lower temperatures.

The crystal structure of the film deposited on SL-400/FTO was further characterized using TEM. Fig. 3(a) displays the cross-sectional TEM image of the film on SL-400/FTO, revealing that the columnar-featured TiO_2 film with a thickness of ∼800 nm was grown on the FTO substrate. The columnar crystals were developed from the seeded FTO substrate as shown in Fig. 3(b). TEM characterizations of the film deposited on SL-400 were then focused on the columnar crystals as well as on the grain boundary regions. The selected area electron diffraction (SAED) pattern taken in the central region of the columnar crystal (zone A denoted in Fig. 3(b)) is shown in the inset of Fig. 3(b). The SAED pattern indicates the single-crystalline anatase TiO_2 phase of the columnar crystal. Fig. 3(c) and (d) show the corresponding SAED patterns taken in zones B and C around the grain boundary regions as denoted in Fig. 3(b), respectively. In addition to the diffraction spots indexed to the anatase TiO_2 structure, as shown in Fig. 3(c) and (d), the diffraction spots pertaining to rutile TiO_2 also present in the SEAD patterns of zones B and C denoted in Fig. 3(b). It indicates that the rutile TiO_2 crystals exist in the grain boundary region of the anatase TiO_2 film. Fig. 3(e) and (f) respectively display the corresponding bright-field and dark-field images acquired from the diffraction spot of rutile TiO_2 (2 1 0) denoted in Fig. 3(d). The dark-field image confirms the rutile TiO_2 crystal appears around the grain boundary region. The formation of rutile TiO_2 crystals in the grain boundary region of the anatase TiO_2 film may be ascribed to the poor crystallinity of the SL-400 seed layer, as shown in the HRTEM image of Fig. S2.

Fig. 4 shows the SEM images of the films grown on the SL-500/FTO substrates using 0.6 mL and 0.8 mL of TnBT. Except for the amount of TnBT, the hydrothermal conditions were no difference from those for the growth of the pure anatase TiO_2 film (Fig. 1(e) and (f)). Nevertheless, a 0.2-μm-thick film with random feature was formed on the substrate by using 0.6 mL of TnBT, as shown in Fig. 4(a) and (b). When the amount of TnBT was increased to 0.8 mL in the hydrothermal process, a film with columnar feature was formed as displayed in Fig. 4(c) and (d). The crystal size and thickness of the film are reduced compared to those prepared using 1 mL of TnBT (Fig. 1(e) and (f)).

The Raman spectra of the films which were hydrothermally prepared using 0.6 mL and 0.8 mL of TnBT are shown in Fig. 5(a) and (b), respectively. The Raman scattering peaks of FTO substrate are present in the Raman spectrum of the film grown using 0.6 mL of TnBT due to the relatively thin film formed on the FTO sub-