

# A monolithic integrated micro direct methanol fuel cell based on sulfo functionalized porous silicon

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**Abstract.** In this paper, we demonstrate a monolithic integrated micro direct methanol fuel cell ( $\mu$ DMFC) for the first time. The monolithic integrated  $\mu$ DMFC combines proton exchange membrane (PEM) and Pt nanocatalysts, in which PEM is achieved by the functionalized porous silicon membrane and 3D Pt nanoflowers being synthesized in situ on it as catalysts. Sulfo groups functionalized porous silicon membrane serves as a PEM and a catalyst support simultaneously. The  $\mu$ DMFC prototype achieves an open circuit voltage of 0.3 V, a maximum power density of 5.5 mW/cm<sup>2</sup>. The monolithic integrated  $\mu$ DMFC offers several desirable features such as compatibility with micro fabrication techniques, an undeformable solid PEM and the convenience of assembly.

## 1. Introduction

With the increasing functions and shrinking sizes of the portable devices, for example, smart phones, the demand for efficient and integrated power sources increases radically. It becomes a huge challenge that how to improve the performance and integration of power sources, so that they can get more energy in the limited volume. Micro direct methanol fuel cells ( $\mu$ DMFCs), have drawn much attention, not only because of their high energy density, room temperature operation, simple and safe handling <sup>[1-2]</sup>, but also because they can make full use of micro fabrication techniques developed for IC and MEMS to optimize the integration and sizes of fuel cells.

In recent years, varieties of  $\mu$ DMFCs have been developed <sup>[3-10]</sup>. Although a promising approach, such  $\mu$ DMFCs require a large volume due to the thickness of each stacked electrode and the inter-electrode space. The power density for such fuel cells is commonly reported in terms of electrode surface area instead of volume as is often the case for other power sources. In order to address the issue, a monolithic integrated  $\mu$ DMFC is a promising way to optimize the assembly and sizes, furthermore, is benefit to enhance the volumetric power density.

Here we present a monolithic  $\mu$ DMFC for the first time, integrated with silicon-based proton exchange membrane (PEM), nanocatalysts and current collector layer together. PEM is achieved by sulfo functionalized porous silicon membrane and 3D Pt nanoflowers are synthesized in situ onto it as nanocatalysts. Ag nanowires film serves as current collector layer. The monolithic  $\mu$ DMFC shows

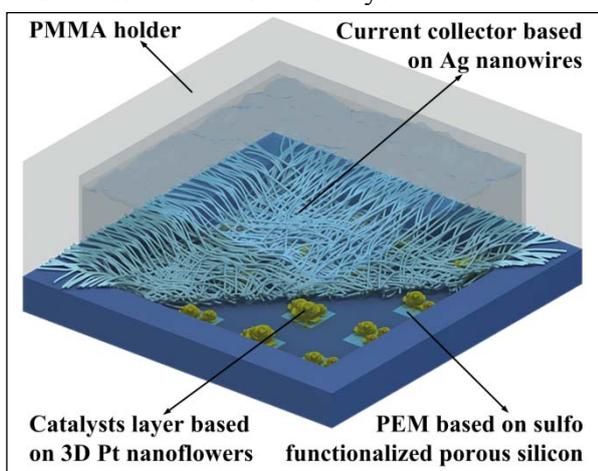


several key advancements in: 1) integrating all components on a chip and simplifying the structure and assembly of fuel cell; 2) solid PEM with little deformation and high proton conductivity; 3) in-situ synthesis of 3D Pt nanoflowers on a fuel cell body without the extra coating process; 4) compatible with micro fabrication techniques. As such, we believe this work is more attractive for system-on-chip.

