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Silicon microhole arrays architecture for stable and efficient photoelectrochemical cells using ionic liquids electrolytes

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HIGHLIGHTS

- Silicon microhole arrays/ionic liquids junction is constructed for solar cells.
- Large holes make better electrochemical contact between electrolytes and SiMHs.
- Ionic liquids offer SiNWs cells better long-term stability than reference ones.

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ABSTRACT

Silicon microhole arrays (SiMHs) structure is constructed and fabricated by a low-cost maskless anodic etching process, which is applied as the photoanode for the silicon photoelectrochemical (PEC) cells. The depths of silicon microhole arrays can be independently controlled by the etching time. The light-scattering properties are also investigated. Additionally, surface morphology analysis show that large hole diameters of SiMHs is very favourable for the full-filling of ionic liquids electrolyte. Therefore, better electrochemical contact as well as high ionic conductivity of the ionic liquids electrolyte renders the PEC SiMHs solar cells to exhibit more excellent performance. After optimization, the maximum PCE could be achieved at 4.04% for the SiMHs cell. The performance of the SiMHs cell is highly comparable to that of silicon nanowires cell. More importantly, the liquid-state electrolyte is confined in the unique microhole structure, which can obviously prevent the leakage of the ionic liquids electrolyte, resulting in much better long-term stability than the reference devices. These preliminary results validate the concept of interpenetrating networks with semiconductor structure/ILs junction to develop stable and efficient PEC cells.

1. Introduction

To address the current problems of increasing climate change and energy crisis, great effort has been devoted to developing the silicon solar energy conversion systems [1]. Unfortunately, the high production cost of the conventional silicon solar cells poses a barrier for solar energy to compete with fossil fuels [2,3]. In the past few years, due to the strong light trapping capability and excellent charge transfer/collection efficiency, silicon nanowire arrays (SiNWs) have been widely exploited for the design of efficient and low-cost silicon inorganic solar cells [4–10]. However, the fabricated processes for silicon p-n/p-i-n junction formation, such as deep reactive ion etching, thermal diffusion, or deep ultraviolet lithography, are complex and costly. To resolve these issues, one area of widespread current interest is using much simpler and low-cost processes to fabricate SiNWs photoelectrochemical (PEC) cells [11–15], since the semiconductor/liquid junction offer the potential cost advantages over their solid-state counterparts. In addition, the use of a liquid junction provided a high-quality, conformal, and rectifying contact to the SiNWs. To date, the performances of SiNWs PEC cells are generally modest. The highest efficiency of power conversion efficiency (PCE) > 10% has been achieved by SiNWs electrode combing with hydrogen bromide (HBr)/bromine (Br_2) aqueous solution acting as the redox pair [11]. Nevertheless, the

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aqueous concentrated HBr/Br_2 electrolyte is toxic, corrosive and volatile, and water could attack the silicon surface. For planar Si PEC cells, ferrocene$^{0/+}$ and their derivatives in acetonitrile, methanol and water have been exploited to achieve promising PCE [16–20]. However, the stability of all these devices has not achieved drastic improvement. The electrolytes, such as aggressive aqueous solution or the volatile and flammable organic solvent, make the cells decay quickly under the light illumination and also hard to be sealed for practical application.

Room temperature ionic liquids (ILs) are a class of organic salts presenting liquid status at or near room temperature, which process many attractive properties such as good chemical and thermal stability, negligible vapor pressure, non-flammability, high conductivity and wide electrochemical windows [21]. Therefore, compared with volatile molecular solvents which would permeate across the cell walls or even cause explosion, ILs electrolytes offer many practical advantages [22]. Up to now, few researches on silicon/ILs PEC cells are reported. Encouragingly, based on the ILs as the electrolyte, we have demonstrated a new type of SiNWs PEC cell displaying better stability than that containing conventional aqueous solution [23]. Under the standard 100 mW cm^{-2} light illumination, the short-circuit photocurrent density (J_{sc}) of the device based on the aqueous solution as the electrolyte decreased to ~10% in less than 4 h, while it can keep about ~90% in 24 h when ILs as the electrolyte. But, due to the high viscosity, ILs are hard to infiltrate into the gaps between the overdense wires. The difficulty in establishing good contact among the SiNWs, ILs and counter electrode limit the electrochemical parameters, *e.g.* low stability and fill factor (FF) value ~0.4 [23]. Moreover, the freestanding Si nanowires are fragile and easily cracked, tending to agglomerate when the wire length increases. These previous research triggers our interest to further explore new silicon nanostructure/ILs junction structure.

In this paper, a kind of large scale silicon microhole arrays (SiMHs) structure is constructed *via* a low-cost maskless approach. With different depths, the light-scattering property and surface morphology of SiMHs are also investigated. Compared to the SiNWs structure, the large hole SiMHs structure is mechanically more robust, and easier to form good junctions. Based on the unique structure combining with ILs electrolyte, the resultant SiMHs PEC solar cells are then fabricated and evaluated. The developed SiMHs/ILs structure paves a new way for high performance PEC cells.

