Fabrication and evaluation of Self Assembled Multi-Walled Carbon Nanotube Electrodes for Electrochemical Analysis

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) can self assemble upon drying driven by capillary force. These self assembled dried MWCNTs can be polished and fabricated as MWCNT electrode. MWCNT is gas impermeable with greater conductivity and chemical stability. The design and method for the making of Multiwalled Carbon Nanotube Electrode for electrochemical analysis has been described. Morphology of MWCNT, alignment pattern, surface roughness, electrical properties and its applications have been described. It is suitable for over the potential range +1.0 to -1.0v Vs SCE. Voltammetric studies have been performed in redox couple containing 10/10mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1M KCl. The fabricated electrode requires no treatment between uses. The Ep and Ip values were reproducible and self assembled MWCNT electrode can be used in the electrochemical analysis of electro-active species.

Key words: Electrochemical analysis, Fabrication, Multi-walled carbon nanotube electrode, Voltammetric studies.

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INTRODUCTION

An electrode is an electrical conductor generally used in electrochemistry to make contact with the electrolyte in a circuit [1]. The use of carbon and its allotropes as electrode in electrochemistry is not new. Carbon being less expensive, chemically inactive in many corrosive medium and greater conductivity has driven the electrochemists around the globe. However in the past years, certain modification has been performed over the carbon based electrodes to enhance the sensitivity and selectivity of the analytes in the medium. Modified pencil graphite has been used for the determination of morphine in biological samples [2]. Graphite electrode has been reported to be modified with functionalized graphene for selective determination of dopamine [3]. Likewise, Glassy carbon electrode was modified with gold nanoparticles for rectopamine and metaproterenol detection [4]. Graphite electrode has been modified with CNTs for the detection of epinephrine [5], DNA hybridization [6], ascorbic acid, dopamine [7] and many. Graphite modified with CNTs has also been used for identification of glucose using glucose oxidase encapsulated in the graphite-CNT composite [8]. Similarly, glassy carbon modified with MWCNTs has been used in the detection and study of furazolidone[9], ascorbic acid [10], dopamine [11] and many. In all the cases, MWCNT was used for its excellent electrical property and surface to volume ratio.

MWCNT can be made as gas impermeable and has greater chemical stability and electrical conductivity. Qingwen et al.[12], first described the drying induced upright sliding and reorganization of MWCNT driven by capillary force. Use of this capillary driven self assembled MWCNT as electrode in electrochemistry has not been reported. Self assembled MWCNT has many properties in common with the conventionally graphite electrode. This paper describes the use of this self assembled MWCNT as electrode and its fabrication for electrochemical analysis.

MATERIALS AND METHODS

1. Reagents

MWCNTs with diameter ranging from 30 to 45nm and height of several microns were obtained from Applied Science Innovation Private Limited, India. All the chemicals were of the analytical grade and used without further purification. Double distilled water were used throughout the experiment.

2. Purification of MWCNT

1g of MWCNT was sonicated in concentrated nitric acid for 1 hour to remove impurities. Later MWCNTs were washed several times with double distilled water to remove trace of nitric acid in the nanotubes. The purified MWCNTs were transferred into a flat bottomed cylindrical container and allowed for drying at 55°C. MWCNT rod of approximate length of 1cm was formed upright inside the tube upon drying.

3. Fabrication of MWCNT electrode

The dried MWCNT rods were carefully removed from the cylindrical container and polished at both the ends by simply rubbing several times until it becomes smooth with alumina cloth. The polished rod was fabricated into electrode by pasting platinum wire at the sides of the rod in order to enable electrical conductivity. The polished rod with platinum wire was sealed using parafilm tape leaving the bottom surface in order to facilitate the electrical contact with the electrolyte.

Fig 1: Fabricated MWCNT electrode

4. Microscopic analysis of MWCNT rod

The polished surface was studied using AFM (Agilent Pico LE) and SEM (FEI Quanta FEG 200) in order to find the surface roughness of the electrode. SEM of the unpolished surface were performed to study the alignment of the MWCNT to form rod.

