Design and implementation of multi-walled carbon nanotube electrodes for electrochemical sensors and thermocells

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**
SINGAPORE

**DESIGN AND IMPLEMENTATION OF MULTI-WALLED
CARBON NANOTUBE ELECTRODES FOR
ELECTROCHEMICAL SENSORS AND THERMOCELLS**

LIN RONGZHOU

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Abstract

Carbon nanotubes (CNTs) have been widely used in electrochemical sensors and thermocells due to their excellent electrochemical, mechanical, chemical, electrical, and thermal properties. Both of electrochemical sensors and thermocells rely on redox reactions happening at the interfaces of electrodes and electrolytes to realize their functions. However, achieving high-performance CNT-based electrochemical sensors and thermocells still faces challenges, notably in achieving high mass transfer coefficient, while keeping time and material consumption during fabrication processes at the minimum.

To address these challenges in CNT-based electrochemical sensors, this thesis first enhances mass transfer coefficient at vertically aligned multi-walled carbon nanotube nanoelectrode arrays (VCNs), which are fabricated by encapsulating multi-walled carbon nanotube (MWCNT) arrays in epoxy and exposing tips of MWCNTs. This thesis investigates the effect of array diameter and forced convection on mass transfer coefficient at VCNs. Compared with macro-sized VCNs in stationary conditions, reducing array diameter to $50\text{ }\mu\text{m}$ achieves a 3-fold enhancement of mass transfer coefficient, while introducing forced convection at a flow rate of $2000\text{ }\mu\text{L}\cdot\text{min}^{-1}$ achieves a 20-fold enhancement. Theoretically, mass transfer coefficient can be further increased by reducing array diameter, increasing flow rate, and reducing channel dimension.

Based on the study of VCNs, this thesis proposes a different configuration of CNT-based electrodes, namely, multi-walled carbon nanotube band electrodes (CBEs). CBEs are prepared by encapsulating MWCNT sheets in epoxy and exposing tips of MWCNTs. The band electrodes are designed with micro-sized width ($\approx 200\text{ nm}$) and macro-sized length ($\geq 3\text{ mm}$) to respectively achieve high mass transfer coefficient and high response current. Compared with macro-size VCNs and individual CNT electrodes, CBEs respectively achieve a 32-fold enhancement on the mass transfer coefficient and a hundred-fold enhancement on the response current.

This thesis further proposes a third kind of CNT-based electrodes, namely, multi-walled carbon nanotube sheet electrodes (CSEs), which are fabricated by pulling MWCNT sheets from spinnable MWCNT arrays and adhering them on insulating polyimide-glass substrates. Compared with other electrode fabrication processes, fabrication of CSEs requires the minimum time (few minutes) and material (no surfactant or binder material).

This thesis systematically investigates the dependence of the electrochemical responses of CSEs on the length of MWCNT leading wires, the layer number of MWCNT sheets, air plasma treatment, and forced convection. By controlling these factors, air plasma treated single layer CSEs can achieve high standard heterogeneous rate constant and high mass transfer coefficient.

To address these challenges, as well as achieving high electrical conductivity, in CNT-based thermocells, this thesis fabricates MWCNT sheets on stainless steel sheets and meshes to respectively form CSSEs and CSMEs, and explores their application in thermocells. By investigating the dependence of output power on the layer number of MWCNT sheets, air plasma treatment, and substrate type, it is found that the mass transfer resistance is the limiting factor and reduces with increasing MWCNTs surface coverage of CSSEs. The small inter-distance between neighboring MWCNTs hinders diffusion of electrolytes into the MWCNT sheets, CSSEs therefore behave as planar electrodes rather than porous electrodes.

This PhD thesis presents detailed studies on designing and implementing VCNs, CBEs, and CSEs for electrochemical sensors, and CSSEs and CSMEs for thermocells. These electrodes successfully achieve high mass transfer coefficient while keeping time and material consumption during fabrication processes at the minimum. The excellent performances of these electrodes in electrochemical sensors and thermocells demonstrate the successful design of these electrodes, and provide guidelines for designing next generation of CNT-based electrodes.

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Acronyms & Symbols

Acronyms

1 mm-VCN	VCN with diameter of 1 mm
400 μm -VCN	VCN with diameter of 400 μm
AP-1-CSEs	1 layer CSEs treating with air plasma
CBE	Carbon nanotube nanoband electrode
CNT	Carbon nanotube
CPE	Constant phase element
CSE	Carbon nanotube sheet electrode on polyimide-glass
CSME	Carbon nanotube sheet electrode on stainless steel mesh
CSSE	Carbon nanotube sheet electrode on stainless steel sheet
CVD	Chemical vapor deposition
DOS	Density of states
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscopy
HMDS	Hexamethyldisilazane
HOPG	Highly oriented pyrolytic graphite
HRTEM	High resolution transmission electron microscopy
MWCNT	Multi-walled carbon nanotube
N-CBE	CBE fabricated from N layers of MWCNT sheets
N-CSE	CSE fabricated from N layers of MWCNT sheets
N-CSSE	CSSE fabricated from N layers of MWCNT sheets
N-CSME	CSME fabricated from N layers of MWCNT sheets
O, R	Oxidant, Reductant
P1, P2, P3	Epoxy curing process 1, 2, 3
PBS	Phosphate buffered saline
SEM	Scanning Electron Microscopy

SSM	Stainless steel mesh
SSS	Stainless steel sheet
SWCNT	Single-walled carbon nanotube
TCVD	Thermal chemical vapor deposition
TEM	Transmission electron microscopy
VCA	Vertically aligned carbon nanotube array
VCN	Vertically aligned multi-walled carbon nanotube nanoelectrode array

