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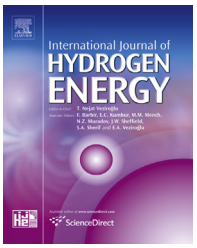

Investigation of porous silicon photocathodes for photoelectrochemical hydrogen production

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ABSTRACT

Solar energy conversion is made possible through the use of silicon as a photoelectrode material. Nanostructuring of the silicon substrate further improves solar energy conversion by virtue of its antireflective surface and tuneable band gap energies. In this work, we investigated the optimal etching conditions to fabricate porous silicon films, in terms of pore size and layer thickness. The stability of the sample was improved by passivating the porous layer with methyl groups via the electrografting of methyl iodide. A bio-inspired iron sulphur carbonyl electrocatalyst loaded on the electrografted porous silicon was studied. A photocurrent density of −2.8 mA/cm^2 and 46.8 μmol/h of hydrogen gas were observed for the electrografted porous silicon coated with bio-inspired iron sulphur carbonyl electrocatalyst.

Introduction

The adverse effects of excessive fossil fuel use on the environment have initiated the need for research into renewable energy sources. Solar energy, in particular, is an attractive source of renewable energy due to its virtually unlimited supply. Solar energy is used in photosynthesis by plants, which contain both a natural photoanode and photocathode to split water molecules. Current research on artificial photosynthesis follows this idea from nature, which involves the use of semiconductor photoelectrodes such as titanium dioxide, zinc oxide, cadmium sulphide or silicon [1–3]. In photoelectrochemical water splitting (PEC), the photoelectrodes absorb sunlight to split water into its constituents of hydrogen (H_2) and oxygen (O_2) [4]. Silicon is an ideal photoelectrode due to its abundance, low price and low band gap of 1.12 eV [5]. The nanostructured form of silicon, namely, porous silicon (pSi), has a tuneable band gap of 1.8–2.2 eV, which becomes useful for PEC water splitting [6–8]. Bulk and nanostructured silicon materials in different forms such as planar silicon [9–11], pSi [6,8], pSi micro/nanoparticles [12–14] and silicon nanowires [15–17] have also been used for water splitting applications. The major issue of using pSi in solar water splitting is its stability. The porous layer in the pSi substrate is prone to oxidation and degrades in electrolyte solutions. Electrografting, in particular, is known to be a superior passivation technique to reduce the oxidation and subsequent degradation of the porous layer [8,18–20]. An enhancement in the photocurrent density using an

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electrografted pSi sample can be achieved through the addition of an inexpensive iron sulphur carbonyl ($Fe_2S_2(CO)_6$) catalyst. This system has previously been shown to improve the efficiency of solar energy conversion [8,11]. Here, we investigated the effect of pore size and thickness of electrochemically anodised pSi in terms of photocurrent generation. We passivated the optimised pSi sample through an electrografting technique by varying electrografting current densities and time. The electrografted pSi sample was loaded with $Fe_2S_2(CO)_6$ catalyst to improve the photocurrent density. The fabricated electrodes were assembled into a three electrode electrochemical cell, which was immersed in 0.1 M sulphuric acid (H_2SO_4) as an electrolyte for photocurrent density measurements. The H_2 gas produced in the headspace was analysed using gas chromatography (GC).

Experimental section

Materials

pSi was fabricated from *p*-type silicon wafers (Czochralski, Siegert Ltd.) with resistivity of <1 mΩ cm, orientation (100). Hydrofluoric acid (HF, 48% Scharlau Chemie Brand) and ethanol 100% undenatured, Chem Supply Brand) was purchased from Chem-Supply, Pty. Ltd. South Australia.

pSi fabrication

Silicon wafers were etched by electrochemical anodisation in 1:1 ratio 48% HF: absolute ethanol with varied etching current density (7–114 mA/cm^2) vs. time (0.5–8 min).