5. Voltammetric studies on MWCNT electrode

The electrochemical properties of MWCNT electrode were studied using cyclic voltammetry in order to study the electrochemical reversibility of the redox probe and the current response at the interface. CV conditions: Potential from -0.7 to +0.7V at scan rate of 50mV/s, Electrolyte: 10/10mM solution of $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1M KCl solution.

RESULTS AND DISCUSSION

1. Microscopic analysis of MWCNT rod

AFM image of the polished MWCNT rod showed a smooth surface with an average roughness of 8.8202 nm. Figure 2 displays the AFM image of the polished MWCNT surface.

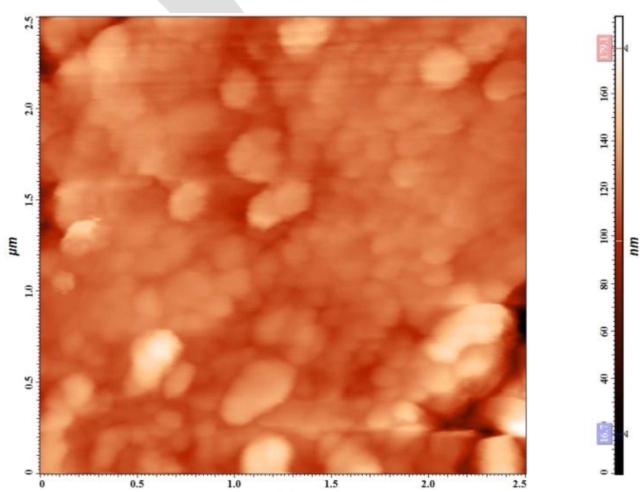

Fig 2a: 2D image of the polished MWCNT surface

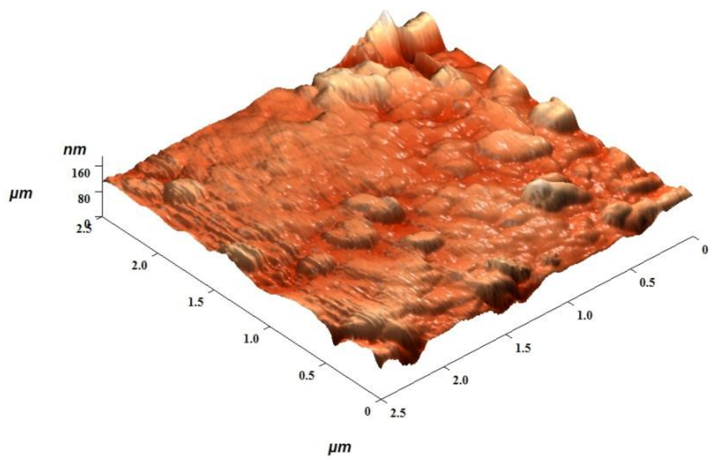

Fig2b: 3D image of the polished MWCNT surface

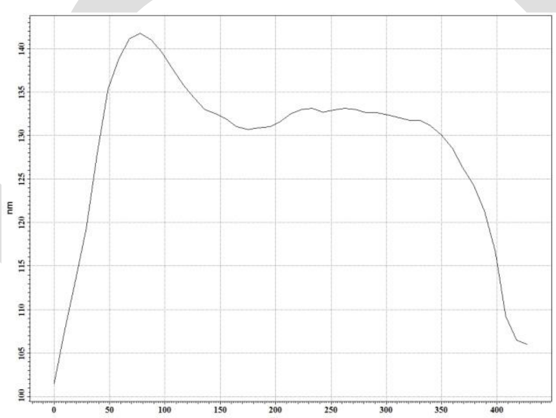

Figure 2c: 2D height- line profile of the polished MWCNT surface

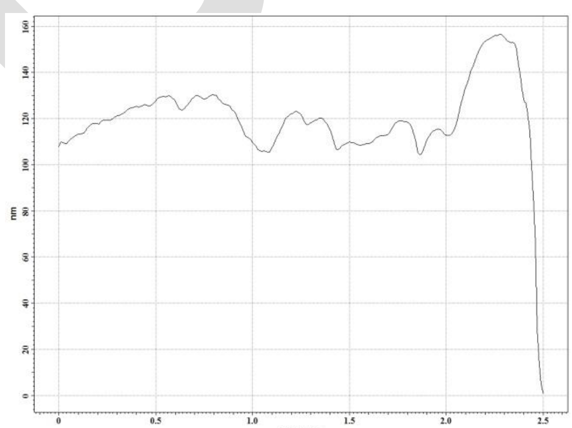

Fig 2d: line profile of vertical cross section @ 840nm of the polished MWCNT surface

