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Facile synthesis of a narrow-gap titanium dioxide anatase/rutile nanofiber film on titanium foil with high photocatalytic activity under sunlight

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ABSTRACT

A narrow-gap TiO₂ nanofiber film was synthesized on Ti foil by chemical polishing and anodization. The morphology, crystal structure, chemical states, and optical properties were characterized by scanning electron microscopy, X-ray diffraction, X-ray photon electron spectroscopy, and ultraviolet-visible-infrared absorption spectroscopy, respectively. Transient photocurrent response, linear sweep voltammetry, and photoconversion efficiency were also measured. The photocatalytic activity was evaluated from both hydrogen generation and methyl orange degradation experiments. Our results suggested that the film was composed of small uniform TiO₂ nanofibers, having interstitial nitrogen-doping, oxygen vacancies and a mixture of anatase and rutile crystal phases. The films exhibited strong and broad optical absorption from 200 to 2500 nm. Owing to this strong absorption and rapid transport of photogenerated electrons, the nanofiber films exhibited a high photoconversion efficiency of 0.62%, and a hydrogen generation rate of 0.62 mL h⁻¹ cm⁻² under visible light irradiation. Under solar irradiation the films also showed remarkable efficiency and stability for the degradation of methyl orange.

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Introduction

Titanium dioxide is widely used in solar-driven pollutant treatments and hydrogen generation because of its low cost, low toxicity, and high chemical stability [1–4]. However, several factors have limited more widespread practical applications of TiO₂, including its wide band gap (3.0 eV for

rutile and 3.2 eV for anatase) [5], rapid recombination of photogenerated electron/hole pairs [6], and the difficulty of separating TiO₂ powder from treated water [7].

To improve the photocatalytic efficiency of TiO₂ under sunlight, many studies have focused on narrowing the band gap of TiO₂ to enhance its absorption of visible light. Doping non-metal elements into TiO₂, such as C, S and N has been shown to improve photoconversion efficiency by introducing

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impurity states into the band gap that extend the optical absorption to longer wavelengths [8–13]. Nitrogen (N)-doped TiO₂ exhibits particularly strong absorption of visible light [14]. N-doping can generally be categorized in two types: substitutional nitrogen (N_s) and interstitial nitrogen (N_i). N_s-doping reduces the band gap by mixing the N 2p level and the O 2p of TiO₂ [15], while N_i-doping induces localized states above the valence band of TiO₂ [16]. Additionally, it has been demonstrated that oxygen vacancies play a critical role in determining the electronic properties and band gap structure of TiO₂. Oxygen vacancies (V_o) can induce shallow levels below conductive band, and further extend the absorption of visible light [17]. The crystal phase and morphology of TiO₂ also affect the photocatalytic activity [18]. A mixture of anatase/rutile (A/R) crystal phases has higher photocatalytic activity than either of the pure TiO₂ phases alone [19–22]. It has been suggested that a built-in electric field at the interface between the phases facilitates charge transfer, which enhances the photocatalytic activity [21]. Recent studies have shown that a thermal treatment of TiO₂ in a hydrogen atmosphere induced structural disorder close to the surface layer, and this material displayed excellent photocatalytic activity and a high stability for hydrogen generation [23].

Here, we developed a novel method to prepare an interstitial N-doped TiO₂ nanofiber film, composed of a mixture of anatase and rutile crystal phases (N_i-TiO₂ (A/R)). The morphology, crystal structure, chemical states, optical absorption, and photoelectrochemical properties of the nanofibers film were investigated. The film displayed good absorption of visible light, and high photoconversion efficiency and photocatalytic activity.

Experimental

Materials

Ti foil (purity 99.6%, 0.2 mm × 30 mm × 40 mm) was purchased from Baoji Jinbu Titanium Equipment Corporation, China. All chemicals were of analytical grade, and purchased from the Sinopharm Chemical Reagent Co., Ltd. China. Deionized water with a resistivity of 18.2 M Ω cm was used in all experiments.

