

DEVELOPMENT OF A CARBON MICROCHANNEL INTEGRATED WITH A HORIZONTAL CARBON SANDWICH ELECTRODE PAIR FOR ULTRA SENSITIVE ELECTROCHEMICAL/BIO SENSORS

Jeong-Il Heo¹, Yeongjin Lim¹, Byungjune Lee¹, Marc Madou², Heungjoo Shin^{1*}

¹UNIST(Ulsan National Institute of Science & Technology), Korea

²University of California, Irvine, USA

ABSTRACT

In this paper, we present carbon sandwich electrode pair as ultrasensitive electrochemical/bio sensors. We introduce simple, easy and low cost batch fabrication method, which is called carbon MEMS. Carbon MEMS process easily converts microstructures to nanostructures using only conventional photolithography and pyrolysis process. The carbon sandwich electrode pair consists of an on-plane electrode and a suspended nanomesh electrode. As electrochemical sensors, redox current amplification was measured with the carbon sandwich electrode pair. The feasibility of the carbon sandwich electrode pairs as highly sensitive electrochemical sensor platforms was demonstrated by measuring current values from the electrode pairs integrated in a pre-defined microchannel. The maximum current signal amplification factor of 89 was achieved by the carbon sandwich electrode pair integrated in a PDMS microchannel of 10 μm channel height. Furthermore, we studied the effect of the aspect ratio of the suspended carbon electrode on the amplification factors.

KEYWORDS

Electrochemical sensor, carbon MEMS, redox cycling, microchannel

INTRODUCTION

The demand of nanostructure sensing systems is emphasized in the areas of healthcare and the life sciences recently. That is because of their advantages; large surface area to volume ratio, high sensitivity, fast response and good electrical property [1]. Recently, many researchers have developed nanostructure based electrochemical sensing systems such as on-plane interdigitated array nanoelectrodes and planar sandwich nanoelectrodes encapsulated in a nanocavity [2, 3]. These systems consist of one pair of electrodes each of which is biased differently such that target molecules experience repeated redox events resulting in electrochemical signal amplification proportional to the number of redox events. The sandwich nanoelectrode pair showed more than one hundred times signal amplification through the redox cycling because the electrodes are tightly spaced and encapsulated in nanocavity so that the diffusion is limited in only the nanocavity [3]. However, the application of this electrochemical sensor is very limited because of difficulties in nanofabrication processes including e-beam lithography and sacrificial layer etching processes, and limited transport of the liquid sample along the nanocavity.

Our group developed the carbon sandwich systems forming a microchannel overcoming the limitation of the nanocavity based sensors. The carbon sandwich system consists of an on-plane carbon electrode and a suspended carbon nanomesh bridging two carbon walls so that a microchannel is defined by carbon exterior (Figure 1a). Moreover, we present novel electrochemical/bio sensing systems based on a horizontal carbon sandwich electrode pair (suspended carbon nanomesh electrode/on-plane carbon electrode) in a channel covered with a pre-defined 10 μm PDMS micro-channel. This novel sensing system utilizes carbon structure as microchannel walls as well as electrochemical sensing electrodes so that the micro-channel can be precisely defined by only bonding a PDMS layer on top of the carbon sandwich electrode (Figure 1b). The horizontal carbon sandwich electrode pair is able to amplify the electrochemical signal by redox cycling of the target molecules between the electrodes. Even this effect of redox cycling is boosted by carbon microchannel/electrode geometries constraining the diffusion of the target molecules only between the electrode pair resulting in more than 80 times signal amplification. In addition, we demonstrate the electrochemical amplification factor depending on the geometries of suspended carbon nanomesh electrodes.