Electrografting of pSi

Freshly etched pSi was rinsed with 1:1 HF: ethanol solution to remove any oxides formed and quickly transferred to a glove box in an argon atmosphere (M Braun Lab Star, 0.01 ppm O_2). pSi was then subjected to electrografting (Keithley, 2601 source metre) with 0.4 M of methyl iodide and 0.2 M lithium iodide in acetonitrile at varied electrografting current density (3.4–9 mA/cm^2) vs. time (45–120 s), under illumination by a tungsten lamp of 50 mW/cm^2. Finally, the samples were rinsed with glacial acetic acid, acetonitrile and left to dry in the glove box.

Electrode fabrication

The porous photoelectrode was soaked in the $Fe_2S_2(CO)_6$ catalyst dissolved in toluene for 1 h in a glove box to avoid surface oxidation. A back contact to the photocathode was formed using In–Ga eutectic applied through a cotton swab. Finally, a copper plate was used as an electrical back contact.

Surface characterisation

Scanning electron microscopy (SEM) images and energy dispersive X-ray absorption spectrum (EDXS) were obtained using a FEI Quanta 450 Environmental Scanning Electron Microscope (ESEM) instrument. Attenuated total reflectance-Infrared (ATR-IR) spectra were acquired on a Bruker Hyperion 1000 IR microscope operating with a Bruker Vertex 80 IR spectrometer. The IR microscope was equipped with a liquid nitrogen cooled MCT detector. ATR spectra were collected over 64 scans, with a resolution of 4 cm^{-1}, using a Ge ATR crystal. Spectra of the pSi layers were recorded and analysed using OPUS version 7.0 software, in the range of 650-4000 cm^{-1}.

Photocurrent and GC measurements

Samples were irradiated using an Abet solar simulator (air mass 1.5–1 sun) and calibrated against a silicon solar cell (New-Spec). Electrochemical measurements were carried out using a PG 310 potentiostat from HEKA Electronics (Germany). Electrolysis was performed using a sealed three-electrode Teflon PEC cell consisting of a platinum (Pt) counter electrode, a Ag | AgCl 3 M reference electrode, and the pSi working electrode. The working electrode with short 12 s dark/light cycle to measure the photocurrents as a function of time. The potential between the working and reference electrodes was adjusted between 0 and -500 mV in 100 mV steps. The sample gas (500 μl) in the headspace above the electrolyte was collected and analysed using a SRI 310C series GC with a thermal conductivity detector and a column held at 70 °C in N_2 as the carrier gas.

Results and discussion

Optimisation of pSi samples at varied thickness of the porous layer

The initial electrochemical anodisation conditions to fabricate pSi samples were followed from our previous published work [8]. The pSi sample fabricated using 57 mA/cm^2 current density in 1:1 HF: ethanol etching solution gave a pore size of ~50 nm, calculated via SEM. In the current work, the etching time was varied from 0.5 to 8 min with a constant current density of 57 mA/cm^2 to fabricate different thickness of the porous layers of pSi. The porous layer became instable after 8 min of etching time and separated from the silicon wafer. Table S1 shows the etching current density, etching time, the corresponding charges and the resulting porous layer thickness of the pSi calculated via SEM. It was observed that an increase in the etch time increased the thickness of the porous layer with a constant current density of 57 mA/cm^2 with the pore size of ~50 nm. The photocurrent density bar graphs are shown in Fig. 1 and are measured at a bias potential of −500 mV. The increase in thickness of the porous layer from 0 (flat silicon) to 1.9 μm led to an increase in the photocurrent density. But upon increasing the thickness further (3.3–9.2 μm) photocurrent densities dropped again.

The photocurrent density measurements demonstrated that a 1.9 μm thick porous layer of pSi showed the highest photocurrent density, with an average of −1.6 mA/cm^2. For an etching current density of 57 mA/cm^2 for 1 min of etching time the charge was calculated to be 3.4 C. With this charge as constant (translating into a more or less constant porous layer thickness), both the etching time and etching current density

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