Polymer coated carbon nanotube probes for Scanning Electrochemical Microscopy

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ABSTRACT

We present a method of fabrication of Scanning Electrochemistry Microscopy (SECM) probes using multiwalled Carbon Nanotube (CNT) coated with Parylene C as a nanoelectrode. Parylene is used to achieve a conformal pin hole free insulating layer, which is a prerequisite for simultaneous topographical and electrochemical imaging applications. A controlled length of the carbon nanotube is exposed, to act as the electrochemically active surface, by local removal of insulating polymer. Calibration of these probes is done by cyclic voltammetry in aqueous solution.

Keywords: Carbon Nanotube, SECM

1 INTRODUCTION

Electrodes of nanometer dimensions provide new tools and opportunities in the area of dynamic electrochemistry. The small electrode dimensions lead to high current density at the electrode surface, thus enabling study of mass transport, molecular interaction and fast heterogeneous electron transfer kinetics at the nanometer scale. The ultimate goal would be the measurement of the activity of a single redox-enzyme coupled to the nanoelectrode.

Combining the unique structural, mechanical and electrical properties of carbon nanotubes, with the spatial resolution and topographical sensitivity of Atomic Force Microscope, will allow probing of local cellular environments leading to innovative biological applications and sensors. Several methods have been reported for fabrication of nanoelectrodes for electrochemistry [1, 2, 3]. However, most fabrication techniques, while challenging, cannot predict the exact geometry of electrode at the nanometer scale. We demonstrate a reproducible method of fabrication of nanoelectrode probe for Scanning Electrochemistry Microscopy with controllable electrode geometry

2 EXPERIMENTAL DETAILS

2.1 Probe preparation

A multiwalled Carbon nanotube was mounted on gold coated Atomic Force Microscope (AFM) tapping mode cantilever in a Scanning Electron Microscope (FEI NovaSEM 200©). Prior to the deposition of a conformal, pinhole free, insulating layer (~300 nm) of Parylene C, by chemical vapor deposition, on assembled structure, the electrical contact resistance between the CNT and the gold surface was measured and found to be typically in the range of few hundred kilo Ohms [4]. Controlled lengths, ranging from a few nanometers up to a micron, of Carbon nanotube were exposed by removing the Parylene from the probing end. This was achieved by heating of selected length of the polymer coated nanotube by controlled introduction into the focal spot of a plane polarized CW green laser (532 nm). Detailed information about controlled removal can be found elsewhere [4].

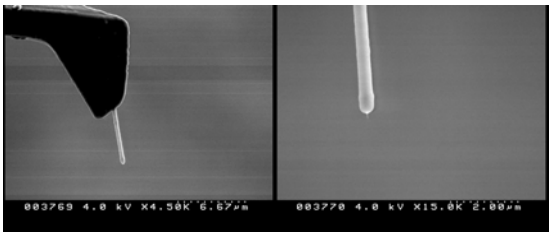

Figure 1: SEM micrograph of a Polymer coated CNT with the probing end free of polymer.

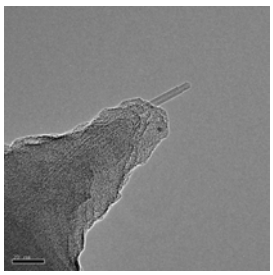

Figure 2: TEM micrograph of probing end of a probe showing a single MWNT free of polymer

2.2 Probe Characterization

Preliminary electrochemical characterization of the probes was done by cyclic voltammetry. With the help of an inverted optical microscope, only the polymer coated Carbon nanotube, with the exposed end and a few microns of the polymer coated AFM cantilever, was dipped in a glass capillary containing a 0.8 milli Molar solution of Ferrocenylmethyl-Trimethyl Ammonium(FcTMA+) and hexaflorophosphate (PF^-_6) (aqueous) as counter ion (no supporting electrolyte was used). A potentiostat (CHI

Instruments©) was used to cycle the potential applied to the electrode between 0.2 to 0.6 volts with respect to a grounded silver/sliver chloride electrode. The entire experimental setup was inside a grounded Faraday's cage.