Symbols

A_c	Cross-section area of chambers
A	Surface area of electrodes
c_{dl}	Specific double-layer capacitance
C_{dl}	Double-layer capacitance
C	Concentration
C_O^*, C_R^*	Initial concentrations of oxidants, reductants
d	Diameter
d_c	Inter-distance between CNTs
d_e	Closest distance between two electrodes in thermocells
D	Diffusion coefficient
D_O, D_R	Diffusion coefficient of oxidants and reductants
$E_{s,p}^a, E_{s,p}^c$	Anodic, cathodic peak potential in cyclic voltammetry
E_{pd}	Potential drop on leading wires
E_d	Discharging voltage
f	Frequency
F	Faradaic constant
h	Height of channels
I_{dl}	Double layer charging current
I_h	Baseline-corrected peak height current
I_{sc}	Short circuit current
I_G, I_D	Intensity at the G-band and the D-band in Raman spectra
$i, I, m; i_b, I_b; j_c;$ $i_{c,l}, I_{c,l}, j_{c,l}, m_{c,l};$ $i_d, I_d; i_{max}, I_{max},$ $j_{max}; I_{s,l}, m_{s,l};$ $i_{s,p}, I_{s,p}, j_{s,p},$ $m_{s,p}; I_{s,p}^a, I_{s,p}^c;$	i , current density; I , current; j , specific current density; m , mass transfer coefficient. Subscript: b, background; c, channel flow condition; d, discharging on load; l, limiting condition; max, maximum; p, peak; s, stationary condition; Superscript: a, anodic peak; c, cathodic peak;
k_o	Standard heterogeneous rate constant
k_b	Heterogeneous rate constant for oxidation
l_c	Length of chambers
l_w	Length of MWCNT leading wires
LN	Layer number

LOD	Limit of detection
n	Number of electrons transferred at each reaction
Pe_s	Shear Peclet number
P_d	Pressure of degassing
P_i	Input power
P_{max}	Maximum output power
P_o	Output power
P_s	Specific power density
$P_{s,max}$	Maximum specific power density
Q	Flow rate
r	Radius
r_m	Weight ratio of epoxy resin and hardener
$\overline{R}$	Universal gas constant
R_{ct}	Electron transfer resistance
R_{lc}	Leading wire and contacting resistance
R_{lo}	Loading resistance
R_{in}	Internal resistance
$R_{in,s}$	Specific internal resistance
R_s	Sheet resistance
R_{so}	Ohmic solution resistance
R_w	Resistance of MWCNT leading wires
Re	Reynolds number
S/N	Signal to noise ratio
S	Sensitivity
Se	Seeback coefficient
t	Time
t_c	Critical time
t_d	Degassing duration
t_p	Plasma exposed duration
T	Temperature
T_c	Curing temperature of epoxy
T_h	Temperature of hot side electrode in thermocells
T_s	Solution temperature

v	Potential scan rate
v_m	Mean velocity
V	Electrode potential
V_{oc}	Open circuit voltage
w	Width of channels
w_e	Width of rectangular channel electrodes
w_w	Width of MWCNT leading wire
x_e	Length of a rectangular channel electrodes
Z_{CPE}	Constant phase element impedance
$Z_{imaginary}, Z_{real}$	Imaginary, real part of complex impedance
Z_w	Warburg impedance or mass transfer resistance

Greek letters

ΔE	Potential step
ΔE_p	Peak potential difference in cyclic voltammetry
ΔT	Temperature difference between two electrodes
ΔS	Reaction entropy
ψ	Dimensionless kinetic parameter
α	Charge transfer coefficient
δ	Diffusion layer thickness
η	Power conversion efficiency
η_c	Relative power conversion efficiency
κ	Thermal conductivity
ν	Kinematic viscosity
σ	Electrical conductivity
σ_b	Standard deviation of baseline currents
ω	Radial frequency

Chapter 1

Introduction

1.1 Background and motivation

Electrochemical sensors have been widely used for detecting various kinds of analytes. Depending on measuring principles, electrochemical sensors are classified as amperometric sensors (measuring current), potentiometric sensors (measuring potential or accumulated charges), conductometric sensors (measuring conductivity) and so on. [1–3] In this thesis, I focus on investigating amperometric sensors. Without specific annotation, electrochemical sensors are amperometric sensors. A electrochemical sensor is generally composed of a working electrode, a reference electrode, and a counter electrode. All these three electrodes are immersed in electrolyte and connected to a potentiostat. The reference electrode is used to provide a controllable potential across the interface of the working electrode and electrolyte. The electrochemical reactions happen at the interface generate response current, which is collected by the counter electrodes and used to measure the analyte concentration.

Thermocells, which are composed of two electrodes at different temperature and electrolyte between them, are galvanic cells used to convert low-grade heat energy into electrical energy using the temperature dependence of electrochemical redox potentials. [4,5] Similar to electrochemical sensors, generation of current in thermocells is dependent on the electrochemical reactions happening at the interface of electrodes and electrolytes.

A general pathway for electrochemical reaction is composed of mass transfer process and electron transfer process. The flux rates for these two processes are represented by mass transfer coefficient and standard heterogeneous rate constant, respectively. The electrochemical reaction is limited by the process with lower flux rate. Enhancing flux rate of the limiting process can increase the reaction rate and subsequently the response

Figure 1.1: Flow chart of this thesis.

current.

Carbon nanotubes (CNTs), which have excellent electrochemical, mechanical, chemical, electrical, and thermal properties, have been widely used in both electrochemical sensors [6–8] and thermocells [9–15]. Several configurations of CNT-based electrodes have been designed and implemented for electrochemical sensors, such as individual CNT electrodes [16–20], CNT film electrodes [21–26], CNT paste and composite electrodes [27–32], vertically aligned CNT nanoelectrode arrays (VCNs, Figure 1.1) [33–38], single-walled carbon nanotube (SWCNT) network electrodes [39–42], and multi-walled carbon nanotube (MWCNT) sheet electrodes [43–45]. Several configurations of CNT-based electrodes have also been designed and implemented for thermocells, such as CNTbucky papers [9], CNT/PVDF composites [14], CNT aerogel sheets [12], vertically-aligned CNT arrays [9], SWCNT/RGO composites [13], and CNT foams [15]. However, achieving high-performance CNT-based electrochemical sensors and thermocells still faces challenges, notably in achieving high mass transfer coefficient, while keeping time and material consumption during the electrode fabrication processes at the minimum.

