FABRICATION AND CHARACTERIZATION OF PURE SINGLE WALLED CARBON NANOTUBES MICROELECTRODE FOR ELECTROCHEMICAL MEASUREMENT

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Introduction

Carbon materials are used extensively in analytical electrochemistry due to several important attributes including ready availability, chemical stability, wide electrochemical potential window in aqueous solution, and biocompatibility [1, 2].

Carbon nanotubes (CNTs) have distinct structural and electronic properties compared with conventional carbon materials used in electrochemistry such as glassy carbon (GC), graphite, and carbon fiber. The combination of high aspect ratio, nanometer sized dimensions, good electrical conductivity, and low capacitance in the pristine state dictates that CNTs have the capability to make excellent electrode materials [1].

In this work, we report a direct and reproducible method for fabrication of pure single walled carbon nanotube (SWCNT) microelectrodes. It means only SWCNT network is exposed to solution during the electrochemical measurements. Fundamental electrochemical properties of the SWCNT microelectrodes were examined. Factors such as redox mediator concentration, and background electrolyte were investigated. SWCNT microelectrode acts like solid Pt microelectrode but with the significant advantages of higher mass transport, and fast response times.

Experimental

1. Device fabrication

a. Making an electric contact on Si wafer.

Briefly, platinum contacts (Pt/Ti: 40/10 nm) were thermally evaporated onto the Si substrate using a conventional photolithography process and a plasma sputtering machine. In order to separate between electrodes, a chromium layer (60 nm) was also sputtering in the middle of platinum contacts. This layer then was removed off after the catalytic process by chromium etchant solution to leave the blank space of Si wafer between electrodes on the same Si wafer (this is illustrated on Fig. 1a).

b. Growth of SWCNT network.

SWNTs were grown on Si substrates (p-type Si (110), with 100 nm of thermally grown SiO_2) using CVD

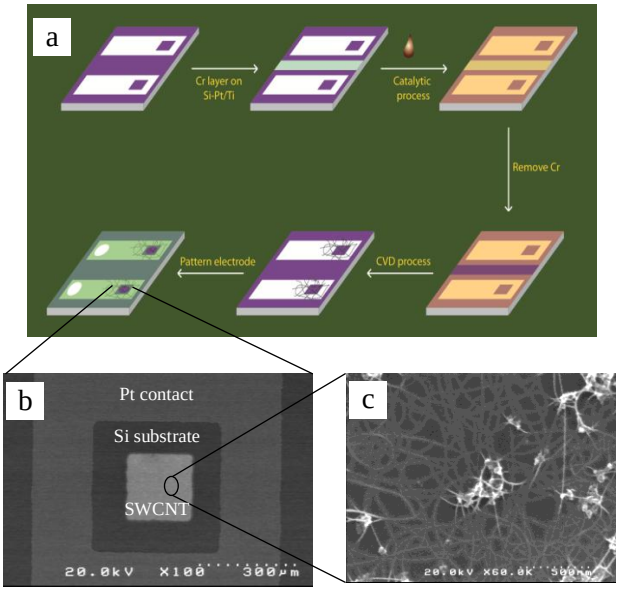

Figure 1: Schematic of procedure for fabricating SWCNT microelectrode

method, employing $Fe(NO_3)_3.9H_2O$, $Mo(acac)_2$, and alumina nanoparticles in the liquid phase as the catalyst [2]. Catalyst deposition involved dipping the substrates in a catalyst solution for 10 minute, followed by gradually taking out and left to dry in the air in 10 minute [3]. The Si substrate was then heated until 825^0C under argon gas and then argon gas was replaced by ethanol vapour. The growth process was conducted in 10 minute. In this way, an array of 24 SWCNT microelectrodes was arrayed on a single substrate.

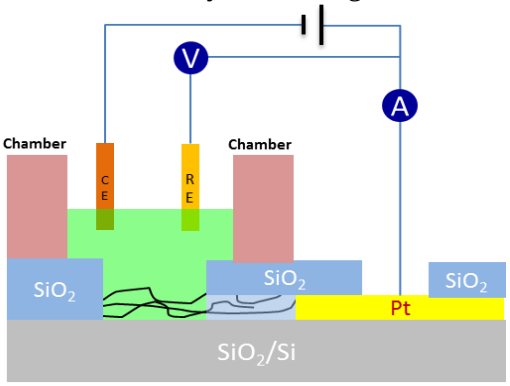

Figure 2: The experimental set-up with SWCNT microelectrode as the working electrode, Pt wire as the counter electrode (CE), and the miniaturized reference electrode (RE, Ag/AgCl).

