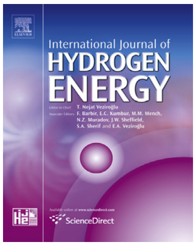
Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/he



The identification and characterization of Pt_x-$Zn_{1-x}O$ photocatalysts for photoelectrochemical water splitting applications

Yu-Ching Weng [a,*], Kuan-Ting Hsiao [a], Ke-Chih Chiu [a], Yuh-Fan Su [b]

[a] Department of Chemical Engineering, Feng Chia University, Taichung 40724, Taiwan
[b] Department of Greenergy Technology, National University of Tainan, Tainan 70005, Taiwan

ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form
27 October 2016
Accepted 4 November 2016
Available online xxx

Keywords:
Scanning electrochemical microscopy (SECM)
Photocatalysts
ZnO
Pt
Water splitting

ABSTRACT

A pico-liter dispensing system is used to fabricate Pt_x-$Zn_{1-x}O$ photocatalyst arrays on a FTO substrate. The photoelectrochemical performance of these arrays is determined quickly, using scanning electrochemical microscopy (SECM), where an optical fiber is connected to a xenon lamp. The spot for the $Pt_{0.2}$-$Zn_{0.8}O$ exhibits the highest photocurrent in 0.1 M Na_2SO_4/Na_2SO_3 solution, it is when irradiated by UV-visible light. This material is characterized using SEM, EDX, XRD, XPS, UV–vis spectroscopy and Mott–Schottky analysis. The $Pt_{0.2}$-$Zn_{0.8}O$ photocatalyst is composed of a binary mixture of 84 mol% ZnO with a Wurtzite structure and 16 mol% Pt with a face center cubic structure. The photoelectrochemical (PEC) properties of the bulk film photoelectrode confirm the SECM results. The superior photocatalytic activity of the $Pt_{0.2}$-$Zn_{0.8}O$ composite is mainly due to its high carrier density, which promotes the separation of photo-induced electrons and holes and gives a reduced probability of recombination.

Introduction

ZnO is a good semiconducting material for photocatalytic applications in energy and environmental fields because of its unique physical properties, such as its direct wide band gap of 3.37 eV and its large exciton binding energy at room temperature of 60 meV [1]. It is also cheap, non-toxic and has a high melting point, a low electron affinity and excellent chemical stability. However, the fast recombination rate for photogenerated electron/hole pairs causes a significant reduction in the photocatalytic efficiency [2,3]. Therefore, charge carriers must usually be rapidly transferred to surface reaction sites. A strategy to negate this involves the formation of a co-catalyst system by enabling noble metal contacts on the surface of ZnO to achieve an efficient charge separation [4–6]. The excited electrons in ZnO then transfer to the metal when the work function of the metal is greater than that of ZnO. Several metals have been used to form metal-ZnO heterostructure photocatalysts, such as Au-ZnO, Ag-ZnO, Pd-ZnO and Pt-ZnO [7–13]. Of the various noble metal co-catalysts, Pt is eminently suitable because of its larger work function of 5.93 eV, which is similar to that for semiconductors [14]. It provides a direct, rapid photogenerated electron transfer channel from an excited semiconductor to the Pt metal and increases the photocatalytic efficiency of a ZnO photocatalyst [15].

---

* *Corresponding author*. Fax: +886 4 24510890.
E-mail address: ycweng@fcu.edu.tw (Y.-C. Weng).

http://dx.doi.org/10.1016/j.ijhydene.2016.11.023

Please cite this article in press as: Weng Y-C, et al., The identification and characterization of Pt_x-$Zn_{1-x}O$ photocatalysts for photoelectrochemical water splitting applications, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.11.023

Some attempts have been made to combine Pt with ZnO as photocatalysts. Xue et al. synthesized ZnO-Pt flowerlike heterostructures that exhibit better catalytic efficiency than commercial TiO_2 nanoparticles [16]. Li et al. reported that a Pt/ZnO nanorod array-modified microreactor exhibits rapid and highly efficient photocatalytic activity during the photodegradation of phenol [17]. Hsu et al. confirmed that Pt-decorated ZnO nanorod (NR) electrodes separate photogenerated electron–hole pairs more efficiently and allow a faster charge transfer than a pristine ZnO NR electrode [18]. However, the effect of Pt on the photocatalytic performance depends significantly on its concentration. This study fabricates Pt_x-$Zn_{1-x}O$ photocatalyst arrays with various Pt/Zn molar ratios on FTO substrates using a pico-liter dispensing system. The arrays are then rapidly screened using scanning electrochemical microscopy (SECM), using an optical fiber in Na_2SO_4/Na_2SO_3 solution. The photocatalytic activity of the spots is measured using the photocurrents at the substrate of the array for water oxidation. Pt_x-$Zn_{1-x}O$ photocatalysts with enhanced photocatalytic activity are identified, characterized and optimized.