Individual CNT electrodes have nano-sized diameters, which result in high mass transfer coefficient, but at the same time cause low response current, as well as suffer from complications in fabrication and utilization. [16, 18, 19] To increase the response current, thousands of CNTs are assembled together to form CNT-based electrodes. Because the averaged inter-distance between CNTs in such electrodes is generally much smaller than

their diffusion thickness, diffusion fields of neighboring CNTs overlap and thus significantly reduces mass transfer towards CNTs. The mass transfer coefficient, however, can be increased by either increasing the inter-distance, [37,46] reducing electrode size, [47–50] or introducing forced convection [51–53] at the cost of increasing fabrication complexity or solution consumption. Currently, fabrication of CNT-based electrodes with high mass transfer coefficient is still a challenge.

This thesis first focuses on enhancing mass transfer coefficient at VCNs, which have several crucial advantages used in electrochemical detection. In such configuration, the electrochemically inert sidewalls of MWCNTs are covered to prevent generation of background current, while the electrochemically active opened ends of MWCNTs are exposed to achieve high electron transfer rate. Encapsulation of MWCNTs in dielectric material provides VCNs high mechanical stability and possibility to be renewed by polishing. The electrons generated at the tips of MWCNTs are transferred directly from the tips through individual MWCNTs to current collectors. [33,46] This configuration makes use of the high electrical conductivity of MWCNTs.

There are several possible methods to increase the mass transfer coefficient at VCNs. The most straightforward method is to reduce the density of CNTs in VCNs to maintain the radial diffusion for each nanoelectrode [37,46,54,55], achieving the pure radial diffusion regime [56]. This method requires low density VCAs ($\approx 7 \times 10^7 \text{ cm}^{-2}$), which are more difficult to synthesize compared with those of higher density. Alternatively, reducing the diameter of VCNs from macro-sizes ($d \geq 1 \text{ mm}$) [33,34] to micro-sizes ($d \leq 100 \mu\text{m}$) [47,48] also changes the behavior towards the VCNs from planar diffusion to radial diffusion under the total overlap regime, although there is a lack of direct and systematic comparison of the mass transfer coefficient at VCNs of varying diameter. The last method involves introduction of forced convection to the solution against electrodes. This method has been used for several variants of CNT-based electrodes [51–53]. The use of forced convection to enhance the mass transfer coefficient, however, has not been demonstrated for VCNs.

This thesis further proposes to use multi-walled carbon nanotube band electrodes (CBEs, Figure 1.1) to achieve high mass transfer coefficient. Metal nanoband electrodes, as the first type of nanoelectrodes, are fabricated by encapsulating continuous thin metal films in dielectric materials and exposing the film edges. [57] The nanoband electrodes have nano-sized width allowing high mass transfer coefficient, and macro-sized length to obtain high response current. [58–60] Spinnable MWCNT array is a special kind of vertically-aligned MWCNT array with the capacity of converting long and high-perfection MWCNTs into continuous MWCNT sheets with well aligned and dispersed morphology.

[61–65] The dimension of MWCNT sheets is highly suitable for mass fabrication of band electrodes. For single layer of CNT sheets, their thickness is about tens of nanometers, width can be up to few centimeters, and length can be up to meter scale. [43, 66] It is possible to fabricate CBEs by encapsulating MWCNT sheets in epoxy and exposing tips of MWCNTs. They can have the dimension of metal nanoband electrodes and electrochemical properties of MWCNTs.

The second challenge in utilizing CNT-based electrodes is to keep the time and material consumption during fabrication processes at the minimum. Currently, fabrication of CNT-based electrodes generally requires long preparation time (few hours) to obtain well dispersing CNT solution by acid treatment or strong ultrasonic [43, 67, 68], or encapsulate CNTs in dielectric materials to reduce background current [33–38]. CNT-based electrodes also need binder materials to increase mechanical strength and stability. [33–38, 43, 67, 68]

This thesis proposes to use single layer MWCNT sheet electrodes (CSEs, Figure 1.1) to address the second challenge. CSEs can be easily fabricated by drawing MWCNT sheets from spinnable MWCNT arrays and laying them on insulating substrates. Current literature reports show that it is necessary to use high layer number (≥ 20) CSEs to obtain both high electrochemical activity and high electrical conductivity. [43–45] As a comparison, SWCNT network electrodes, which are two-dimensional networks on Si substrates with $< 1\%$ SWCNTs surface coverage, have been used to detect a wide range of analytes such as dopamine, H_2O_2 , FcTMA^+ and so on. [39, 41, 51, 53, 69] The successful application of SWCNT network electrodes in electrochemical detection is highly dependent on both high electrochemical activity of sidewall of SWCNTs towards various species and low intrinsic capacitance of SWCNTs (*i.e.*, low electrical double layer charging current). [39–42, 70, 71] Even though MWCNTs do not have these two special properties in nature, their electrochemical activity can be improved by functionalization and the electrical double layer charging current can be minimized by using steady-state measurement method such as chronoamperometry. Single layer CSEs therefore have the potential to overcome the excessive time and material consumption in the fabrication process, as well as achieve excellent detection performance.

The aforementioned challenges for utilizing CNT-based electrodes in electrochemical sensors, as well as achieving high electrical conductivity, are existing in using CNT-based electrodes in thermocells. In thermocells, CNTs are generally assembled in the form of porous structure, *e.g.*, MWCNT bucky papers [9] and MWCNTs aerogel sheets [12], to increase surface area of electrodes and subsequently response current. Those electrodes are generally fabricated by the similar methods used for fabricating CNT-based electrodes for electrochemical sensors. They therefore also suffer from the problem of high material

and time consumption during the electrode fabrication process. In these porous CNT-based electrodes, the small inter-distance between CNTs results in overlapping of diffusion layers of CNTs and hinders diffusion of electrolytes to the porous electrodes. Besides, due to the porous structure, electrons generated at the top surface need to transfer across connections between CNTs and then across interfaces between CNTs and metal current collectors to be collected. This resulting connecting resistance may significantly increase the internal resistance of thermocell and subsequently reduce current and power output. To address these challenges, this thesis fabricates MWCNT sheets on stainless steel sheets and stainless steel meshes to respectively form CSSEs and CSMEs (Figure 1.1), and investigates the dependence of internal resistance and output power of thermocells on the layer number of MWCNT sheets, air plasma treatment, and substrate type.

