



Molybdenum-doped and anatase/rutile mixed-phase TiO₂ nanotube photoelectrode for high photoelectrochemical performance



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HIGHLIGHTS

- Aligned TiO₂ NTs with Mo-doping and mixed phase are achieved by one step hydrothermal process.
- Oxygen vacancies are increased and recombination of photo-excited charge is reduced.
- The photocurrent density is doubled.
- Mo-doped TiO₂ NTs show visible-light absorption and high stability.

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ABSTRACT

Molybdenum-doped TiO₂ nanotube arrays (Mo-doped TiO₂ NTs) photoelectrodes with anatase/rutile mixed phase are successfully fabricated via two-step anodization of titanium followed by a hydrothermal doping treatment process. The Mo-doped TiO₂ NT material shows higher photocurrent density and enhanced incident photon to current conversion efficiency (IPCE) compared with the pristine TiO₂ NTs for photoelectrochemical (PEC) water-splitting. The improvement of PEC response results from not only the increasing of oxygen vacancies and reducing of the recombination of photoexcited charges by Mo-doping, but also the new formed heterojunctions of anatase/rutile mixed-phase by hydrothermal treatment. Moreover, the Mo-doped TiO₂ NTs show high stability and obvious visible absorption with considerable photocurrent density under visible light ($\lambda > 420$ nm).

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1. Introduction

The discovery of the photoelectrochemical (PEC) water-splitting based on TiO₂ electrode in 1972 has prompted the investigations on nanostructured TiO₂ materials, especially in recent years for the energy and environmental issues [1]. Due to high chemical stability, strong optical absorption, environmental benignity and inexpensive cost, TiO₂ has been considered as one of the most promising candidates to generate clean hydrogen energy from water [2,3]. In particular, one-dimensional TiO₂ nanostructures, such as nanorods, nanowires and nanotubes, have already attracted more and more attention, owing to their large surface area and short diffusion distance for photo-excited charge carriers, which can facilitate the charge separation and inhibit recombination [4–7].

In principle, the PEC water splitting based on a photocatalyst membrane electrode occurs in three steps, similar to the powder photocatalytic water splitting [8]. First of all, the photocatalyst absorbs photon energy greater than the band gap energy to generate photo-excited electrons and holes ($h\nu \geq E_g$) [9]. Secondly, the photo-excited carriers separate and migrate to the surface of the photocatalyst without recombination. Thirdly, the electrons and holes migrate to the surfaces of the cathode and anode to reduce and oxidize water to produce H₂ and O₂, respectively. Through the PEC water splitting processes, all the three steps are strongly dependent on the structure and composition of the photocatalysts. The visible light driven photocatalysts are more promising and beneficial for the practical applications under solar light irradiation. The ordered structure and high crystallinity are key factors to accelerate the separation and transmission of photoexciton as well as increase the photon-to-hydrogen energy conversion efficiency. Thus, it is very important to design both the

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architecture and band gap structure of the photocatalysts so as to obtain high photocatalytic activity.

So far, there are lots of reports about PEC water splitting based on TiO₂ nanomaterials with different preparation methods [10–12]. Among them, the *in situ* anodization of Ti to prepare TiO₂ NTs was widely studied. However, the wide band gap nature of TiO₂ ($E_g = 3\text{--}3.2$ eV) and low hydrogen generation efficiency are still crucial deficiencies to limit the applications of this material. In previous studies, various strategies were adopted including doping [13–20], composite, heterostructures, and structural improvement to adjust the band gap of TiO₂ and enhance the photocatalytic performance [21,22]. For example, suitable metal ions doping within TiO₂ lattice can result in a smaller energy gap for visible light absorption, and create oxygen vacancies to improve the photocatalytic activity. On the other hand, the high crystallinity also has a positive effect on the photocatalytic activity since the defects decrease with increasing the crystallinity. Furthermore, it has also been reported that mixed-phase of anatase with a certain amount of rutile to form TiO₂ phase heterostructures has better photocatalytic activity than the pure anatase TiO₂, because the interface formed between anatase and rutile phases can act as electron traps to suppress the recombination owing to their different Fermi level [23,24]. However, every factor mentioned above is crucial, and it is not enough to improve the PEC performance by considering only one of them. Thus, designing the TiO₂ photocatalyst simultaneously with ordered structure, suitable doping ion, good crystallinity and mixed-phases is highly important and urgent, which is still a difficulty and challenge now.

Herein, we demonstrated a simple one-step hydrothermal doping method to prepare TiO₂ NTs photoelectrode with Mo-doping, good crystallinity, and anatase/rutile mixture phase for high PEC performance. Due to the similarity in the ionic radii of Mo⁶⁺ (0.062 nm) and Ti⁴⁺ (0.068 nm), Mo⁶⁺ was selected as the doping element to replace Ti⁴⁺ in the lattice to form oxygen vacancy and adjust the band gap [25,26]. The hydrothermal method was used to *in situ* dope Mo ions into TiO₂ NTs and form mixed phase with high crystallinity, which could increase the photocurrent density and water splitting efficiency.