2.3 Results and Discussion

Preliminary results indicate that the steady state electrochemical current (scan rate 0.005V/s sample interval 0.001 V) scales with the length of the electrode, as shown by the steady state voltammograms of two electrodes of different lengths (figures 3 &4).

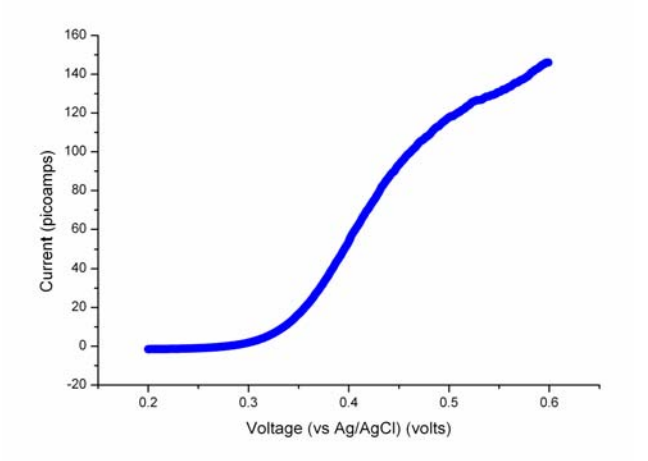

Figure 3: Averaged Steady-state voltammograms of $FcTMA^+$ with electrode length of ~1 micron.

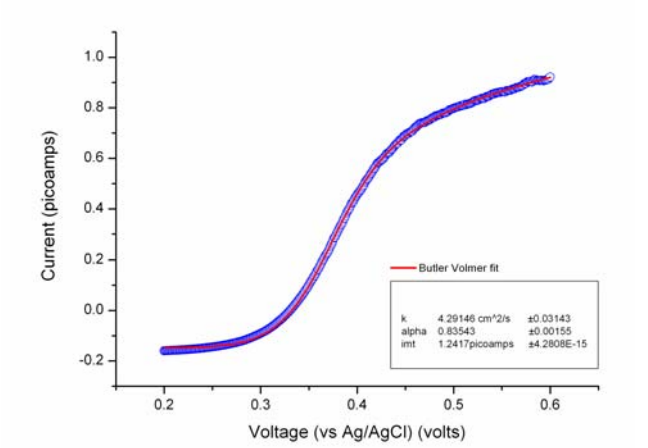

Figure 4: Averaged Steady state voltammograms of $FcTMA^+$ with electrode length of 10 nm. Fit carried out with Butler-Volmer kinetics.

The obtained voltametric curves can be described by Butler Volmer kinetics, showing the high electron transfer rate for these electrodes. Values obtained for heterogeneous rate constant (k) are in good agreement with published literature [5].Within scanned potential window range, the diffusion limited plateau was not observed in the voltammograms. This could be attributed to enhanced diffusion caused by the nanoscale dimensions of the electrode or due to the leakage of the electrolyte, over a period of time, between the CNT and the polymer coating.

Thus further characterization of probe and its geometry is being done before its experimental application as SECM probe.

3 CONCLUSIONS

We have presented a reproducible fabrication method for nanoscale electrodes, with controllable geometry. We have obtained steady state electrochemical current and a high rate of electron transfer through the CNT. The nanoelectrode allows probing of fast electrode kinetics with relatively high steady state current density values and coupled with the spatial resolution and topographical sensitivity of Atomic Force Microscope will be a superior SECM probe

4 FUTURE PLANS

The use of carbon as electroactive surface limits the potential range over which electrode can function. A way to overcome the limitation, imposed by carbon, would be to replace the CNT by a metal nanowire of identical dimensions.

REFERENCES

[1] C. Kranz, G.Friedbacher et al, Anal. Chem, *73*, 2492, 2001
[2] Y. Shao and Michael V. Mirkin, Anal. Chem, *69*, 1627, 1997
[3] C. Wang, Y. Chen, et al, Electrochimica Acta, *50*, 5588, 2005
[4] A.V. Patil, Jennifer Sippell et al, Nano Letters, *4*, 303, 2004.
[5] I. Heller, J. Kong et al, Nano Letters, *5*, 137, 2005