1.2 Objectives

This thesis focuses on achieving high mass transfer coefficient at MWCNT electrodes used in both electrochemical sensors and thermocells, as well as keeping time and material consumption in fabrication processes at the minimum. In order to accomplish these objectives, several specific objectives are proposed:

- To enhance mass transfer coefficient at vertically aligned multi-walled carbon nanotube nanoelectrode arrays.
- To design and implement multi-walled carbon nanotube band electrodes for electrochemical sensors.
- To design and implement single layer multi-walled carbon nanotube sheet electrodes for electrochemical sensors.
- To design and implement multi-walled carbon nanotube sheet on stainless steel sheets and meshes for thermocells.

1.3 Outline of thesis

This PhD thesis contains seven chapters.

In Chapter 1, I introduces background and objectives of this study.

In Chapter 2, I presents background knowledge by reviewing electrode processes, electrochemistry methods, synthesis of CNTs, CNT properties, and CNT-based electrodes used in electrochemical sensors and thermocells.

In Chapter 3, I introduces experimental details which include synthesis of MWCNT arrays, fabrication of CNT-based electrodes, and experimental setups and measurements.

In Chapter 4, I optimizes the fabrication process of vertically aligned MWCNT nano-electrode arrays (VCNs). I then systematically investigates the effect of array diameter and forced convection on mass transfer coefficient towards VCNs, and finally designs and implementates MWCNT band electrodes (CBEs) in electrochemical sensors.

In Chapter 5, I designs and implements MWCNT sheet electrodes (CSEs) in electrochemical sensors, and investigates the dependence of electrochemical responses of CSEs on the length of MWCNT leading wires, the layer number of MWCNT sheets, air plasma treatment, and forced convection. I implements VCNs, CBEs, and CSEs in channel flow voltammetry to detect both $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine, and compares their performances with literature results.

In Chapter 6, I presents and calibrates a new design of thermocell, and then designs and fabricates new configuration of electrodes: multi-walled carbon nanotube sheets on stainless steel sheets (CSSEs) and stainless steel meshes (CSMEs). I investigates the dependence of output power of thermocells on the layer number of MWCNT sheets, air plasma treatment, and substrate type.

In Chapter 7, I presents conclusions of this thesis and recommendation for future work.

Chapter 2

Literature Review

2.1 Electrode processes

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. [1, 2, 72] A large part of this field deals with the chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. The exchange of electrical and chemical energy is achieved through two kinds of electrode processes: non-faradaic processes and faradaic processes.

At the non-faradaic processes, no charges are transferred across the electrode-electrolyte interface. One of the important non-faradaic processes is electrical double layer charging. When an electrode with charges contacts with an electrolyte solution, in the solution side, counter charges accumulate at the electrode surface to maintain charge neutrality at the interface. The charge layers at electrode and solution side form an electrical double layer, which has been experimentally shown to behave like a capacitor. During transient experiment, the double layer is charged or discharged, and subsequently generates electrical double layer charging or discharging current. Even though this current can be neglected generally, it can be much higher than the faradaic current in reactions involving low concentration analytes (*e.g.*, few nM).

At the faradaic processes, electrons are transferred across the electrode-electrolyte interface, either from electrodes to species (reduction) or reverse (oxidation). The faradaic processes can happen spontaneously at galvanic cells to convert chemical energies to electrical energies; or happen under driving of external potential at electrolytic cells to induce desired chemical reactions. The faradaic processes are independent of whether they happen in galvanic cells or electrolytic cells. They can be explained by using an overall electrode reaction. Figure 2.1 shows a general pathway for an overall electrode

Figure 2.1: Pathway of a general electrode reaction. [1]

reaction $O + ne \rightleftharpoons R$, which is composed of several intermediate reaction steps. The faradaic process (to be specific, the faradaic current) of this reaction is governed by the rates of following processes: mass transfer, which is the movement of material from one location in solution to another; electron transfer, which is the transfer of electron across the interface; chemical reactions preceding or following the electron transfer, and other surface reactions, such as adsorption, desorption, or crystallization. At the steady state, the rates of all processes are the same, and they are determined by the inherently most sluggish one.

Here, the reaction is simplified by assuming that the electron transfer rate is fast, no intermediate reaction step or adsorption happens, diffusion is the only mass transfer way, and only O exists in the solution at the beginning of experiment. By using linear sweep voltammetry, the potential at the electrode is gradually reduced to increase energy of electrons in the electrode. When the potential at the electrode is more negative than formal potential of the redox couple, electrons may jump out of the electrode and be obtained by O at the electrode surface, which are subsequently reduced to R . The consumption of O generates a concentration difference at the bulk solution and at the electrode surface, and subsequently induce diffusion of O to the electrode surface. By further lowering the applied potential, the heterogeneous rate constant for oxidation k_b increases, while the diffusion layer becomes thicker and the mass transfer coefficient m reduces. At the condition that $k_b < m$, the response current keeps increasing with lowering potential. While at the condition that $k_b > m$, O at the electrode surface are consumed and no new O is supplied timely, the response current reduces gradually and a peak shape shows in the voltammogram. In this case, the faradaic process is controlled by the mass transfer process, and the faradaic current is limited by the mass transfer

coefficient.

There are three modes of mass transfer in electrode processes: migration, diffusion, and convection. Migration is the movement of charging species under electrostatic forces. In an electrochemical cell, a potential difference is applied between two electrodes and forms an electrical field within electrolyte solution. Charging species are moved by electrostatic forces within the electrical field. The migration speed can be increased by increasing the electrical field. However, this results in a higher potential drop on the electrolyte, and increase difficulty of controlling the potential at the electrode. Generally, high concentration supporting electrolytes (*e.g.*, 1 M KCl) are used to increase conductivity of electrolytes and eliminate the potential drop.