## 2. Experimental

### 2.1. Design

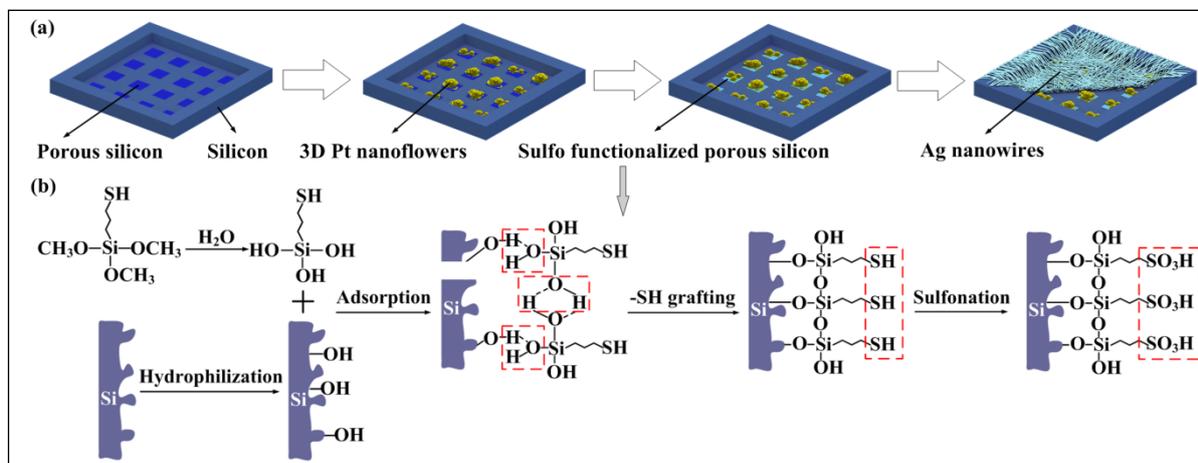
The monolithic integrated  $\mu$ DMFC was designed as illustrated in Figure 1. The fuel cell combined PEM, nanocatalysts and current collector layer together on a chip, in which PEM was achieved by sulfo functionalized porous silicon membrane, Pt nanocatalysts were synthesized in situ on it and Ag nanowires were coated as current collector layer.



**Figure 1.** Schematic of a monolithic integrated  $\mu$ DMFC based on sulfo functionalized porous silicon membrane.

### 2.2. Fabrication

The fabrication process of the monolithic integrated  $\mu$ DMFC divided into four steps, shown as Figure 2(a). Porous silicon membranes were fabricated and 3D Pt nanoflowers were synthesized in situ onto them using by the method proposed in our previous work<sup>[11-12]</sup>. After that, porous silicon membranes were functionalized with sulfonic acid groups via chemical grafting method. Then the collecting layer was formed by dropping Ag nanowires dispersion on the PEM and baking 30 min at 50 °C to dry. Finally, the monolithic integrated  $\mu$ DMFC prototype was obtained after assembly by PMMA holders.



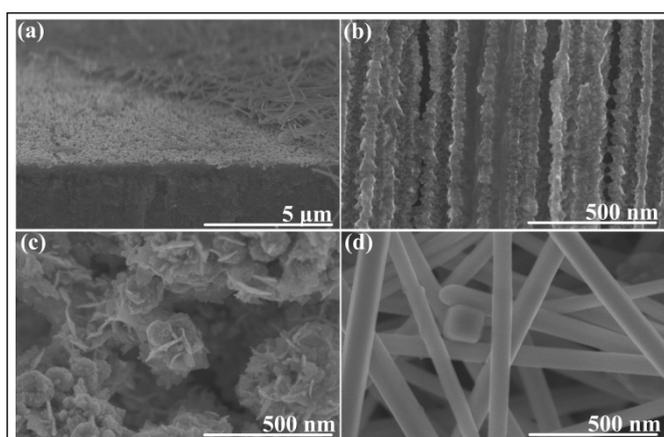
**Figure 2.** Fabrication of a monolithic integrated  $\mu$ DMFC (a); sulfo functionalization of the porous silicon membrane (b).

The porous silicon membranes were functionalized with sulfonic acid groups, according to the following steps, shown as Figure 2(b). Firstly, fabricated porous silicon membranes were immersed in a mixed solution of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  at the volume ratio of 3:1 for 30 minutes at 60 °C for hydrophilization. Simultaneously, Si-O-CH<sub>3</sub> groups in 3-mercaptopropyltrimethoxysilane (MPTMS) molecules were hydrolyzed to form Si-OH groups in mixed benzene solutions, with the MPTMS concentration of 30 wt. % and glacial acetic acid (GAA) concentration of 5 wt. %. Secondly, Si-OH groups in hydrolyzed MPTMS were absorbed onto the walls of porous silicon nanoholes by immersing the hydrophilic porous silicon membrane into mixed benzene solutions. Thirdly, mercapto groups were grafted via dehydration condensation reaction with ultrasonically activating for 48 hours. Finally, mercapto groups were oxidized to sulfonic acid groups in an 30 wt. %  $\text{HNO}_3$  aqueous solution for 3.5 hours with ultrasound at room temperature. Eventually, a functionalized porous silicon membranes were obtained, which were proton-conductive as a result of sulfonic acid terminal.

### 3. Results and discussion

Various tests had been done to describe the monolithic integrated  $\mu\text{DMFC}$ . The morphology characterizations were investigated by scanning electron microscopy (SEM), which were performed on a HITACHI S-5500 operating at an accelerating voltage of 5 kV. The performance of the monolithic integrated  $\mu\text{DMFC}$  were characterized using by a Solartron 1287 electrochemical interface coupled with a Solartron 1260B frequency response analyzer at room temperature.