2. Experimental procedure

2.1. SiMHs preparation

The SiMHs structure is fabricated with the electrochemical etching method according to the previous reports [24,25]. The polished side of the clean silicon wafers (n-doped, 100) with resistivity of 5–7 Ω cm are exposed to etching solution of 5% HF (aq) that contained 10 mM sodium dodecylsulfate (SDS). The etching is performed potentiostatically at 5 V in a Teflon cell equipped with a Pt counter electrode. During the etching, the mixed solution is stirred vigorously to reduce hydrogen bubble formation. The illumination intensity is adjusted to maintain the etching current of 12 mA/cm^2, with the light intensity controlled by connecting the lamp power supply to a variable resistor. Samples are etched for 15, 30, 45, and 60 min respectively. After etching, samples are rinsed completely in water and dried with nitrogen flowing, and then are etched in 10% KOH (aq) for 10 s to remove the disordered microporous silicon layer. Subsequently, the samples are rinsed with water, acetone, methanol, acetone and water respectively.

2.2. SiNWs preparation

SiNWs are prepared by immersing the clean silicon wafers in 5 M HF/0.02 M $AgNO_3$ solution, according to previous reports [26,27]. Typically, the etching time is about 15 min, and the length of the SiNWs is about 10 μm. In order to remove the silver dendrites from the nanowire surface, after etching, the prepared SiNWs is immersed in a concentrated HNO_3 solution for at least 1 h.

2.3. Silicon surface modifications

The hydrogen terminated (−H) silicon surface is obtained by dipping silicon wafer in 5 M HF for 10 min, followed by immersing in deionized water for 1 min. In order to obtain a better surface density of state and lower surface recombination velocity, a two-step process is employed to methylate the silicon surface [28,29]. First, the −H substrates are immersed in a saturated chlorobenzene solution of PCl_5 at 100 °C for 1 h, in which Si–H bonds are transformed into meta stable Si–Cl ones. Second, the substrates are dipped into $MgCH_3Cl$ in THF solution at 80 °C overnight, converting surface Si–Cl bonds to Si–C ones. After that the substrates are washed with THF, acetone and methanol subsequently. All of these processes are operated in nitrogen filled glove box. Ultrafine Pt nanodots have also been explored to enhance the Silicon PEC cells performance *via* its 'catalyst effect' [23]. In order to decorate platinum (Pt) nanodots, the substrates are immersed in 2 mg/ml ethanol H_2PtCl_6 solution for 1 min and dried with nitrogen flowing, then annealed under nitrogen atmosphere at 200 °C for 10 min.

2.4. SiMHs characterizations

The reflectivity light ratio of the substrates was measured by Perkin-Elmer Lamda 750 with integrating sphere. The morphologies of SiMHs are observed using a scanning electron microscope (SEM, FEI/Quanta 200 FEG) and the components of ILs-coated SiMHs are analyzed using an energy dispersive X-ray spectrometer (EDS) attached to SEM.

2.5. Device fabrication and evaluation

1-Propyl-3-methylimidazolium iodide (PMII) and 1-ethyl-3-methylimidazolium thiocyanate (EMISCN) are prepared according to previous report [30]. The mixture ILs electrolyte of PMII and EMISCN (volume ratio of 13:7) employed contains 0.05 M I_2 and 0.1 M LiI. The devices have a sandwich structure consisting of silicon electrode, counter electrode, spacer, and ILs electrolyte. Here, the transparent counter electrodes are prepared by chemically decorating Pt onto the cleaned ITO-coated glass slides *via* dipping into 2 mg/ml H_2PtCl_6 ethanol solution and then annealing at 200 °C for 10 min. Insulating tapes (10 μm) is used as spacer between the Silicon electrode and ITO-coated glass. Once the electrolyte is loaded, two electrodes are encapsulated with acrylic acid adhesive. Ohmic contacts are obtained on the rear face of the silicon electrode with indium gallium alloy. To further optimize the performance, more careful and complete filling of the electrolyte is carried out. Meanwhile, rear contact is thermal evaporating 2 nm 8-hydroxyquinolinolato-lithium (Liq) and 150 nm Al on to the backside of the SiMHs substrate.

The electrochemical impedance spectra (EIS) of the PEC cells were acquired on a CHI660c electrochemical workstation using the AC impedance method at the forward bias voltage of −0.25 V and the frequency of 0.1–10^5 Hz under dark conditions and the amplitude is 5 mV. The equivalent circuit model for EIS analysis was used by Autolab (PGSTAT30). The photovoltaic characteristics of the silicon PEC cells are evaluated using a Keithley 2612 source meter in