Diffusion is the movement of species driven by concentration difference. There are two kinds of diffusion mode: planar diffusion and radial diffusion. The diffusion mode is affected by both electrode size and experimental time. Here, I use a simple case as an example to explain this principle. For a simple electrode process with fast electron transfer process in stationary conditions, by applying a potential step from a value where no current flows to one where the reaction is diffusion controlled, the species at the electrode surface are consumed and subsequently causes diffusion. At short times, the diffusion layer is very thin relative to the electrode (Figure 2.2A). The mass transfer is dominated by planar diffusion, irrespective of the electrode dimension. As time increases, the diffusion layer thickness increases, and becomes much larger than the electrode dimension (Figure 2.2B). Correspondingly, the diffusion mode is changed from planar diffusion to radial diffusion. The critical time t_c can be estimated by

$$t_c = \frac{r^2}{\pi D}, \quad (2.1)$$

where r is radius of electrode and D is diffusion coefficient of species. At general experimental time, *i.e.*, tens of seconds, the diffusion mode is planar diffusion at macro-size electrodes with $r > 0.5$ mm (Figure 2.2C), and is radial diffusion at micro-size electrodes with $r < 0.05$ mm (Figure 2.2D). These two diffusion modes can be observed by using cyclic voltammetry. The corresponding voltammograms demonstrate peak-shape (Figure 2.2E) and sigmoidal-shape (Figure 2.2F), respectively.

In reversible systems using planar electrodes, the peak current $I_{s,p}$ and steady-state limiting current $I_{s,l}$ at the voltammograms (as shown in Figure 2.2E and F) can be estimated by [1, 2, 72]

$$I_{s,p} = 0.45AC \left(\frac{n^3 F^3 D v}{RT} \right)^{1/2}, \quad (2.2)$$

Figure 2.2: Transition from (A) planar diffusion mode at short times to (B) radial diffusion mode at long times. Transition from (C) planar diffusion mode at a macro-size electrode to (D) radial diffusion mode at a micro-size electrode. (E) Peak-shape and (F) sigmoidal-shape voltammogram at planar diffusion mode and radial diffusion mode, respectively. [2]

$$I_{s,l} = 4nFDCr, \quad (2.3)$$

where A is the surface area of electrode, C is the concentration of specie, n is the number of transferred electron at each reaction, $F = 96485.3 \text{ C} \cdot \text{mol}^{-1}$ is the faradaic constant, $\bar{R} = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the universal gas constant, $T = 298 \text{ K}$ is the solution temperature, and v is the scan rate.

Convection consists of natural convection and forced convection. Natural convection is resulted from density difference in the solution, and forced convection is caused by the relative motion between electrode and solution. Introducing forced convection have the advantages of quick formation of steady-state mass transfer, measurement with high precision, and high mass transfer coefficient compared to diffusion in general. However, compared to stationary electrodes, it is more difficult to construct hydrodynamic electrodes with predictable and reproducible mass transfer processes.

Channel electrodes are one of typical hydrodynamic electrodes. As shown in Fig-

Figure 2.3: (A) Schematic diagram of a channel electrode and (B) the corresponding flow profile. [72]

Figure 2.3A, in channel electrodes, a rectangular electrode (length x_e and width w_e) is constructed on one of the channel walls, and the solution containing analytes flows in the channel (height h and width w). The mass transfer coefficient can be easily controlled through the channel size, the electrode size and the flow rate. Moreover, this setup enables the incorporation of electrochemical measurements to flow systems as well as its use in spectroelectrochemistry and photoelectrochemistry.

To obtain predictable and reproducible mass transfer in channel electrodes, there are several conditions. The first condition is that a laminar flow is fully developed across the electrode surface. This requires adjusting the cell design (dimension and position of electrode) and flow rate Q to obtain a Reynolds number $Re = hv_m/\nu < 2300$. Here $v_m = Q/wh$ is the mean velocity of the solution, and ν is the kinematic viscosity of the solution. Under this condition, the solution velocity profile in laminar flow can be simplified as parabolic shape (Figure 2.3B). The second condition is that the flow velocity is high enough to neglect mass transfer from diffusion in the flow direction. This requires the shear Peclet number $Pe_s = 6Qx_e^2/Dwh^2 \gg 1$. The third condition is that edge effects can be neglected. This requires that $x_e \ll w_e \ll w$ and $h \ll w$. Under these three conditions, the mass-transfer limiting current $I_{c,l}$ at a rectangle electrode can be estimated by [72–74]

$$I_{c,l} = 1.47nFCw_e(D^2Qx_e^2)^{1/3}(wh^2)^{-1/3}. \quad (2.4)$$

When the rectangle electrode is replaced by a circular electrode with diameter d , the shear Peclet number $Pe_s = 3Qd^2/2Dwh^2 \gg 1$, $I_{c,l}$ can be estimated by [73, 74]

$$I_{c,l} = 1.23nFCd(D^2Qd^2)^{1/3}(wh^2)^{-1/3}. \quad (2.5)$$

Figure 2.4: Cyclic voltammogram recorded in (A) 1 M KCl solution, and (B) 1 mM $K_3Fe(CN)_6$ in 1 M KCl solution.

2.2 Electrochemical methods

2.2.1 Cyclic voltammetry

Cyclic Voltammetry is the most widely used technique to acquire quantitative information about electrochemical reactions, *e.g.*, redox potentials and peak currents. [1, 2] In this technique, potentiostats apply potential at working electrodes versus reference electrodes by using a triangular potential waveform, and measure the corresponding response currents, resulting from the electrochemical reactions of analytes happening at the surface of the working electrode. The cyclic voltammogram is a plot of the response current versus the applied potential.

At the condition that no reactive species in electrolytes, the voltammogram is in a rectangle shape as shown in Figure 2.4A. The response current is mainly from electrical double layer charging or discharging current I_{dl} , which is proportional to the area inside the voltammogram. The charging current I_{dl} at planar electrodes can be estimated by

$$I_{dl} = vAc_{dl}, \quad (2.6)$$

where c_{dl} is the specific double-layer capacitance of the electrode material.

