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Sunlight driven photoelectrochemical light-to-electricity conversion of screen-printed surface nanostructured TiO_2 decorated with plasmonic Au nanoparticles

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ABSTRACT

In this paper, we report a promising sunlight-driven screen-printed TiO_2 porous nanorods (PNR) photoanode decorated with Au plasmonic nanostructures for photoelectrochemical (PEC) light-to-electricity conversion. Fabricated photoanodes were characterized using field emission scanning electron microscopy, high-resolution transmission electron microscopy, energy dispersive spectroscopy, X-Ray diffraction analysis, X-ray photoelectron spectroscopy, N_2 adsorption-desorption isotherms, UV–vis spectroscopy and electrochemical impedance spectroscopy in detail. The Au-PNR-TiO_2 photoanode demonstrates superior PEC activities both under simulated sunlight and visible light irradiation. Interestingly, the Au-PNR-TiO_2 shows high photocurrent density of 0.71 mA cm^{-2} at +0.4 V vs. Ag/AgCl, which is 65% higher than the pristine PNR-TiO_2. It is shown that enhanced surface area, roughness factor, high crystallinity and one-dimensional framework which are offered by screen-printed porous TiO_2 nanorods make a great microenvironment for more accessible reactive sites, light capturing ability, efficient charge generation and smooth transfer of photogenerated charge carriers. Decoration with Au nanoparticles is also shown that play an important role in improving the PEC performance by injecting hot electrons and excellent catalytic effect.

1. Introduction

Photoelectrochemical (PEC) light-to-electricity conversion is one of the highly efficient and eco-friendly methods of production of H_2 for renewable green fuel application [1–6]. TiO_2 is one of the most promising photocatalysts candidates as it is nontoxic, stable, inexpensive, and exhibits strong photocatalytic activity [7–11]. The efficiency of charge carriers in TiO_2 is significantly influenced by two important factors: (i) geometry of nanostructure, and (ii) properties of the surface, where the catalytic reaction takes place, are the two most important parameters which determine the PEC performance of TiO_2 crystals [12].

Compared with irregular-shaped nanoparticles, one-dimensional (1D) nanostructures (like nanorods and nanotubes), possess greater charge mobility along the longitudinal dimension as they offer direct pathways for charge carriers [13]. However, the reaction rate of 1D nanostructures is low as the electrode–electrolyte interfacial area is typically insufficient. Therefore, various TiO_2 architectures such as nanofibers [14], three-dimensional (3D) nanostructured [15], and branched nanorods [16,17] photoanodes have recently been introduced because of their unique characteristics such as improved specific surface area, efficient charge separation, high carrier mobility and ease of nanoscale integration of different functional materials which are favorable for PEC light-to-electricity conversion [18,19]. Most of these proposed TiO_2 architectures were synthesized using the hydrothermal method. Even though high quality of 1D

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nanostructured TiO_2 are produced by this method, the process cannot be applied to large-scale fabrication. On the other hand, screen-printing is a well-established commercialized technology for the large-scale fabrication of sensors and photoanodes [20,21]. Particularly, screen-printing of TiO_2-based photoanodes is an extensive industrial, low-cost and fast technique with a possibility to attain very precise position and thickness control. To prepare the efficient TiO_2 based PEC light-to-electricity conversion, it is also important to design a photoanode with a large roughness factor (defined as the total surface area per unit substrate area) and high optical absorption.

Since PEC light-to-electricity conversion takes place at a high overpotential to form O_2 molecules, the reactions between photogenerated holes and water molecules primarily control the performance of PEC [22]. However, the water oxidation through photogenerated valence band holes is kinetically ineffective, so extra anodic biases are required for PEC light-to-electricity conversion [23]. In addition, electron–hole recombination and other side reactions induce a large accumulation of photoholes at the interface of electrode/electrolyte [24,25]. Incorporation of nanomaterials and nanostructures is an effective method to reduce the recombination velocity and enhance the kinetics of electrode reactions. Therefore, efficiently coating TiO_2 with nanostructure catalyst can be used to improve the performance of TiO_2 based PEC light-to-electricity conversion.

Among different nanostructured catalysts, Au plasmonic nanostructure is considered as one of the most promising nanostructured catalyst for PEC applications due to its excellent photostability and tunable interactions with visible light via localized surface plasmon resonance (LSPR) [26–28].

In this study, we demonstrate a novel facile and industrial method to fabricate nanostructured porous TiO_2 nanorods (PNR-TiO_2) via screen-printing method for efficient PEC light-to-electricity conversion. To the best of our knowledge, this is the first report on exploiting screen printed nanostructured TiO_2 electrode (in other researches, electrodes were mostly fabricated through hydrothermal method [1,15,16]) for PEC applications which is vitally important because practical and industrial methods have to be used for commercial application. PNR-TiO_2 have superior charge transport and optical absorption properties and larger surface area for more proficient carrier collection as compared with pristine NR-TiO_2. Furthermore, the results show that PNR-TiO_2 surface decoration with Au nanoparticles (NPs) catalyst leads to an enhanced PEC activity under simulated sunlight and visible-light irradiation. This boosted PEC activity is mainly attributed to the lower charge carrier recombination, a well-established Schottky barrier, hot electron transfer between metal and oxide and ultimately catalytic effect of Au NPs. This work demonstrates the unique approach for preparing the high-performance visible-light-driven PEC light-to-electricity conversion by coupling plasmonic Au nanoparticles with screen-printed nanostructured TiO_2 nanorods.

