



Preparation of polypyrrole sensitized TiO₂ nanotube arrays hybrids for efficient photoelectrochemical water splitting



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ABSTRACT

Stable polypyrrole-TiO₂ nanotube arrays hybrids (PPy-TNTs) have been prepared by facile anodization and potentiostatic polymerization methods. The morphology and structure of PPy-TNTs are characterized by SEM, XRD, XPS. The amount of deposited PPy can be easily adjusted by electropolymerization time. UV–vis diffuse reflection spectra show that the polypyrrole can act as visible-light photosensitizer and the electrochemical impedance spectra suggest that the formed p–n junctions between PPy and TNTs can facilitate the charge separation and transfer. The photocurrent density of PPy-TNTs under simulated solar illumination (AM1.5, 100 mW/cm²) is about 2.5 times compared with that of pristine TNTs. Incident photon to current conversion efficiency (IPCE) spectrum of PPy-TNTs increases in UV and visible light region. Moreover, The PPy-TNTs hybrids show much higher photoelectrochemical stability than the pure TNTs.

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1. Introduction

One dimensional TiO₂ nanotube arrays (TNTs) prepared electrochemical anodization has been extensively studied as a promising photoanode for photoelectrochemical (PEC) water splitting due to its excellent electron pathways, favourable band-edge positions and easy preparation [1–3]. However, the PEC water splitting efficiency of TNTs photoanodes is still low with the fact that their limited light absorption spectrum range and relatively fast charge carriers recombination. In order to solve these problems, sensitized the pristine TNTs with various sensitizers such as organic dye [4–6], organometallic complexes [7], and narrow band semiconductor quantum dots [8–10] has been demonstrated to be a feasible way to improve its PEC water splitting efficiency. Nevertheless, these sensitizers are either highly unstable during light irradiation process or poisonous [11,12]. Therefore, it is necessary to explore new sensitizers to expand the light absorption range of TNTs and thus further enhance its PEC performance.

The conjugated polymers with extending π -conjugated electron systems such as polyaniline, polypyrrole (PPy), and

polythiophene have been widely used to couple with TiO₂ due to their high absorption coefficient, superb mobility of charge carriers and excellent stability [13–16]. Among all the conducting polymers, the PPy has attracted most attention because of its high conductivity and easy preparation. In the PPy-TiO₂ systems, the PPy with band gap of about 2.2 eV can act as a sensitizer to harvest the visible light and then inject the photoexcited electrons to the conduction band of TiO₂, thus facilitating the separation of photoinduced electron-hole pairs and improving the photoconversion efficiency [17,18]. Recently, Wang et al. [19] reported the preparation of coaxial PPy nanowire/TNTs hybrids by electropolymerization of pyrrole into TNTs. Janaky et al. [20] investigated the influence on PPy grafted onto the TNTs posed by different electrochemical deposition methods. Jia and co-workers [21] explored the PEC properties of PPy-TNTs fabricated by potentiostatic polymerization of pyrrole into the TNTs. However, these previous literatures are mainly focus the preparation process of PPy-TNTs hybrids rather than their efficient PEC water splitting application.

Therefore, in the present work, we first prepare the PPy-TNTs hybrids by potentiostatic polymerization of pyrrole onto the surface and into the inner walls of TNTs. The optimized deposition amount of PPy is tuned by electropolymerization time. The PPy-TNTs show more excellent PEC water splitting performance than the pristine TNTs.

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2. Experimental

2.1. Preparation of PPy-TNTs hybrids

A two-electrode electrochemical cell, with a working electrode of Ti foil ($1.2 \times 1 \times 0.02$ cm) and a counter electrode of Pt foil, was used for the preparation of TiO₂ nanotube arrays (TNTs). The titanium foils were firstly anodized in ethylene glycol (EG) electrolyte containing 0.3 wt% NH₄F and 5 vol% deionized water under 60 V for 2 h. Then the as-prepared TiO₂ layer was peeled off by ultrasonic in deionized water. Subsequently, the print-left titanium foils were subjected to a second anodization in the same electrolyte at 60 V for 30 min. The resulting TNTs on Ti substrate were rinsed by deionized water. Finally, the as-anodized TNTs were annealed at 450 °C for 2 h with a heating and cooling rate of 10 °C/min. The PPy-TNTs hybrids were electrochemically polymerized on a CHI660C electrochemical workstation in a traditional three electrode system with the annealed TNTs as working electrode, Pt foil as counter electrode, and Ag/AgCl as reference electrode. Electropolymerization was conducted potentiostatically at 0.8 V for different time (1 min, 5 min, and 10 min), corresponding to the three samples named PPy1-TNTs, PPy5-TNTs, and PPy10-TNTs, respectively. The aqueous electrolyte contains 0.1 M LiClO₄ and 0.2 M pyrrole acetone solution. All the electrochemical anodization experiments were carried out at the ambient temperature (25 °C).

The morphologies of the samples were characterized by field-emission scanning electron microscopy (NOVA NANOSEM 430) at an acceleration voltage of 15 KV. X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Bruker D8 ADVANCE) using Cu K α radiation and operating at 30 kV/30 mA. Fourier transform infrared (FTIR) spectra were recorded using an FTIR (Perkin Elmer, 2200) spectrophotometer. UV-Vis light absorption spectra were obtained from a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly and using BaSO₄ as reference to measure all the samples. Optical filters range in 600–800 nm are used to exclude the double wavelength effect. X-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD) was used to detect the chemical composition of the as-prepared samples.