At the condition that reactive species are added to electrolytes and planar diffusion dominates the mass transfer process, the voltammogram is in a peak shape as shown in Figure 2.4B. The voltammogram can provide several important parameters of the electrochemical response, *e.g.*, the cathodic peak potential $E_{s,p}^c$ and anodic peak potential $E_{s,p}^a$, and the corresponding peak current $I_{s,p}^c$ and $I_{s,p}^a$. The peak potentials are used to calculate peak potential difference by $\Delta E_p = E_{s,p}^a - E_{s,p}^c$, which provides information about electrochemical activity of electrodes towards specific redox couples. Based on

Figure 2.5: Working curves showing the dependence of $\Delta E_p \times n$ on a dimensionless kinetic parameter ψ . [75]

Equation 2.2, the peak current can be used to estimate A , C , or D , depending on the design of experiments.

In Nicholson's method, the standard heterogeneous rate constant k_o is estimated from ΔE_p . [1, 72, 75] Figure 2.5 shows a plot of $\Delta E_p \times n$ versus ψ . The dimensionless kinetic parameter ψ is defined as

$$\psi = \frac{\gamma^\alpha k_o}{\sqrt{\pi \varphi D_O}}, \quad (2.7)$$

where $\gamma = (D_O/D_R)^{1/2}$, $\varphi = nFv/\bar{R}T$, D_O and D_R are the diffusion coefficients of oxidants and reductants, respectively, and α is the charge transfer coefficient. In order to simplify the calculation, $\gamma^\alpha = 1$ is generally used. [72, 75] After obtaining ΔE_p from voltammogram as shown in Figure 2.4B, ψ can be obtained from Figure 2.5. Subsequently, k_o can be calculated using Equation 2.7.

2.2.2 Linear sweep voltammetry

Linear sweep voltammetry is a technique similar to cyclic voltammetry and it only performs forward scanning potential. [1, 2] This technique is specially dedicated to be used in hydrodynamic conditions to investigate effects of forced convection on the electrochemical response happening at the electrode surface. Figure 2.6A shows representative voltammograms recorded with varying flow rate Q . At each flow rate, the response current increases along the scan direction and approaches a steady-state, which suggests the electrochemical response is limited by mass transfer process and is important to do quantitative study. The mass transfer limiting current $I_{c,l}$ is measured at the steady-state range and investigated against Q . In ideal conditions, as shown in Figure 2.6B, $I_{c,l}$ increases linearly with $Q^{1/3}$ and can be predicted by Equation 2.4. Both the potential and the flow rate to achieve the steady-state can be used in chronoamperometry to do real-time detection. By further increasing Q to the condition that the mass trans-

Figure 2.6: (A) Typical linear sweep voltammogram with varying flow rate Q in hydrodynamic experiment. (B) Plot of limiting current $I_{c,l}$ versus $Q^{1/3}$. [53]

fer coefficient is higher than heterogeneous rate constant for oxidation or reduction, the mass-transfer-limited condition is not satisfied anymore, and the response current will keep increasing along the scan direction.

2.2.3 Chronoamperometry

In chronoamperometry, potentiostats apply constant potentials at working electrodes to cause electrochemical reactions of analytes, and measure response currents at the same time. [1,2] This method is simple and compatible with micro-fluidic systems for real-time detections. Besides, it can achieve low background currents and subsequently facilitates detections of low concentration analytes. The background currents are mainly electrical double layer charging currents I_{dl} , which decrease with experimental time t following

$$I_{dl} = \frac{\Delta E}{R_{so}} e^{-t/R_{so}C_{dl}}, \quad (2.8)$$

where ΔE is the potential step, R_{so} is the Ohmic solution resistance, and C_{dl} is the electrical double layer capacitance. I_{dl} reduces 95% for $t = 3R_{so}C_{dl}$. As shown in Figure 2.7, after background current is stabilized, injection of analyte causes faradaic reaction at the electrode surface, and subsequently generates signal current, which is proportional to the concentration of analyte.

2.2.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a powerful technique used to investigate electrochemical cells. Generally, electrochemical impedance spectroscopy (EIS) consists of the following steps: perturb an electrochemical cell by using an alternative potential with small amplitude (generally in sinusoidal shape) over a range of frequencies; record

Figure 2.7: Current response for the injection of analyte with different concentration in chronoamperometry. [52]

Figure 2.8: A four-element Randles equivalent circuit. [2]

corresponding response current; relate key physical or chemical characteristics of the cell to equivalent electrical components and form a Randles equivalent circuit; fit the experimental data with the circuit to obtain values of each component. [1, 2]

The key step in EIS is to construct the Randles equivalent circuit to mimic the electrical behavior of the cell. Generally, an electrochemical sensor is composed of four elements (Figure 2.8): the Ohmic solution resistance R_{so} , the electron transfer resistance R_{ct} , the constant phase element (CPE) with impedance Z_{CPE} , the Warburg impedance or mass transfer resistance Z_W . The Ohmic solution resistance R_{so} is the resistance of the solution between the working electrode and the reference electrode. In a bounded space with area A_c and length l_c , R_{so} can be estimated by

$$R_{so} = \frac{1}{\sigma} \frac{l_c}{A_c}, \quad (2.9)$$

where σ is the electrical conductivity of the electrolyte.

The electron transfer resistance R_{ct} reflects the speed of electron transfer across the interface of the electrode and electrolyte. It is affected by redox couples, solution temperature, concentration of the redox couples, and applied potential. When the applied potential is equal or similar to the equilibrium potential of the redox couple, the cell is at equilibrium state and the current-potential relationship can be linearized. There, R_{ct}

can be estimated by

$$R_{\text{ct}} = \frac{\overline{RT}}{n^2 F^2 A C k_o}. \quad (2.10)$$

An electrical double layer exists at the interface between an electrode and its surrounding electrolyte, and it has been shown to behave as a capacitor. However, its capacitance is affected by electrode potential, solution temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, and so on. It generally behaves as a CPE rather than an ideal capacitor. The impedance of a CPE can be expressed as

$$Z_{\text{CPE}} = \frac{1}{(j\omega)^a C_{\text{dl}}}, \quad (2.11)$$

where $\omega = 2\pi f$ is the radial frequency, f is the frequency of the alternative potential, a is a constant in the range $0.5 < a < 1$ ($a = 1$ or $a = 0.5$ corresponds to an ideal capacitor or a Warburg element), C_{dl} is the capacitance of the electrical double layer capacitor.

