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Unique photoelectrochemical behavior of TiO₂ nanorods wrapped with novel titanium Oxy-Nitride (TiO_xN_y) nanoparticles

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ABSTRACT

In this work, we developed novel titanium oxynitride (TiO_xN_y) nanoparticles with diameter of 25 ± 2 nm and crystalline size of ~15 nm on hydrothermally grown one-dimensional (1D) TiO₂ nanorod (TNR) arrays. Herein, the TiO_xN_y nanoparticles were synthesized by facile nitridation using TiO₂ powder at 100% NH₃ gas atmosphere. Titanium oxynitride composed of potentially energetic metal-nitrogen bonds (Ti–N), compared to the weaker Ti–O bond, becomes chemically stable in the alkaline environment, and is considered as a suitable material for photoelectrochemical (PEC) system. The PEC performance of TiO_xN_y decorated TNR (abbreviated as TiO_xN_y@TNR) films was evaluated in 0.1 M KOH solution under solar illumination condition, and achieved the potentially high photocurrent density (*J*) of 2.1 mA/cm² at 1.23 V versus reversible hydrogen electrode (RHE) (abbreviated as V_{RHE}) in the TiO_xN_y@TNR arrays, in comparison with the poor photoresponse (0.7 mA/cm² at 1.23 V_{RHE}) of the pristine TNR arrays. A nearly three-fold enhancement was attained in the TiO_xN_y decorated TNR arrays, attributed to the high visible light absorption and fast carrier separation, due to the hybridization with the visible active TiO_xN_y nanoparticles in the cascading band alignment between the TiO_xN_y and TNR materials. Furthermore, the introduction of TiO_xN_y layer on the TNR surface quite reduces the interfacial resistance in the solid-liquid interface region, and further, the TiO_xN_y layer contributes to the passivation of the surface states (e.g., defect, trap sites etc.) where the charge recombination reaction frequently happens, leading to the improvement of PEC performance.

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Introduction

Photoelectrochemical (PEC) water splitting can convert water into chemical fuels, H_2 and O_2 with no harmful chemical emission, in the circumstance where only solar energy can be illuminated to the device [1–3]. PEC water splitting mainly consists of two processes: hydrogen evolution reaction (HER), requiring the transfer of two electrons on the photocathode, and oxygen evolution reaction (OER), by the transfer of four electrons on the photoanode. Rather than HER where two protons and two electrons take part in the reaction, the OER is the rate-limiting step, due to the requisite coupling of four electrons and four protons to yield two bond-making steps ($\sigma + \pi$ of O_2). Accordingly, the rate that the photocatalysts should catalyze OER by forming the O–O bond is a critical factor to determine the overall efficiency of water splitting, and as a result, significant effort has been dedicated to developing new and functional structure, as well as discovering novel materials. Titanium oxide (TiO_2) has widely facilitated this process by virtue of its chemical stability, nontoxicity, widespread availability, and low cost, starting with the pioneering work of Fujishima and Honda using *n*-type TiO_2 in the 1970s [4]. However, TiO_2 inherently suffers from instability in capturing visible light (only utilizing light $\lambda < 420$ nm), owing to the large band gap (>3.0 eV). Hence, the broad band gap energy of TiO_2 restricts the maximum theoretical solar to hydrogen (STH) conversion efficiency to 2.2%, which is quite less than the expected 10% of STH conversion efficiency required for commercial utility. Nevertheless, a variety of research toward TiO_2 , including other metal oxides such as α - Fe_2O_3 , WO_3 , $BiVO_4$ etc., has established these materials as the only chemical systems capable of the long-term stability necessary for practical use. As a consequence, several attempts have been reported to overcome the poor performance of TiO_2 . For example, structural modification toward 1D and 3D structures, elemental doping, sensitization with dye molecules or through semiconductor nanocrystals, post-treatments including oxygen, hydrogen, carbon monoxide, and sulfur, heterojunctions, and the deposition of co-catalysts have been extensively studied to enhance the intrinsic TiO_2 properties for the PEC reaction [5–10]. Moreover, the technological promises of dual-band-gap heterojunctions based semiconductor photoanode and photocathode are attracting interest to achieve the insufficient light absorption of the respective oxidation and reduction reactions [11]. This approach allows for the use of lower-band-gap materials that can absorb complementary portions of the solar spectrum and yield higher solar-to-fuel efficiencies. In addition, photoelectrode in the form of heterojunction can provide new functionality to enhance charge separation and overcome charge recombination; preserve the narrow-band-gap semiconductor from photo-corrosion [12–22].