Photoelectrochemical measurements were carried out in 1 M KOH electrolyte with a standard three-electrode cell composed of the obtained sample, platinum foil and Ag/AgCl as the working, counter and reference electrode, respectively. The samples were illuminated by a stimulated solar light (AM1.5, 100 mW/cm²) provided by a PLS-SXE300UV Xe lamp. The intensity of the light source was calibrated with a Si diode (Model 818, Newport). The incident photon to current conversion efficiency (IPCE) measurement was performed at 0.23 V (vs. Ag/AgCl) in a three-electrode model, with prepared samples as anode, Pt as cathode and the Ag/AgCl as reference. Gases generated during water splitting under entire solar light irradiation were collected via a homemade photo-reactor. The photoanode (PPy-TNTs) and the counter electrode (Pt foil) were separated in different tubular chambers, which were made of quartz. The design of the photo-reactor avoids mixing of hydrogen generated on the Pt electrode and oxygen generated on the photoanode and thus the hydrogen and oxygen gases can be separately collected. The electrochemical spectra (EIS) were performed under illumination (100 mW/cm²) at open circuit voltage over a frequency range from 10⁵ to 0.1 Hz with an AC voltage at 10 mV. Simultaneously, the Mott-Schottky plots were obtained at a fixed frequency of 5 kHz in dark to determine the flat band potential and carrier density. All experiments were carried out under ambient conditions.

3. Results and Discussion

The scanning electron microscopy (SEM) images of the pristine TNTs, PPy-TNTs are shown in Fig. 1. The pure TNTs have a uniform-arranged tubular structure with an average inner pore diameter of 120 nm and a length of about 12 μ m (Fig. 1a). The effect of electropolymerization time on the morphology of PPy-TNTs is shown in the Fig. 1c, d and e. As shown in Fig. 1b, a relatively small amount of PPy is randomly and discontinuously covering the top surface of TNTs. When the electropolymerization time increase to 5 min, PPy is filling a majority of the top pores and forming continuous film within partial region (Fig. 1c). In addition, the PPy particles also deposited into the inner walls of tube (inset in Fig. 1c), which will significantly increase the p-n junctions area between PPy and TNTs. Fig. 1d exhibits a continuous PPy film completely covering the surface of TNTs when the electropolymerization time is fixed at 10 min.

X-ray diffraction (XRD) was adopted to investigate the crystal phase of the unannealed and annealed pristine TNTs and PPy-TNTs. As showing in Fig. 2a, XRD diffraction peaks centered at 25.1°, 37.5°, 47.8°, 54.2° suggest that the annealed TNTs are highly crystallized with pure anatase phase compared with the unannealed TNTs [22,23]. After the PPy deposited on the TNTs for 5 min, the PPy-TNTs also exhibit strong anatase diffraction similar to the annealed TNTs, but a close observation of the XRD pattern in the range of 20–30°, a small peak located at 24.1° which can be ascribed to the characteristic of the doped PPy (inset of Fig. 2a) [18,24]. This result indeed confirms the existence of PPy in the hybrids. To further determine the existence of PPy, FTIR spectra of TNTs and PPy-TNTs are shown in Fig. 2b. The peak at 1636.5 cm⁻¹ is ascribed to the N-H in-of plane bending vibration. 1541.5 and 1455.2 cm⁻¹ are the characteristic peaks of PPy, which is result of the C=C symmetric and anti-symmetric stretching vibration in PPy ring. The band at 1296.6 cm⁻¹ is attributed to the C–N stretching vibration. The peaks at 1164.3 and 786.4 cm⁻¹ are typical stretching vibration of C–C and the peaks at 1035.0 and 668.0 cm⁻¹ are assigned to the out-of-plane bending vibration [21]. All the above characteristic peaks of PPy confirm the existence of PPy in the PPy/TNTs hybrids.

X-ray photoelectron spectroscopy (XPS) is a useful tool to explore the minor surface elements. Fig. 3a displays the XPS survey spectra of the PPy5-TNTs hybrids. Five elements, they are C, N, O, F, and Ti exist in the nanocomposites. The small amount of carbon may originates from the adventitious hydrocarbon contamination and the fluorine species are come from the anodizing electrolyte which containing etching agent of fluorine ions [25]. As seen in Fig. 3b, after being coupled with PPy, the concentration of nitrogen in the PPy5-TNTs obviously higher than that in pristine TNTs, which indicates the presence of PPy in the hybrids.

The UV-vis diffuse reflectance spectra (DRS) of pure TNTs, PPy1-TNTs, PPy5-TNTs and PPy10-TNTs are shown in Fig. 4. All the PPy-TNTs hybrids show higher absorption intensity than the pure TNTs, which is ascribed to that the PPy can act as sensitizer for trapping a large number of visible light photons. Moreover, the PPy5-TNTs and PPy10-TNTs exhibit higher absorption intensity in the visible light region than that of PPy1-TNTs due to that the longer electropolymerization time results in more deposited sensitizer of PPy. While the absorption of PPy10-TNTs in the visible light range is lower than that of PPy5-TNTs, which can be attributed to that the continues PPy film completely covering the surface of TNTs goes against the light absorption of inner tubes and lead to partial light reflection.

Transient photocurrent response measurements were conducted over the pristine TNTs, PPy1-TNTs, PPy5-TNTs and PPy10-TNTs during repeated on/off light irradiation (AM 1.5, 100 mW/cm²) cycles at 0.23 V vs. Ag/AgCl (Fig. 5a). All samples

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