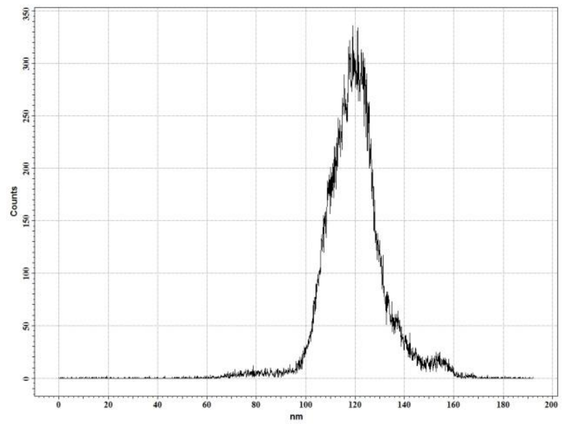

Fig 2e: histogram analysis of the polished MWCNT surface

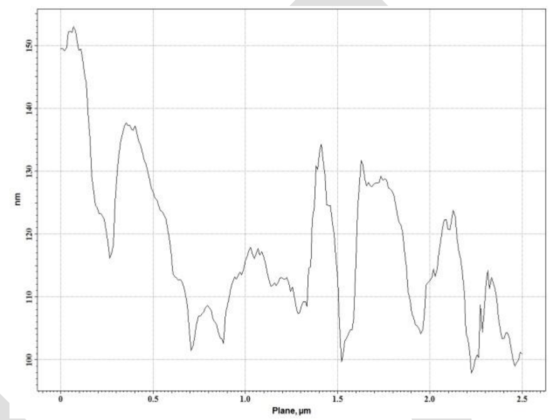

Fig 2f: line profile of vertical cross section @ 1090nm of the polished MWCNT surface

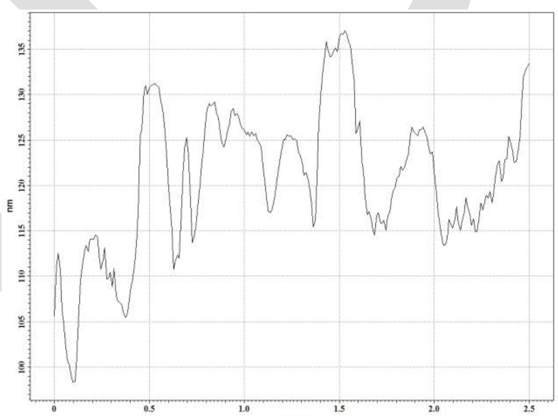

Fig 2g: line profile of vertical cross section @ 740nm of the polished MWCNT surface

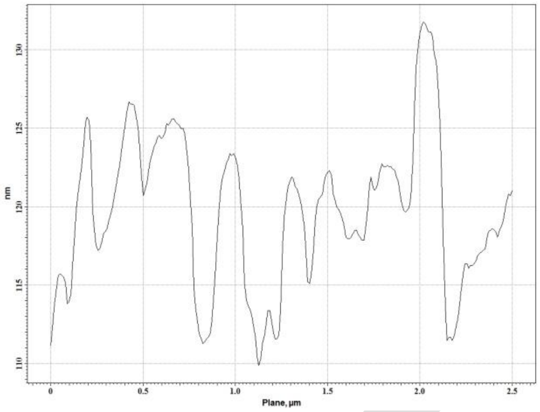

Fig 2h: line profile of vertical cross section @ 1200nm of the polished MWCNT surface

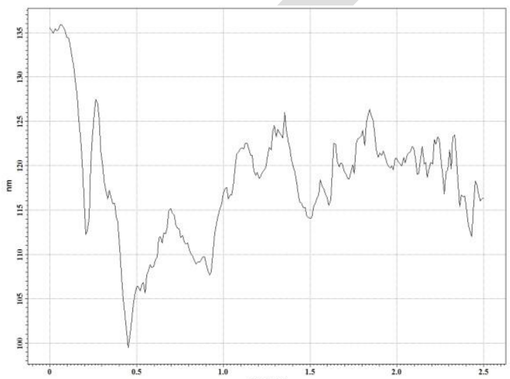

Fig 2i: line profile of vertical cross section @ 1580nm of the polished MWCNT surface