For example, α - Fe_2O_3 @ TiO_2 core-shell architectures improved the fast interfacial charge-transfer process, and the wide spectral response toward the visible wavelength could be the driving force for enhanced PEC performance [23]. In order to extend the photoresponse from ultraviolet (UV) to visible light, the use of transition-metals (Fe, Mn and Co) doped TiO_2 nanorod arrays was reported. Among them, Fe doping is the

most effective route to enhance the photoactivity of TiO_2 , reaching a J of 2.92 mA cm^{-2} at 0.25 V vs. Ag/AgCl, which is five times higher than that of the undoped TiO_2 , attributed to the enhanced activity in the visible light from the impurity states, the increased carrier density of TiO_2 , effective carrier separation, and longer electron lifetime [24]. Also, surface modification of the N-doped TiO_2 nanotubes exploring an amorphous thin TaO_xN_y layer fabricated by nitridation induced a further red shift of the absorption edge toward the visible region, leading to efficient charge separation, and finally achieving a markedly enhanced PEC performance [25].

Recently, oxynitride based photoelectrodes have emerged as an attractive opportunity for PEC water oxidation, due to the proper band positions being well straddled to the water oxidation/reduction potential, as well as the narrower bandgap to extend the visible light absorption [26,27]. For example, nitrogen enriched GaON/ZnO nanoflower sheet architecture as photoanode exhibited a J of $\sim 1.2 \text{ mA/cm}^2$ at 1.1 V vs. SCE [28]. Recently, Ag nanoparticles-decorated $TiON$ (Ag/ $TiON$) nanotube arrays showed a significant increase to reveal a J of $\sim 6 \text{ mA/cm}^2$ under one sun condition, closely related to the increased electrical conductivity and surface plasmonic effect of Ag nanoparticles [29]. On the basis of the established concepts and ideas, a strategy on new material structure and design is highly desirable to boost the PEC performance via the surface modification of the TNR arrays [17–22]. As a strong candidate, TiO_xN_y is a cost-effective *n*-type semiconductor that shows unique physico-chemical properties and large-scale applicability in various fields, including nanoelectronics, catalysis, sensors, photonics, biomaterials, and biomedicine [30–32]. To the best of our knowledge, no relevant research combining TNR arrays and TiO_xN_y has been reported for PEC water oxidation. Therefore, the formation of a heterojunction (TiO_xN_y @TNR) based on the oxynitride and TNR arrays can overcome the drawbacks of the TNR array with coupling to the favorable features of TiO_xN_y nanoparticles having a size of ~ 15 nm, contributing to the increase of PEC performance. In particular, solution-based colloidal methods for preparing oxide/oxynitride semiconductor photoanode allow the use of inexpensive processing techniques like spin-coating or dip coating, and can form stable thin film with 1D morphology. Herein, according to the number of TiO_xN_y layers from 1 to 3 layers by a spin-coating method, the PEC activity is evaluated and optimized, and finally discussed in terms of several aspects of the TNR@ TiO_xN_y system.

Experimental procedures

First, the fluorine doped SnO_2 (FTO) conducting substrates were chemically treated by using a $H_2SO_4:H_2O_2:H_2O$ solution of 3:1:1 vol ratio for 20 min to improve the surface roughness. The TNR arrays were synthesized by a facile hydrothermal method, where the aqueous solution containing 22 ml of deionized (DI) water and 22 ml of hydrochloric acid (HCl, 35.5%) is mixed with titanium (IV) butoxide (0.378 ml, 97%) in a 50 ml beaker under constant magnetic stirring for 20 min at room temperature. Subsequently, the surface treated FTO substrates (2 cm \times 2 cm) were placed inside a Teflon vessel. The resulting homogeneous mixture was then transferred

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