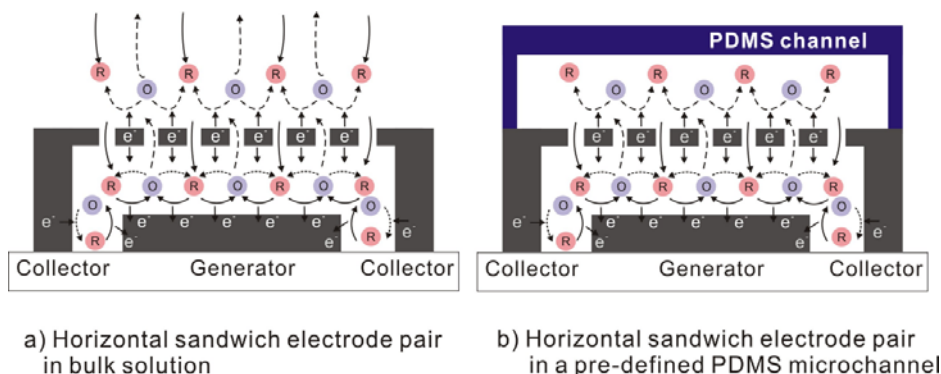


Figure 1. Redox cycling effect of the horizontal carbon sandwich electrode pairs a) in bulk solution, b) in a pre-defined microchannel (generator: anode, collector: cathode).

Experimentals

Fabrication

Using a photolithography process, 4 μm thick planar polymer (SU-8 photoresist) pads were patterned on a 6 inch silicon wafer insulated by a thermally grown SiO_2 layer. The planar polymer pads were converted to carbon planar electrodes in a pyrolysis process. Second, 25 μm thick SU-8 photoresist was spin-coated on the first photoresist patterns. Then, UV light was illuminated onto the photoresist layer through a photomask for contact pads which support suspended photoresist microwire meshes. Without a developing process, another UV exposure process is performed defining suspended photoresist microwire meshes. Next, a developing process to release the photoresist patterns was performed. Finally the entire polymer structures were converted into carbon structures at 900 $^\circ\text{C}$ in inert gas condition.

Microchannel integration

The carbon sandwich systems were passivated except sensing area including the suspended carbon electrode and the planar electrode just below the suspended electrode before PDMS channel bonding. PDMS microchannel molds of 10 μm high SU-8 photoresist structures were prepared on a silicon wafer using photolithography. Then, PDMS solution was poured on the SU-8 molds. The molds were cured in an oven. At last, the microchannel detached from the molds was integrated on top of the carbon sandwich systems.

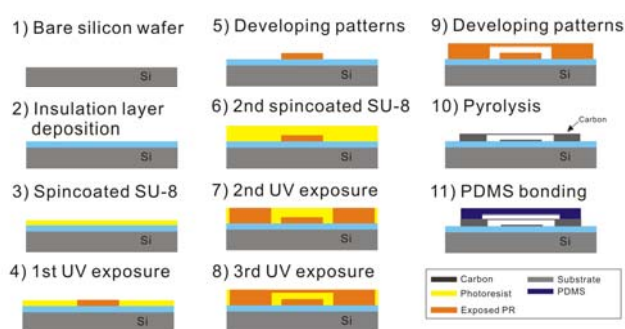


Figure 2. Fabrication steps of the horizontal carbon sandwich systems.

Electrochemical methods

0.01 M $[\text{Fe}(\text{CN})_6]^{4-}$ (Sigma-Aldrich, USA) in a 0.5 M KCl (Bioshop, Canada) solution was used as redox species for the cyclic voltammetry. The potential of the planar electrode was scanned from 0 to 0.6 V against Ag/AgCl reference electrode without any bias applied to the suspended carbon nanowire mesh electrode (single mode) using a multichannel potentiostat (CHI 1020; CH Instruments, Inc.). Then, the same potential was scanned while the suspended carbon nanowire mesh electrode was biased at a constant -0.3 V (dual mode) in order to measure the current amplification caused by redox cycling.

RESULTS AND DISCUSSION

Several geometries of carbon nanomeshes are shown in Figure 3. The geometry of nanomesh structures is determined by the photomask design of third UV exposure (Figure 2 (8)). The polymer micromesh structure of 1 μm width and 2 μm thickness was converted into the carbon nanomesh structure with dimensions of 500 nm width and 800 nm thickness (Figure 3(a)).

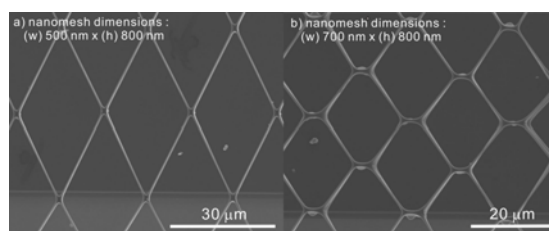


Figure 3. SEM images of various nanomeshes with dimensions of a) width = 500 nm, height = 800 nm, b) width = 700 nm, height = 800 nm.