2. Experimental

2.1. Photoanodes preparation

The (NP, NR, PNR)-TiO_2 were synthesized using the method published elsewhere [29]. Briefly, NP-TiO_2 was synthesized via hydrothermal method by 12 g of acetic acid (CH_3COOH) and 58.6 g of titanium tetra iso propoxide (TTIP) with a purity of 97% (Sigma-Aldrich, UK), 300 ml deionized water, 10 ml of 65% nitric acid (Merck). The mixture was heated at 70 °C and peptized for 75 minutes. Then after it was hydrothermaled at 180 °C for 24 h. To grow NR-TiO_2, 1 g of NP was used as a precursor powder that was mixed in 40 ml of a 10 M aqueous NaOH solution followed by hydrothermal at 180 °C for 72 h and rinsed with HCl. In the second step, the above solution was dispersed in 40 ml ethanol/water (1:1) solution and 2 ml of dimethylamine and stirred for 30 minutes. The finalized solution was hydrothermaled at 180 °C for 10 h. For synthesizing PNR-TiO_2, the same steps as for NR were repeated, except that ethylene glycol was used instead of ethanol in the second step (Corresponding micrographs of as-prepared NR-TiO_2 and PNR-TiO_2 powders via hydrothermal synthesis are shown in Fig. S1a and b).

In the next step, pastes of (NP, NR, PNR)-TiO_2 were made as described previously [30]. Briefly, 1 ml acetic acid, 5 ml deionized water, 130 ml ethanol, 20 g terpineol and 10% ethyl cellulose, were added dropwise to 6 g of synthesized (NP, NR, PNR)-TiO_2 powders, followed by grinding, stirring and sonication. The final paste was acquired after evaporation and homogenization. A layer of paste was screen-printed with appropriate stencil designs using a SP-1400 screen-printing machine (90T mesh/cm) onto $TiCl_4$ pre-treated fluorine doped tin oxide (TEC15 FTO from Pilkington) with a 40° rubber squeegee and printing speed of 10 mm/s. To decorate PNR-TiO_2 with Au NP cocatalyst cyclic voltammetry (CV) technique was utilized at a scan rate of 20 mV s^{-1} for 1 cycle in the range of potentials from +0.1 to −1 V vs. open circuit potential (OCP) from

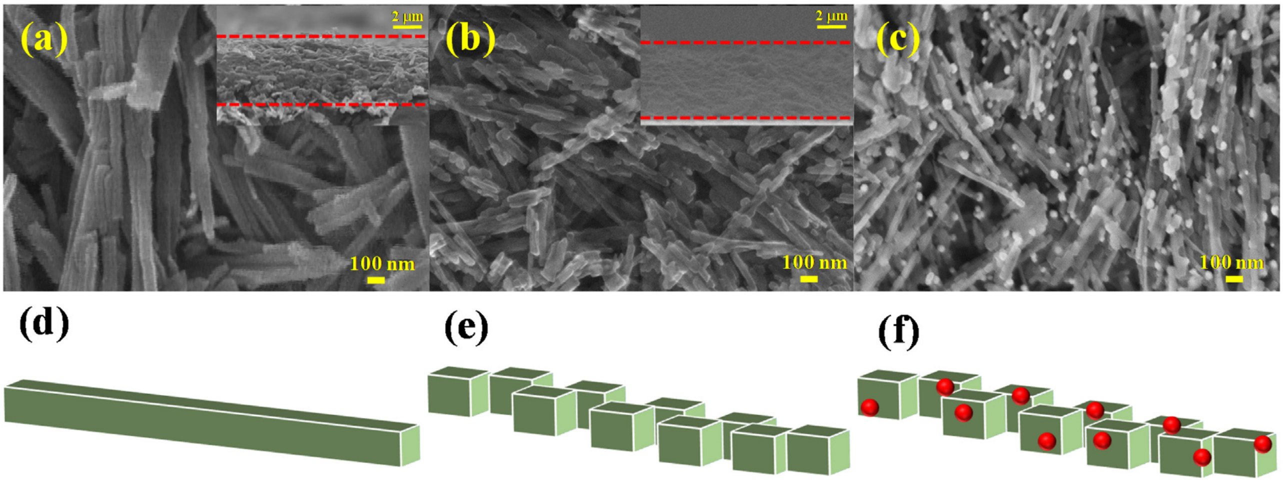

Fig. 1. Top view FESEM micrographs of (a) NR-TiO_2 film (inset: cross sectional image) (b) PNR-TiO_2 film (inset: cross sectional image) (c) Au-PNR-TiO_2 film; their schematic illustrations are depicted in (d)–(f), respectively.