Fabrication of N_i-TiO₂ (A/R) nanofiber film

The N_i-TiO₂ (A/R) nanofiber film was prepared by a two-step method using chemical polishing and anodization processes. The Ti foil was ultrasonically degreased in acetone, ethanol and distilled water, each for 15 min, and then dried at room temperature. Chemical polishing was performed in a mixed solution of HNO₃ (68%) and HF (volume ratio 5:1) for 20 s. For anodization, the polished Ti foil was used as the anode and a Pt sheet as the cathode, in an ethylene glycol solution containing 1.5 wt% HNO₃ and 1.0 wt% H₂O for 10 min at 50 V in an ultrasonic bath at room temperature. A direct-current power supply (HB172000SL 3A) was used for the anodization. After rinsing in ethanol and distilled water, the anodized samples were calcined for 1 h at 773 K with a 273.34 K s⁻¹ heating and cooling rate in muffle furnace.

Characterization of the N_i-TiO₂ (A/R) nanofiber film

The morphology was studied using a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi). The crystal structure was investigated by grazing incidence X-ray diffraction (XRD) using Cu-Kα (0.15418 nm) radiation at 40 kV and 30 mA. Raman measurement (Horiba Jobin Yvon LabRAM HR800) was recorded in the range 100–1000 cm⁻¹ using a 532 nm laser excitation source. The chemical composition was evaluated by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer Corporation, Eden Prairie, MN) with an Mg K anode (1253.6 eV photon energy, 15 kV, 300 W) at a takeoff angle of 45°. The binding energy values were calibrated from the C 1s peak of carbon contaminants (C 1s = 284.4 eV). Electron spin resonance spectroscopy (ESR, JES FA-200) was used to identify V_o. UV-vis-NIR absorption spectra were obtained using a TU-1901 spectrometer over the range 200–2500 nm.

Photoelectrochemical measurements

The photoelectrochemical measurements were carried out in aqueous 1.0 M NaOH in a three-electrode cell using a CHI electrochemical workstation (CHI 830C Instruments, Shanghai Chenhua Device Company, China). A N_i-TiO₂ (A/R) nanofiber film was used as the working electrode, and Ag/AgCl and Pt foil were used as the reference and counter electrodes, respectively. A 300 W xenon lamp was used as the light source. All measurements were carried out at room temperature. The photoconversion efficiency was calculated from Ref. [24]:

$$\eta(\%) = \frac{[(\text{total power output} - \text{electrical power input}) / (\text{light power input})] \times 100}{= j_p [(E_{rev}^0 - |E_{app}|) / I_0] \times 100,} \quad (1)$$

where j_p is the photocurrent density (mA cm⁻²), $E_{rev}^0 = 1.23$ V is the standard potential for H₂ evolution. The applied potential $E_{app} = E_{means} - E_{aoc}$, where E_{means} is the electrode potential of the working electrode (vs Ag/AgCl) at which j_p is measured and E_{aoc} is the open circuit electrode potential of the working electrode (vs Ag/AgCl) under the same conditions. The voltage at which the photocurrent becomes zero is taken as E_{aoc} . I_0 is the power density of incident light (100 mW cm⁻²).

Photoelectrocatalytic activity evaluation

The photoelectrocatalytic activity of the N_i-TiO₂ (A/R) nanofiber film was evaluated from hydrogen generation and methyl orange degradation experiments. Hydrogen generation was carried out in a quartz cell with 1.0 M NaOH electrolyte. The N_i-TiO₂ (A/R) nanofiber film was used as the photoanode, and Pt foil was used as the cathode. The two electrodes were separated by a Nafion membrane. A 300 W Xenon lamp served as the light source. The hydrogen gas generated at the Pt electrode was collected in an inverted burette. The methyl orange degradation experiments were performed under sunlight with 40 mL solutions of methyl orange (20 mg L⁻¹, pH = 6.8) and 0.5 M NaCl as the supporting electrolyte. Cycling tests were conducted for 2.5 h at the same time of day (12:00 to 14:30) under direct sunlight for 10 days.

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