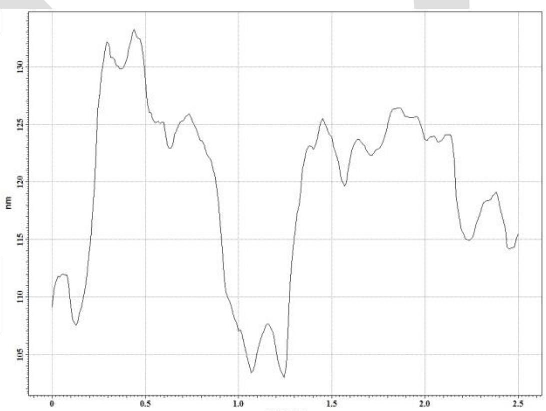

Fig 2j: line profile of vertical cross section @ 1950nm of the polished MWCNT surface

SEM image of the unpolished surface reveals the formation of MWCNT rod upon drying. SEM image of the rod displays the interlocking of the rod. This could have happened during the presence of solvent during purification process. Upon dryness the rods remain interlocked driven by capillary effect of MWCNT forming a stable rod. Excellent mechanical property and capillary force of MWCNT might have formed a major role in the formation of rod after dryness. It should be noted that no other carbon allotrope follow this pattern upon dryness.