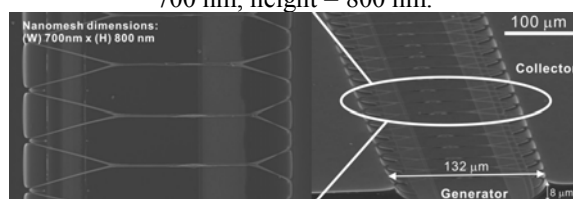


Figure 4. SEM images of the horizontal carbon sandwich system.

After fabrication process, a PDMS layer was bonded on top of the pre-defined carbon cavity with a pre-defined microchannel. The cavities of nanomeshes ensure effective mass transport between generator and collector electrodes.

In the previous study, we demonstrated the amplification factor of 89 with the horizontal sandwich electrode pair in 10 μm high microchannel (nanomesh dimensions; width 1.3 μm , height 2.2 μm , 15 μm separated from substrate) [5]. Redox species experience redox cycling between the nanowire mesh electrode (collector) and the planar electrode (generator). PDMS microchannel plays a role in the increase of amplification because of restrained mass transport of redox species receding from the electrode in microchannel. As well, redox cycling current depends on the geometry of nanowire mesh electrode and the planar electrode. To study the effect of geometries, we fabricate horizontal sandwich electrode pairs with different thickness of nanomesh electrode and the fixed size planar electrode. In figure 5c, 34.5 times amplified current signal was achieved from a sandwich electrode pair with an 1:1 aspect ratio suspended carbon nanomesh electrode (width : 800 nm, thickness : 800 nm) and a planar electrode. It means that 3-D shaped nanomesh electrodes have significant effect on electrochemical signal amplification.

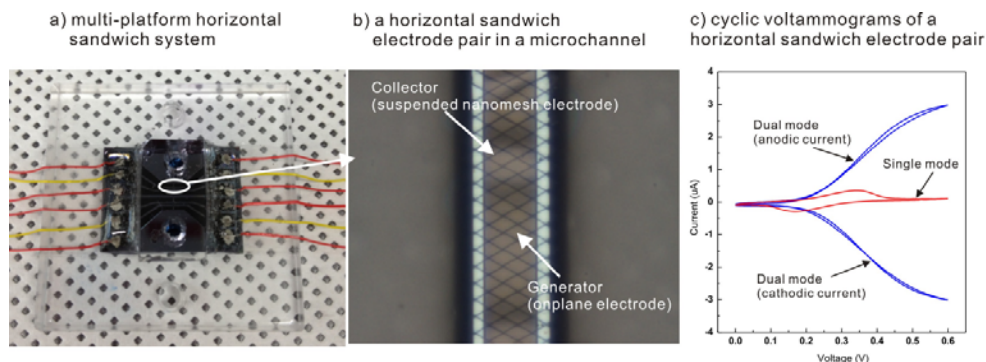


Figure 5. a) image of a multi-platform horizontal sandwich system, b) microscopic image of a horizontal sandwich electrode pair in 10 μm high PDMS microchannel (nanomesh dimensions; width = 800 nm, height = 800 nm, length = 130 μm , 8 μm separated from the substrate), c) cyclic voltammograms in 10 mM $[\text{Fe}(\text{CN})_6]^{4-}$ with 0.5 M KCl (the same electrode pair as figure 5b).

CONCLUSION

We demonstrate the prospect of electrochemical sensors using C-MEMS process that is a low cost and simple batch fabrication consisting of only two step process; conventional photolithography and pyrolysis process. Electrochemical signal amplification of 89 times was accomplished with the horizontal carbon sandwich electrode pair in the microchannel which can overcome the limitation of on-plane nanostructures in a nanocavity. The microchannel was constructed by bonding a pre-defined PDMS layer on top of the carbon structures so that the development of highly sensitive electrochemical/biosensors of very simple configuration expected. The electrochemical current amplification could be even more enhanced by increasing the aspect ratio of the suspended carbon nanomeshes.

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CONTACT

*Heungjoo Shin, tel: +82-52-217-2315; hjshin@unist.ac.kr