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Photosensitive polymer and semiconductors bridged by Au plasmon for photoelectrochemical water splitting

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ABSTRACT

Heterogeneous semiconductor has received increasing attention as promising photoelectrode matrix in photoelectrochemical (PEC) water splitting. However, the composition and optimization of heterostructure still limited the photoelectric transformation and PEC water splitting efficiencies. Here, an effective strategy was introduced to enhance PEC performance by sandwiching Au plasmon inside inorganic-organic hybrid heterostructure. We successfully fabricated TiO_2 and polythiophene (PTh) heterostructure bridged by Au nanoparticles, and applied it in PEC water splitting for the first time. Compared with traditional TiO_2 and TiO_2/PTh, the as-prepared heterostructure photoelectrode exhibited the optimal photoelectric conversion (0.11%, at 0.22 V vs Ag/AgCl) and PEC hydrogen production rate (2.929 mmol h^{-1} m^{-2}, at 50 mW/cm^2 and 0.4 V vs Ag/AgCl). The enhanced water splitting can be mainly contributed to the transparent PTh nanowires as the photosensitizer and Au nanoparticles as both electron-transport bridge and plasmonic sites.

1. Introduction

Environmental pollution from carbon-based fuel has become an inevitable threat to human survival and development. Hydrogen is an ideal green energy, and the hydrogen production by direct photoelectrochemical (PEC) water splitting could effectively converse solar energy into a sustainable green energy for industries and vehicles [1]. Abundant metal oxide semiconductors especially titanium oxide (TiO_2) have been considered as effective matrixes for PEC water splitting, because TiO_2 possesses several unique natures for fabricating PEC photoelectrodes, such as photosensitivity, suitable band edge positions, long-term stability and low cost [2,3]. However, the large band and electron-hole separation cause the bare TiO_2 photoelectrodes just to respond to UV light with significant charge recombination, so it is still a challenge to design high effective photoelectrodes based TiO_2 [4]. Various compositing strategies have been explored to improve TiO_2 photoelectrodes with optimal solar energy conversion for PEC water splitting [5], which can be realized by narrow band semiconductor modifying, selective elements doping [6] or noble metals decorating [7]. Although TiO_2 could form heterojunction with some semiconductors like ZnO, CdS or MoS_2, the major problem it faces is the instability performance which mainly results from photochemical corrosion [8–10]. Taking account of above problems, organic polymer with better chemical stability and photo-absorption coefficient may offered a new opportunity in the fabrication of hybrid TiO_2 photoelectrodes, which might substitute the traditional inorganic material to decorate TiO_2 photoelectrodes [11,12].

Polythiophene (PTh), a classical photosensitive polymer, has been widely investigated as organic semiconductor and applied in many fields like photocatalysis, solar cells, sensors and so on, due to its favorable transparency and plasticity [13–15]. As possible as we known, there are still very few reports about PTh for hydrogen production by PEC water splitting. Since Katsumi Yoshino and Shigenori Hayashi had synthesized structured PTh by using anhydrous $FeCl_3$ as catalyst in 20 century 80 years [16], some different synthesis methods for PTh have been further reported subsequently, while the electrochemical method can carry out at room temperature and take less time [17,18]. Moreover, PTh plays an important role in the photosensitization, but the conductivity of PTh is relative lower than inorganic materials, so PTh can be only used as the modified materials but not the main matrix in the compound [19], and which also limits the charge transfer between PTh and inorganic semiconductor. Therefore, it will be another strategy to further optimize the intersuface between PTh and inorganic semiconductor.

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Noble metal such as gold (Au) would be a suitable link to further optimize the interface between PTh and inorganic semiconductor, since Au has excellent electronic transmission capability [20]. Moreover, the plasmon effect and chemical stability of Au also endow photoelectrode with wider spectral response range [21,22]. In addition, Au could also effectively retard the recombination of photogenerated electron and hole (e^-/h^+) pairs in TiO_2 due to surface plasmon resonance of noble metal nanoparticles [23,24].

Herein, we fabricate a ternary bybird structure TiO_2/Au/PTh to improve the PEC water splitting efficiency of bare TiO_2. The TiO_2 serves as a supporting platform which makes it possible that building a composite structure on FTO surface for PEC photocatalysis, while PTh could further increase the absorption of visible light and provide more photogenerated e^-/h^+ pairs. The PTh can be synthesized as nanowires structure, which benefits for the contact between electrolyte and internal layer TiO_2. More importantly, the Au nanoparticles have been induced between TiO_2 and PTh, and Au nanoparticles can act as a "bridge" to accelerate the electron transport between organic and inorganic materials. The PEC properties and hydrogen production rate have been effective enhanced compared with bare TiO_2 photoelectrode.

2. Experimental

2.1. Chemicals

Tetrabutyl titanate (TBTI), thiophene, chloroauric acid ($HAuCl_4$), potassium chloride (KCl), lithium hydroxide (LiOH) were purchased from Sigma-Aldrich. Ethanol (≥99.7%), hydrochloric acid (HCl, 63–66%) and perchloric acid ($HClO_4$, 70–72%) were supplied by Sinopharm Chemical Reagent Co., Ltd., of China.