2. Experiment section

2.1. Synthesis of TiO₂ nanotube arrays

The pristine ordered TiO₂ nanotube arrays were synthesized on titanium foil substrates using a modified two-step anodization process in a two-electrode electrochemical cell [27,28]. The commercial titanium foil (0.25 mm thick) was used as the working electrode, and the graphite slice was served as a counter electrode. Before anodizing, the titanium foils were degreased with ethanol, acetone and deionized (DI) water by ultrasonication, and dried off with N₂ gas. The clean foils were then anodized in an ethylene glycol solution containing NH₄F (0.5 wt%) and HF (0.5 vol%) at 70 V and 25 °C for 2–10 h. The resulting TiO₂ NTs layer was then peeled off by ultrasonication in 1 M HNO₃ aqueous solution. Subsequently, the second anodization was performed for 4 h under the condition identical to those in the first anodization step. After that, the as-prepared sample was thoroughly washed by DI water and dried by N₂, and then annealed in air at 450 °C for 2 h.

2.2. Preparation of Mo-doped TiO₂ nanotube arrays

The precursor solution was prepared by dissolving 0.145 g of hydroxylamine hydrochloride (NH₂OH·HCl), 0.24 g of sodium sulfide nonahydrate (Na₂S·9H₂O) in 60 mL of DI water in a 100 mL beaker to provide a weakly alkaline condition [29] followed by

adding 0.242 g of sodium molybdatedihydrate (Na₂MoO₄·2H₂O). Then the solution was transferred to a 100 mL sealed Teflon reactor, followed by the as-prepared TiO₂ NTs on a titanium foil placed in the reactor which was kept in an oven at 180 °C for 10 h. After that, the sample was thoroughly rinsed with DI water and dried by compressed N₂. To obtain the TiO₂ NTs with different amount of Mo⁶⁺ doping, the same hydrothermal process was used by changing the amount of Na₂MoO₄·2H₂O from 0.242 g to 0.121 g and 0.484 g, marked as Mo-doped TiO₂, 1/2Mo-doped TiO₂ and 2Mo-doped TiO₂, respectively.

2.3. Photoelectrochemical measurement

The PEC measurement was carried out using a three-electrode electrochemical cell, with a saturated calomel electrode (SCE) and a Pt wire as reference electrode and counter electrode, under the irradiation of a 300 W xenon lamp with the light density of 370 mW/cm² (Beijing Perfect light Technology Co. Lt, PLS-SXE300UV), and simulated sunlight of a 450 W Xenon lamp coupled with an AM 1.5G filter with the light density of 100 mW/cm² (Newport 94023A, USA). The TiO₂ NTs samples were used as the working electrodes with an area about 3.4 cm². The measured potentials vs Hg/Hg₂Cl₂ were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation. NaOH aqueous solution (0.1 M, pH = 13) was used as an electrolyte for PEC measurements. The electrolyte was stirred and purged with Ar gas for 20 min before the measurements. An electrochemical workstation (CHI660B) was used to measure current–voltage (*I*–*V*), amperometric *I*-*t* photoresponse characteristics of the electrode, with a scan rate of 10 mV/s. The IPCE was tested under the illumination of a 150 W xenon lamp of SM-25 Hyper Monolight (Japan). The light intensity of the illumination source was calibrated by using a standard silicon photodiode.

2.4. Structural characterization

Scanning electron microscopy (SEM) images were carried out on a field-emission scanning electron microscopy (JSM-6701F, JEOL Inc., Japan). Transmission electron microscopy (TEM) images were obtained from a FEI Tecnai G2 TF20 transmission electron microscope with a field emission gun operating at 200 kV. X-ray diffraction (XRD) data were collected on a X-ray Single Crystal Diffractometer (XRD, Philips Corp) with Cu-K α radiation ($\lambda = 1.5418$ Å), 2θ ranging from 20 to 80°. X-ray photoelectron spectroscopy (XPS) spectra are recorded under ultra high vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV on a ESCALAB 250Xi system equipped with a dual X-ray source by using Mg anode and a hemispherical energy analyser. All the energies are calibrated with contaminant carbon (C1s = 284.6 eV) as a reference. UV–Vis absorption spectra were measured on a UV–Vis spectrophotometer (UV-2600, Shimadzu) with an integrating sphere attachment.

3. Results and discussions

Fig. 1 shows the SEM images of the ordered TiO₂ NTs before and after Mo-doping by *in situ* hydrothermal treatment. The average diameter and nanotube length are about 100 nm and 12 μ m, respectively. From the top views (Fig. 1a and d) and the cross-sectional images (Fig. 1b and e) of the samples, there are no obvious changes of the TiO₂ NTs before and after Mo-doping. From the magnified images in Fig. 1c and f, there is also no impurity such as molybdenum oxide nanoparticles or other precipitates, detected either on the top surface or on the wall of the smooth NT, indicating the Mo ions doped into the TiO₂ lattice.

Transmission electron microscope images and the energy-

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