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Full Length Article

Enhanced photo-assistant electrocatalysis of anodization TiO_2 nanotubes via surrounded surface decoration with MoS_2 for hydrogen evolution reaction

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ABSTRACT

A highly ordered TiO_2 nanotube array covered with MoS_2 is fabricated through a facile anodization of a metallic Ti followed by electrochemical deposition approach. The morphologies characterization of v-TiO_2@MoS_2 indicate that a whole scale of 1D TiO_2nanotube uniformly covered with the MoS_2 layer inside and outside, and the pathway inside the TiO_2nanotube is kept flow-through. The as-synthesized v-TiO_2@MoS_2 hybrid exhibits higher efficient and stable visible light activities than that of either pure TiO_2 nanotubes or nv-TiO_2@MoS_2 nanostructures. By electrochemical measurements such as linear sweep voltammetry(LSV) and electrochemical impedance spectroscope (EIS) under light illumination or in dark, we find that the v-TiO_2@MoS_2hybrid shows markedly enhanced photoelectrochemical performance. Furthermore, we compare the electrocatalytic behavior of v-TiO_2@MoS_2under illumination in H_2SO_4/Lactic acid within Na_2S/$NaSO_3$ solution. The results show that the photo-assistant electrocatalytic activity in acidic environment is much better than in alkaline environment. The highly directional and orthogonal separation of charge carriers between TiO_2 nanotubes and MoS_2 layer, together with maximally exposed MoS_2 edges, light harvesting and junctions formed between TiO_2 and MoS_2 is supposed to be mainly responsible for the enhanced photo-assistant electrocatalytic activity of v-TiO_2@MoS_2.

1. Introduction

The utilizing of solar energy to hydrogen fuel from water via photocatalysis has been considered to be an effective strategy for tackling the global energy and environmental crisis. Generally, the semiconductors generate charge-carrier (electron–hole) pairs due to solar light harvesting [1–3] and suitable energy band alignment for reduction of H^+ to H_2 [4–9] and therefore be widely used for photocatalysis of HER. Among the numerous candidates, titanium dioxide (TiO_2) is often employed as a photocatalyst [10] for self-cleaning and solar energy conversion [11–13] for its chemical stability and biological benign [14–17]. However, the wide band gap of pure TiO_2($\sim$3.1 eV) results in only $\sim$5% of the entire solar spectrum absorbed, and is very inefficient for visible solar light harvesting. To improve the photoelectrocatalytic activities under visible light, many investigations have developed to reduce the TiO_2 bandgap by doping [18–20] or band gap engineering [21], aiming to broaden its light harvesting window to visible range [22,23] and to construct suitable electronic heterojunction for charge separation and transportation [24–26]. As most photocatalytic reactions are carried out in the electrolyte, it is necessary to consider the nature of the semiconductor/electrolyte interface, which determines both energetics of phase boundaries and kinetics of the reaction. Therefore, optimizing crystal structures (polymorphs and faceting) [27–29] or morphologies is another effective strategy to enhance the photocatalytic performance of TiO_2. Among a plethora of crystal structures and morphologies of TiO_2 such as nanowires, nanosheets, and nanotubes [22,30–33], anatase TiO_2 nanotube have been prepared with different synthesis strategies, and show advantages of 1D nanostructures [34–43]. Therein, the vertically oriented anatase TiO_2 nanotube arrays prepared by a facile electrochemical anodization method exhibits the highest photocatalytic activity due to high specific surface and excellent electron transportation [32,44,45]. Recently, layered MoS_2, a well known *p*-type semiconductor [25,46–50], has been reported the band gap (Eg) of $\sim$ 1.9 eV [51,52] on going transition from direct to indirect band gap semiconductor, which opens a possibility for visible light

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adsorption. Coupling with TiO_2, a regular *n*-type semiconductor, to form 1D MoS_2/TiO_2 nanotube hybrid, the as prepared hybrid composite not only creates the *p-n* heterojunction between MoS_2 and TiO_2, thus enhancing the separation of photoinduced electro-hole pairs, but also broadens its light harvesting window to visible range in the quest of visible light photocatalysis. More importantly, MoS_2 with a layered structure is considered a promising electroatalyst for HER due to its similar free energy of adsorbed H ($\triangle G_H$) on crystalline MoS_2 (010) edge sites with those of Pt [53,54]. Together with the desirable designation of the architectural structure morphology enabling synergistic impacts on photocatalytic activity, 1D MoS_2/TiO_2 nanotube composite is anticipated to perform a superior integrated performance of photocatalytic and electrochemical activity.

In this work, a highly ordered TiO_2 nanotube array covered with MoS_2 was fabricated through a facile anodization of a metallic Ti substrate followed by electrochemical deposition approach. In contrast to conventional composite prepared from 1D TiO_2 nanotubes in which the introduction of foreign species is preferentially deposited only at top surface of the TiO_2 nanotubes and blocked the tube openings [55], the composite prepared with this approach presents a whole scale of 1D TiO_2 nanotube uniformly covered with the MoS_2 layer inside and outside, and the pathway inside the TiO_2 nanotube is kept flow-through. This characteristic of the as-prepared hybrid structure favors for both light harvesting and band gap engineering. More meaningful, 1D TiO_2 nanotube wrapped with MoS_2 layer not only maximally expose the MoS_2 edges, but also offers enlarged interfacial contact area between 1D MoS_2/TiO_2 nanotube and electrolyte. Together with the highly directional and orthogonal separation of charge carriers between 1D TiO_2 nanotubes and MoS_2 layer, which is exploited for a fast transport, the as-synthesized composites showed a superior electrocatalytic activity for HER by assistance of visible light. In addition, directly anodic 1D TiO_2 on Ti substrates is binder free, and was chosen to be a cathode. Different from classical powder assemblies, requiring additives/binders to prepare the electrodes, the as prepared composite provides a facile way for recycling use. Due to advantageous directional charge transfer, increased active facet exposure the interfacial contact, and sufficient electrochemical reaction of individual nanostructures, the as-synthesized composites integrate electro- and photocatalysis toward HER.