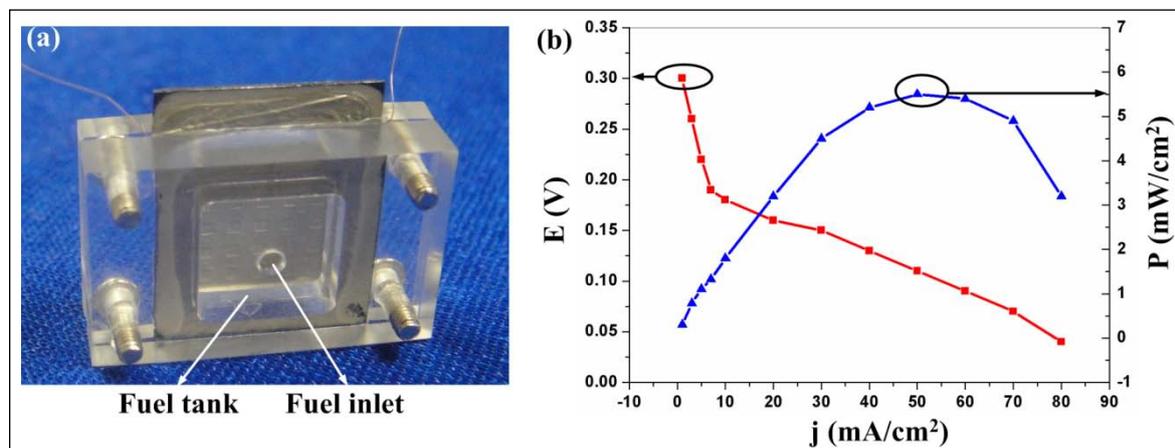
SEM images of a monolithic integrated  $\mu\text{DMFC}$  based on sulfo functionalized porous silicon membrane are shown as Figure 3. As we can see, the monolithic integrated  $\mu\text{DMFC}$  is made up of PEM based on porous silicon, Pt nanoflowers and Ag nanowires layer by layer. The porous silicon membrane shows distinct nanoholes structure with the bore diameter of 50 nm, and there are many organic molecules attached onto the walls of porous silicon nanoholes, which are grafted  $-\text{SO}_3\text{H}$  groups. The sulfonic acid groups attached on the walls of porous silicon nanoholes will hydrolyze in water, thus the walls of porous silicon nanoholes will be negatively charged and the protons can transfer between neighboring oxygen atoms at the gradient of potential and concentration. 3D Pt nanoflowers are assembled on the PEM based on sulfo-functionalized porous silicon membrane, with the size of about 200-400 nm. Due to the unique morphology, 3D Pt nanoflowers exhibit excellent catalytic activity<sup>[12]</sup>. A uniform film formed by Ag nanowires with diameter of 40-60 nm serves as a collecting layer.



**Figure 3.** SEM images of a monolithic integrated  $\mu\text{DMFC}$  based on sulfo functionalized porous silicon: cross-sectional view (a); high resolution SEM image of sulfo functionalized porous silicon membrane (b), Pt nanoflowers (c) and Ag nanowires (d).

The novel fabricated monolithic integrated  $\mu\text{DMFC}$  prototype based on sulfo functionalized porous silicon membrane and its corresponding I-V curves were shown as Figure 4. When filled with 2M methanol, a constant voltage was applied and the output current was monitored for a period of 50 s until the final steady-state value was recorded, and the I-V curve was obtained. The results clearly

show that the  $\mu$ DMFCs achieve an open circuit voltage of 0.3 V, a maximum power density of 5.5  $\text{mW}/\text{cm}^2$  and a maximum current density of 80  $\text{mA}/\text{cm}^2$ .



**Figure 4.** The monolithic integrated  $\mu$ DMFC prototype based on sulfo functionalized porous silicon membrane (a) and its corresponding I-V curves (b).

#### 4. Conclusions

A monolithic  $\mu$ DMFC is demonstrated for the first time, integrated with silicon-based PEM, nanocatalysts and current collector layer together. The  $\mu$ DMFC prototype achieves an open circuit voltage of 0.3 V, a maximum power density of 5.5  $\text{mW}/\text{cm}^2$ . These results demonstrate the proposed monolithic integrated  $\mu$ DMFC shows great potentials for optimizing the size and performance of  $\mu$ DMFCs, furthermore, are quite promising for integrated micro systems.

#### Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 61474071) and 973 program (No. 2015CB352100).

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