2.2. Preparation of photoelectrodes

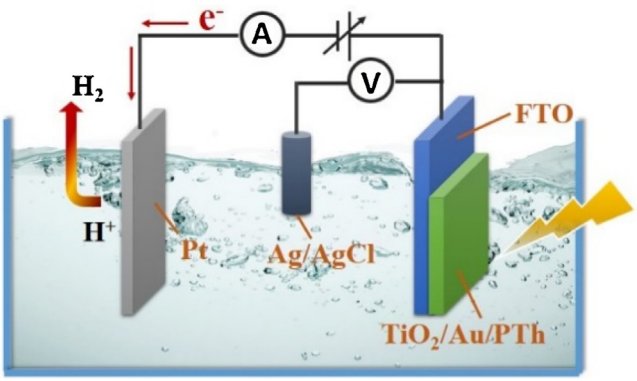
The synthesis of TiO_2 photoelectrode was according to the traditional hydrothermal method [25]. A mixing precursor solution with 1.4 mL TBTI, 30 mL HCl and 30 mL H_2O was stirred for 1 h, then put into a Teflon-lined stainless steel autoclave containing with a FTO substrate, and the Teflon-lined stainless steel autoclave was heated in oven at 180 °C for 5 h. Subsequently, the original formation of TiO_2 substrate was steep into a solution with 1.5 mL TBTI, 2 mL acetic acid and 100 mL ethanol for 1 h, and finally placed into a muffle furnace to be annealed at 450 °C for 2 h in air.

Au nanoparticles were loaded on the surface of TiO_2 by electrodeposition method [26]. The electrodeposition was performed in a three-electrode cell by using 0.1 M $HAuCl_4$ and KCl solution with TiO_2 electrode as the working electrode, a Pt foil as the counter electrode and the Ag/AgCl electrode as a reference electrode. The deposition was achieved at room temperature with constant potential of −0.2 V for 30 s.

Similarly, PTh was also synthesized by electrodeposition, using 0.1 M $LiClO_4$ as electrolyte, and dispersing 0.5 M thiophene into acetonitrile solution. PTh was polymerized on surface of TiO_2 with bias voltage of 1.8 V for 2 min.

2.3. Characterization

Morphologies of samples were characterized by scanning electron microscopy (SEM) on S-4800 II field-emission scanning electron microanalyzer. Transmission electron microscopy (TEM) was measured by JEM-2100 (HR) microscopes. The phases of samples were confirmed by X-ray powder diffraction (XRD) (Cu-Kα radiation, λ = 1.541 Å, Bruker or D8 Advance), and the 2θ range was from 5° to 60°. X-ray photoelectron spectroscopy (XPS) measurements were achieved with an ESCALAB 250 photoelectron spectrometer. Fourier transform infrared (FTIR) spectra were recorded by Bruker Vector. Raman spectra of the samples were investigated by Jobin-Yvon HR-800 spectrometer (532 nm Ar^+ ion laser) at room temperature. UV–vis absorbance spectra were obtained using Shimadzu UV-2550 spectrometer.



Scheme 1. PEC performance test and process of hydrogen production.

2.4. PEC performance test

PEC Measurements were performed in a three-electrode cell (as shown in Scheme 1) by using 0.5 M $NaSO_4$ electrolyte with simples as the working electrode, a Pt foil as the counter electrode and an Ag/AgCl electrode as a reference electrode. The solid lines represent that samples with an area of 1 cm^2 are exposed upon visible light irradiation at 50 mW/cm^2 provided by a 150 W xenon lamp. The potential and other parameters were set up through an electrochemical workstation (CH Instruments, CHI 852C).

3. Results and discussion

The classical morphology of TiO_2 rod-like array structure which vertically grows on FTO by hydrothermal treatment has been shown in Fig. 1a. From the top of view, it can be clearly observed that the diameter of TiO_2 rod-like array is about 200 nm and obvious interspaces exist among the array. However, when TiO_2 has been further modified by PTh as shown in Fig. 1b, a thin and transparent film will cover on the top of TiO_2 array. Taking account of the viscosity of colloid PTh, the interspaces have been filled, and the PTh encapsulates on the surface of TiO_2 array, which finally makes TiO_2 array unapparent in Fig. 1b and the sectional drawing (Fig. S1).

TEM is conducted for detailed investigation of microstructure, the image of which is shown in Fig. 1c and d. A few fragmentary black rod-like materials in the sample can be attributed to the TiO_2, since the sample used for TEM characterization was previously stripped from photoelectrodes and then ultrasonic dispersed in ethanol, which may cause the break of TiO_2 array. In addition, microstructure of PTh has been observed as another kind of one-dimensional nanowires, and PTh nanowires further form as a dense network structure, which may result from the self-assembly behavior of organic polymers. The inset image of Fig. 1d shows some Au nanoparticles about 10 nm on the surface of TiO_2, indicating that the Au nanoparticles has been successfully loaded by electrodeposition method. Therefore, TEM images give a preliminary proof for the fabrication of ternary composite system based on TiO_2, Au and PTh, and the Au nanoparticles are at the position between TiO_2 and PTh.

In Fig. 2, both high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images are measured for TiO_2 and Au in the composite material, but except for PTh nanowires, because the organic polymer is unstable in the electron field emission and the amorphous carbon in cop-