Experimental procedure

Materials and chemicals

F-doped tin oxide (FTO)-coated conducting glasses (TEC 7, C. P Solar Co.) were used as substrates and cut into 1.5 × 3 × 0.2 cm^3 pieces, for use as both spot arrays and bulk electrodes. These substrates were cleaned and rinsed using isopropanol and deionized water. $Zn(NO_3)_2 \cdot 6H_2O$ (Showa), $H_2PtCl_6 \cdot xH_2O$ (UR), glycerol (J. T. Baker), $NaSO_4$ (Showa) and Na_2SO_3 (Showa) were used as received. Deionized water was used as a solvent in all of the electrochemical experiments.

Preparation of photocatalyst arrays

The dispensing system (CHI model 1550, CH Instruments) was used to fabricate the photocatalyst arrays. The position of the piezo-electronic dispenser was controlled using stepper-motors that operated an XYZ stage in a pre-programmed pattern. When the FTO substrate had been placed on the platform of the dispensing system, a voltage pulse of 80 V was applied to the dispenser, in order to eject the desired number of drops of metal precursor solution onto the substrate. All precursor solutions used a 3:1 solution of water/glycerol with a metal salt concentration of 0.2 M. The Zn precursor solutions were first loaded and dispensed in a specific pattern onto the FTO substrate. When the dispenser had been flushed and washed, the Pt solutions were loaded and dispensed onto the overlaying pattern. Each spot had a total of 20 drops and the number of moles of metal ions on each spot was constant. The prepared arrays were then stored at 600 °C for 3 h in an air atmosphere, using a tube furnace (21,100, Barnstead).

Screening of the photocatalyst arrays

The screening of the photocatalyst arrays used a PC-controlled CHI model 900c SECM (CHI Instruments, Austin, TX), as described in the literature [19]. A 200 μm optical fiber (FIA-P200-SR, Ocean Optics) that was coupled to a 150 W xenon lamp (SXE-150, Collimage International Co.) was connected to the tip holder of the SECM. The photocatalyst arrays on the FTO substrate constituted the working electrode and were placed on the bottom of the Teflon cell with an exposed area of 1.0 cm^2. A Pt wire and an Ag/AgCl electrode respectively constituted the counter and reference electrodes. The electrolyte consisted of 0.1 M Na_2SO_4 and 0.1 M Na_2SO_3. The Teflon cell was filled with SO_3^{2-}, which was used as a sacrificial electron donor. Light from a Xenon lamp was passed through the optical fiber, which was positioned perpendicular to the array surface at a distance of 500 μm. This scanned over the surface at 500 μm/s and illuminated one spot at a time. During the scan, a potential of 0 V vs Ag/AgCl was applied to the substrate, using the SECM potentiostat. A 425 nm long-pass filter was used to block the ultraviolet portion of light during irradiation by visible light. The photocurrent during the scan was used to produce a color-coded two-dimensional image and the optimal spot in the array was selected for the PEC application in the form of a bulk electrode.

Preparation and photoelectrochemical measurements for the bulk film electrodes

The premixed precursor solutions with a specific composition that was determined from the screening results were prepared using a drop-casting method for bulk film electrodes. 200 μL of 0.02 M metal salt in a water/glycerol solution was pipetted onto the FTO substrate (1.5 × 1.5 cm^2), using a micropipette, and then annealed in an air atmosphere at 600 °C for 3 h at a heating rate of 1°/min. The resulting bulk film electrode constituted the working electrode in a three-electrode cell. The Ag/AgCl electrode and a Pt foil were respectively used as the reference and counter electrodes. The surface of the bulk film electrode, which had a geometric area of 0.5 cm^2, was irradiated by a Xenon lamp. The photocurrent was measured under UV-visible or visible light irradiation in a 0.1 M Na_2SO_3/Na_2SO_4 solution, using chronoamperometry.

Physicochemical characterization

The surface morphology and the composition of the ZnO-Pt arrays were determined using a scanning electron microscope (SEM, S3400-N, Hitachi Co.) that was equipped with an energy dispersive X-ray spectroscope (EDX). The crystalline structure of the photocatalysts was determined using a high-resolution X-ray diffractometer (HRXRD, D8, Burker-Nonius) with CuKα radiation. The scanning rate was 3°/min in a 2θ range from 20 to 80°. The patterns obtained were identified using the Power Diffraction File (PCPDFWIN software). The chemical composition and binding states of the photocatalyst at the surface were determined using X-ray photoelectron spectroscopy (XPS, Phi5000 Ulvac-Phi Co.) with a monochromatic Al Kα X-ray source operating at 15 kV. The light absorption spectra for the photocatalysts were measured using a UV-visible spectrometer (UV–vis, V-670, JASCO) with a diffuse reflectance module.

Please cite this article in press as: Weng Y-C, et al., The identification and characterization of Pt_x-$Zn_{1-x}O$ photocatalysts for photoelectrochemical water splitting applications, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.11.023