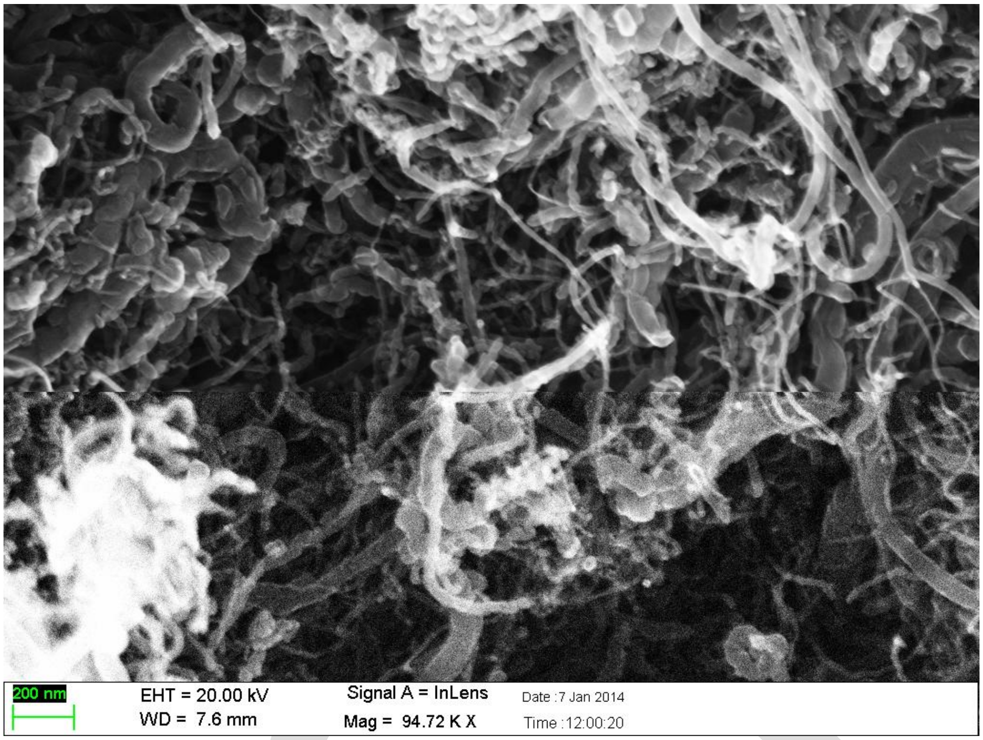

Fig 3a: SEM image of the unpolished surface of MWCNT rod

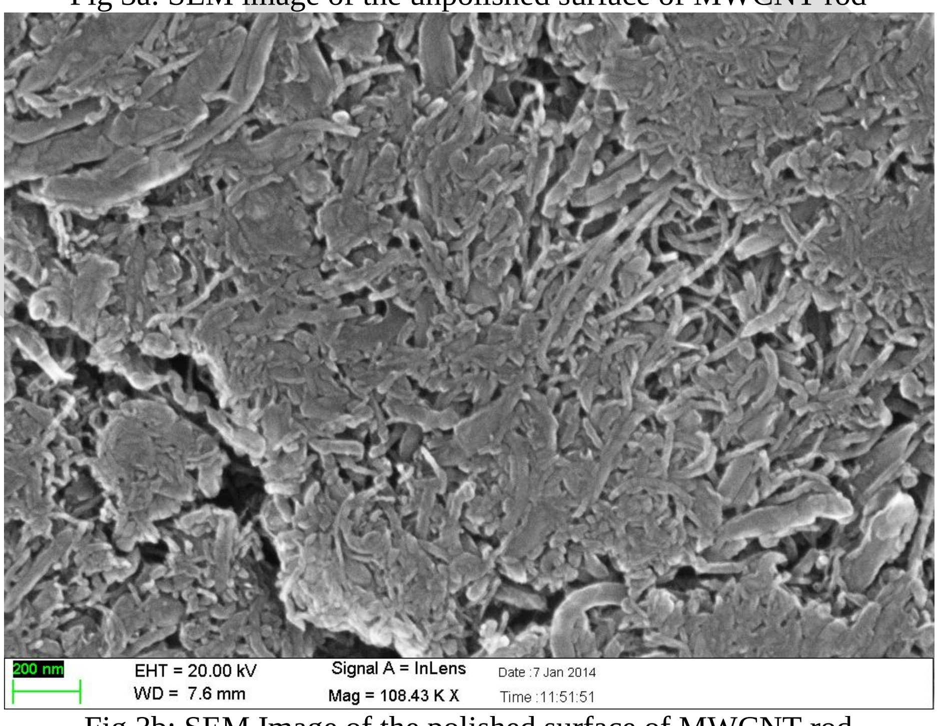

Fig 3b: SEM Image of the polished surface of MWCNT rod

2. Voltammetric analysis

Cyclic voltammetry was performed to determine the electron transfer and redox potential at the interface of the fabricated MWCNT electrode for its possible application in electrochemical analysis. The CV of the redox couple is characterized by anodic to cathodic peak potential separation of 0.21±0.05V and anodic to cathodic peak current ratio of 0.98, signifies the electrochemical reversibility of the redox probe. With the known greater surface to volume ratio possessed by MWCNT and from the CV response in redox couple, the fabricated electrode could be used in voltammetry for analytical applications.

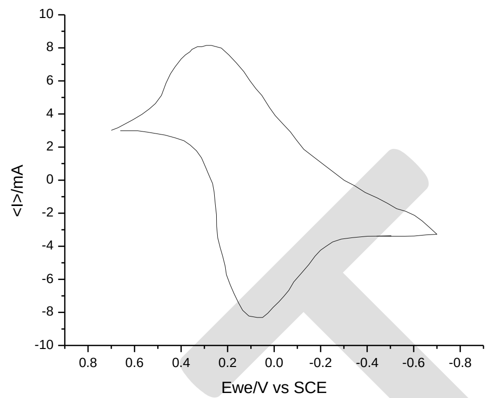

Fig 4: CV of the MWCNT rod in 10/10mM solution of $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1M KCl solution.

CONCLUSION

Since the discovery of multi-walled carbon nanotubes in 1992, lots of research focused on its physical, chemical, mechanical and electrical properties. Multiwalled carbon nanotube being a semi-conductor has greater surface area which facilitates electron transfer between electrochemically active compounds. The self assembled MWCNT upon dryness were found to possess greater stability and could be used in replacement with other carbon based electrodes. The average roughness of the polished surface was found to be 8.82nm. This signifies the surface smoothness exhibited by the fabricated electrode for the even distribution of the analytes over the electrode. The greater electrical conductivity, greater surface area and higher stability of the electrode are well understood form its CV response in redox couple.

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