2. Experimental

2.1. Materials

Lactic acid, sulfuric acid, potassium chloride, sodium sulfite anhydrous and hydrofluoric acid aqueous solution was obtained from Sinopharm Chemical Reagent Co., Ltd. Ammonium tetrathromolybdate and Sodium sulfide nonahydrate was obtained from J&K. Ti foil (200*100*0.2 mm, 99.7% purity) was purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Limited. Deionized water (DI water) (Resistivity > 18.2MΩ cm^{-1}) was prepared by a pure water equipment (TTL-6B). All chemical reagents were used as received.

2.2. Preparation of anodic TiO_2 nanotube array wrapped with MoS_2(labeled TiO_2@MoS_2)

An electrochemical anodization and a followed electrochemical deposition were preferred to prepare the TiO_2@MoS_2 nanotube array structure. Firstly, Ti foil (40*20*0.2 mm) were ultrasonically washed in ethanol, acetone and DI water for 15 min each, respectively, and then dried in a nitrogen atmosphere prior to anodization. Then the highly ordered TiO_2 nanotubes were prepared by anodic oxidation in a HF aqueous electrolyte (0.8vol.%), following that described by previous work [56]. In a typical reaction, Ti foils were immersed in a HF aqueous solution (0.8vol.%), and suffered from a constant 20 V potential for 1hr at room temperature in a two-electrode electrochemical cell supplied with a DC power. After anodic oxidation, the as-prepared products were washed with DI water, and dried in a N_2 stream.

For preparation of TiO_2@MoS_2 nanotube array, the as prepared anodic TiO_2 nanotube array was immersed in aqueous solution composed of 2 mM $(NH_4)_2MoS_4$, 2 mM Na_2S•$9H_2O$ and 0.1MKCl, and then vacuumed for 30 min. The above pretreated system was electrodeposited for 10–30 min, and the film obtained was washed with DI water. The as prepared product was annealed at 400 °Cfor 2hr under the argon atmosphere to obtain TiO_2@MoS_2 nanotube array electrode (labeled v-TiO_2@MoS_2). For comparison, the TiO_2@MoS_2 nanotube was prepared by immersing in the aqueous precursor solution without vacuuming (labeled nv-TiO_2@MoS_2). Another control sample of Ti foil covered with MoS_2 (labeled MoS_2/Ti) is prepared by similar process with that of TiO_2@MoS_2 nanotube arrays, except that the anodization process is rule out.

2.3. Characterization

Scanning electron microscopy (SEM) was conducted using a JEOL-6701F field emission scanning electron microscope at 10 μA of scanning current and 5 kV of accelerating voltage. High resolution transmission electron microscopy (HRTEM) images are obtained from a JEOL JSM-3010 instrument which was operated at 200 kV. X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2500B2+/PCX system which is operated at 40 kV and 30 mA using Cu Kα radiation with a scan rate of 4° min^{-1}. X-ray photoelectron spectroscopy (XPS) was conducted by an ESCALAB250. The optical properties were investigated by UV–vis diffuse reflectance spectra using a UV–vis spectrophotometer (Shimadzu UV2450, Japan) with an integrating sphere attachment. Photoluminescence measurements (PL) were conducted on a Hitachi F-4500 FL spectrophotometer with an excitation light at 410 nm induced from a Xe laser source. PL decay dynamics measurement was carried out by fluorescence lifetime spectrometer (FLS980 Edinburgh Instruments).

2.4. Electrochemical measurements

We performed the electrochemical experiments in a three-electrode cell which was made of quartz. A Pt wire and calomel (Hg/Hg_2Cl_2, SCE) were employed as the counter and reference electrodes, respectively, and the as prepared catalysts were used as the working electrode which has an area of 0.16 cm^2. Linear sweep voltammetry (LSV) with scan rate of 10 mV $s^{-1}$was conducted in 0.5 M H_2SO_4/lactic acid (pH = 0.52) and 0.5 M $Na_2S/NaSO_3$ (pH = 12.8) solution, respectively, using an electrochemical workstation (CHI660E, Chenhua, China). Both of lactic acid and Na_2S function as a sacrificial agent. Prior to the test measurements, N_2 was introduced into the electrolyte solution to eliminate the dissolved oxygen. A 300W Xe arc lamp (CEL-HXF300) was employed as a light source. The integrated visible light intensity was 150 mW/cm^2. IPCE was measured at 0 V versus RHE with a monochromator in the range of 380−700 nm. The light intensity was measured with a photometer (Newport, 840-C, USA). The typical monochromatic photon power density in the IPCE measurements was 0.7 mW/cm^2. The IPCE is expressed as IPCE = (1240I)/(λ J_{light}), where I represents the measured photocurrent density, λ represents the incident light wavelength, and J_{light} represents the recorded incident light power density.