The mass transfer impedance depends on the mode of mass transfer. A typical mode is the semi-infinite linear diffusion, which results in a infinite Warburg impedance Z_{w} , and can be estimated by

$$Z_{\text{w}} = \frac{\sigma(1-j)}{\omega^{1/2}}, \quad (2.12)$$

with

$$\sigma = \frac{\overline{RT}}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right), \quad (2.13)$$

where C_R^* and C_O^* are the initial concentrations of reductant and oxidant, respectively. The impedance Z_{w} depends on the frequency of the alternative potential. At high frequencies, Z_{w} is small since the species do not have to move very far. At low frequencies, Z_{w} is large as the species have to diffuse farther.

The frequency response of electrochemical cells can be illustrated by a Nyquist plot, which is a plot of the imaginary part of complex impedance $-Z_{\text{imaginary}}$ versus the real part of complex impedance Z_{real} . Figure 2.9 shows a typical Nyquist plot of a electrochemical sensor composed of four elements (equivalent circuit is shown in Figure 2.8). At high frequency ($\omega \rightarrow \infty$), Z_{CPE} becomes zero and current flow through the capacitor directly, the impedance of the whole cell is R_{so} . A rough estimation of R_{ct} is related with the diameter of the semicircle. The C_{dl} can be estimated from $\omega = 1/R_{\text{ct}}C_{\text{dl}}$ with ω obtained at the maximum $-Z_{\text{imaginary}}$ of the semicircle. At low frequency ($\omega \rightarrow 0$), Z_{w} appears as a diagonal line with an slope of 45° . The semicircle and the straight line respectively represents kinetic control and mass transfer control.

Figure 2.9: A typical Nyquist plot for an electrochemical cell. [2]

2.3 Carbon nanotubes: novel electrode materials

2.3.1 Structure and properties

Carbon is one of the most fundamental and rich atoms in the world. It has four electrons available to form covalent bonds. Until a few decades ago, the well-known allotropes of carbon are diamond (sp^3 material), graphite (sp^2 material), and amorphous carbon (non-crystalline form). The discovery of C60 in 1985 and multi-walled carbon nanotubes (MWCNTs) in 1991 open a new era for the carbon chemistry and novel materials.

Carbon nanotube (CNT, a one-dimension structure) is a member of sp^2 carbon family, along with graphene (a two-dimension structure), and highly oriented pyrolytic graphite (HOPG, a three-dimension structure). As shown in Figure 2.10A, HOPG is composed of multi-layer of graphene, single-walled carbon nanotube (SWCNT) is a scroll of individual graphene, and MWCNT is a scroll of multiple graphene with concentric structure. SWCNTs have typical outer-diameter of 0.4-1.5 nm, and MWCNTs have outer-diameter ranging from 2 nm to 100 nm. [69, 76]

Graphene is composed of benzene-type hexagonal rings of carbon atoms, it can be rolled up along different directions of the hexagonal lattice to form SWCNT with different properties. As shown in Figure 2.10B, the rolling direction is represented by a vector, $\vec{C} = n\vec{a}_1 + m\vec{a}_2$. $\vec{a}_1$ and $\vec{a}_2$ are the directions along the hexagonal lattice, and n and m are the number of lattice along $\vec{a}_1$ and $\vec{a}_2$, respectively. The direction is usually described by a pair of index (n,m) . Depending on the rolling direction, SWCNTs can show metallic ($n - m = 3N$, N is integer) or semiconducting behavior (other vectors). It has been estimated that only 1/3 tubes are metallic. [76, 78]

The difference of metallic SWCNTs and semiconducting SWCNTs can be found in their density of states (DOS). Figure 2.10C shows the DOS for two representative SWCNTs: one metallic tube (5,5) and one semiconducting tube (7,0). They present discon-

Figure 2.10: (A) Schematic of structure connection between HOPG, graphene, SWCNT and MWCNT. [69] (B) Schematic of rolling a graphene into SWCNT along three directions (14,0), (11,4), and (8,8). [77] (C) Density of state (DOS) for a metallic SWCNT (5,5) and a semiconducting SWCNT (7,0). [78]

tinuous spikes, which are typical for one-dimension material. Compared to the metallic tube, the semiconducting tube has a band gap ($\text{DOS} = 0$) around Fermi level. The band gap for the tube with diameter d can be estimated by $E_g = 0.9\text{eV}/d$. [79] MWCNTs are different from SWCNTs, *i.e.*, generally demonstrate metallic behavior. The whole tube is metallic when only one of the concentric tube is metallic. [69]

CNTs have high electrical and thermal conductivity. The nano-sized diameters of CNTs restrict transportation of electrons along their axes without scattering. A perfect metallic SWCNT (or MWCNT) has electrical conductance as high as $2G_0$ (or G_0). Here $G_0 = 7.75 \times 10^{-5}S$ is the conductance of a single ballistic quantum channel. Besides, the absence of scattering minimizes Joule heating. Both SWCNTs and MWCNTs can withstand current density up to $10^9 \text{A} \cdot \text{cm}^{-2}$, which is orders of magnitude higher than that of metals. [79–82] CNTs are also very conductive for phonons. MWCNTs have been reported with thermal conductivity of $3000 \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. [83]

CNTs have excellent mechanical properties, resulted from sp^2 bonds between carbon

atoms, nano-sized diameter, and high aspect ratio. However, the mechanical properties of CNTs are affected by their structure quality significantly. [84] MWCNTs synthesized by arc-discharge methods (ARC-MWCNTs) have fewer defects than MWCNTs synthesized by CVD methods (CVD-MWCNTs). ARC-MWCNTs have Young's modulus ranging 0.27-1.28 TPa, tensile strength ranging 11-63 GP, and fracture at strains up to 12%. [85-87] CVD-MWCNTs have Young's modulus ranging 12-450 GPa, and tensile strength 4 GPa. [86, 88] CNTs are stiff along their axes, but flexible in the orthogonal direction.