2. Electrochemical measurement

The electrochemical measurement was performed with ALS/CH Instruments electrochemical analyzer, model 730C (USA). The fig 2 shows the schematic structure of the experimental set up for the SWCNT microelectrode.

Results and discussion

The SEM image in fig 1b and 1c were recorded to illustrate the pristine network of SWCNT. They show that the SWCNT network was high density and the diameter of SWCNT was estimated to be 1-3 nm by Raman scattering measurement [2].

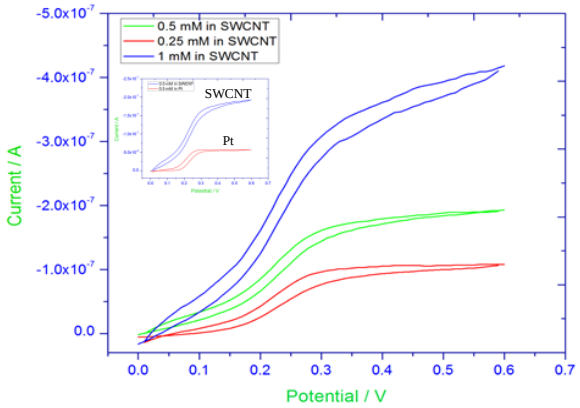

Figure 3: Cyclic voltammograms of an SWCNT electrode in 0.1 M KCl solution containing 0.25 mM, 0.5 mM and 1 mM $K_3Fe(CN)_6$ /$K_4Fe(CN)_6$. The scan rate is 4 mV s^{-1}.

The electrochemical properties of SWCNT microelectrode was investigated using cyclic voltammetry (CV). The voltametric curves obtained from SWCNT microelectrodes (fig 3) deviate from the classic Nernstian curve-shape controlled by thermo-dynamics and mass transport. In the scanned potential window, we do not observe a diffusion-limited plateau and the voltametric waves appear stretched. This may be due to the heterogeneous electrode kinetics that controls the rate of the electrode reaction. Because of the small critical dimension of SWCNT, mass transport is highly effective, and the rate of mass transport may become comparable to or larger than the rate of electron transfer. In this case there will be a deviation from thermo-dynamic equilibrium between oxidized and reduced species at the electrode surface and the voltammetric curve will depart from the Nernstial limit [4]. The CV measurement also show (inset on the fig 3) that the SWCNT microelectrode performed much better than solid Pt microelectrode of the same size and dimension.

The time response of the SWCNT microelectrode was investigated using chronoamperometry. For the measurement, the potential of the SWCNT microelectrode and Pt microelectrode, which are the same size, were stepped from 0.0 to 0.2 V vs Ag/AgCl, in solution containing 0.1 M NaCl. The charging current decreases exponentially with time as shown in fig 4, at a rate dictated by RC, the cell time constant. However, the exponential decay of the charging current can be clearly seen to be significantly faster for the SWCNT microelectrode compared with a Pt microelectrode at the same size. This is because of low intrinsic capacitance [5].

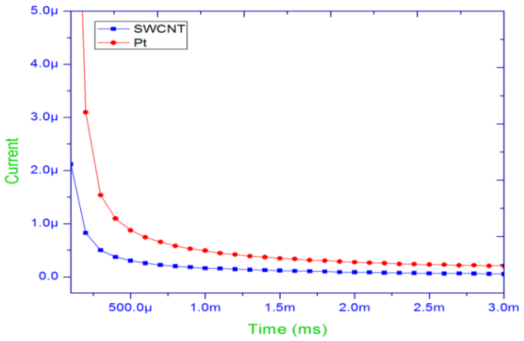

Figure 4: Current – time discharge curves of SWCNT and Pt microelectrode in 0.1M KCl solution. The potential was stepped from 0.0-0.2 V vs Ag/AgCl.

Conclusion

A CVD method based on ethanol vapor as the carbon source has shown successful for the fabrication of SWCNT networks on insulating surface. The using simple post growing process that it possible to fabricate SWCNT network microelectrode which offers superior characteristics over conventional metal microelectrode. The SWCNT network microelectrodes also show to have very fast response time than for conventional Pt microelectrode, sealed in glass.

References

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