The unique structures of CNTs, including sp^2 bonds and nano-sized diameter, also enable CNTs special electrochemical properties. CNTs are widely used in electrochemical application with the advantages of high electrochemical activity, wide scanning potential window, low electrical double layer charging current, bio-compatibility, and so on. According to energy conservation, electrons prefer to transfer between electrodes and redox couples which have overlapping electron energy levels. High DOS at these energy levels increases the possibility of transferring electrons, and subsequently increases the heterogeneous rate constant of oxidation or reduction. [89, 90] As shown in Figure 2.10C, SWCNTs rolled along different directions have different DOS. It has been shown that SWCNTs have much slower heterogeneous rate constant towards those redox couples with formal potential locating at the band gap than other redox couples. [89, 91, 92] Besides, the low DOS facilitate SWCNTs low capacitance, and subsequent low electrical double layer charging current. The high curvature at the sidewall of SWCNTs distorts π -orbitals and facilitates electron transfer. Several works have demonstrated reversible electron transfer at the sidewall of pristine SWCNTs. [70, 71, 92] MWCNTs are generally accepted to have similar electrochemical properties as graphite. They have high electrochemical activity at the edge and low activity at the basal plane. The disorder such as edges and defects can increase local DOS and subsequently electrochemical activity. [69, 91, 93, 94]

Oxygen-containing functional groups, *e.g.*, -OH and -COOH, also affect electrochemical properties of CNTs. Gong *et al.* [95] compare electrochemical activity of several species at sidewalls or tips of MWCNTs with/without the functional groups. MWCNTs tips with the functional groups have the highest activity towards $K_3Fe(CN)_6$, while MWCNTs sidewalls have the highest activity to oxidize H_2O_2 , which is not affected by the functional groups. However, decorating functional groups also induces defects at MWCNTs, which is not considered in this work. [91] In order to separate effects from defects and the functional groups, acid-treated MWCNTs are annealed at 900 °C to remove the functional groups while remain defects. [93] The investigation concludes that the high electrochemical activity of MWCNT towards $K_3Fe(CN)_6$ is originated from defects not

from the functional groups. This conclusion can be supported by recent reports that basal planes of freshly prepared HOPG have high electrochemical activity for reducing $\text{K}_3\text{Fe}(\text{CN})_6$, and the activity is deteriorated with exposing the planes to ambient environment. [96,97] McCreey has also reviewed that the surface condition and oxidizing condition of electrodes may affect their electrochemical activity depending on species. [89]

Residual catalysts in CNTs (*e.g.*, Fe, Ni, and Co) can also influence their electrochemical activity, and even dominate the activity towards special species. [69,91] For example, iron nano-particles in MWCNTs are responsible for oxidation of hydrazine and reduction of H_2O_2 . Catalysts encapsulated within CNTs as deep as 12 nm can still participate in electrochemical reactions. [98,99]

2.3.2 Growth of carbon nanotubes

Carbon nanotubes can have different structures, morphologies and properties, depending on both growth methods and post processing. [100] There are three typical growth methods: electrical arc discharge, laser ablation, and chemical vapor deposition (CVD). [76,101,102] Both of electrical arc discharge and laser ablation use solid-state carbon as carbon sources and evaporate carbon at high temperature (thousands of degrees Celsius). They can synthesize CNTs with high crystallinity. However, the yield and purity are low, and the byproducts (amorphous carbon and residual catalyst) are high. [76,101] CVD uses hydrocarbon gases as carbon sources and metal catalysts as CNT nucleation sites. It is carried out at a relative low temperature ($< 1000^\circ\text{C}$). Compared to other two methods, CVD has great advantages in tenability, purity, cost and productivity. Depending on energy source, CVD can be further categorized as thermal CVD (TCVD), plasma enhanced CVD, hot-filament CVD, and radio-frequency CVD. [76,101,102] Among these methods, TCVD is the most widely used method considering its simplicity and ability to synthesize spinnable MWCNT arrays. In the following parts, I introduces the spinnable MWCNT arrays, spinnable mechanisms, their growth process and effects of several parameters on the spinnability.

Spinnable MWCNT arrays are a special kind of vertically-aligned MWCNT array that can be converted into continuous MWCNT yarns (Figure 2.11A) or MWCNT sheets (Figure 2.11B). [65] Since its discovery by Fan *et al.* [61] in 2002, spinnable MWCNT arrays have attracted great attention as they are able to convert microscopic MWCNTs into macroscopic MWCNT devices easily and have been used in a variety of applications. There are two mechanisms to explain the spinnability. Fan *et al.* [61,103] observe the process of pulling MWCNT yarns from spinnable arrays by using scanning electron mi-

Figure 2.11: (A) SEM images showing MWCNT bundles simultaneously pulled and twisted from the spinnable array to form MWCNT yarns. [62] (B) (left) Image of a transparent self-supporting MWCNT sheet, and (right) SEM images showing the conversion of a vertically-aligned MWCNT forest into a single MWCNT sheet and a two-dimensionally reinforced structure fabricated by overlaying four MWCNT sheets with a 45° shift in orientation between successive sheets. [63]

croscope and optical microscope, and find that MWCNTs are connected end-to-end to form continuous yarns (Figure 2.12A). They propose that the clean surface and super-alignment morphology of MWCNTs increase the Van der Waals forces between individual MWCNTs and subsequently cause conjunction. Kuznetsov *et al.* [104] and Zhu *et al.* [105] propose that the spinnability depend not only upon good alignment of MWCNT bundles (nearby MWCNTs usually stick together to form small bundles), but also upon structural interconnections between MWCNTs. As shown in Figure 2.12B, MWCNT bundles are interconnected by cross MWCNTs at the beginning, pulling the bundles densifies these interconnections at the top or bottom of the bundles, which increase adhesion between bundles and enable the continuous drawing of MWCNTs [104]. Both of mechanisms require MWCNTs in the spinnable array to have clean surface and super-aligned morphology, which subsequently require strict control of the growth process.

Currently, the spinnable MWCNT arrays are synthesized by using TCVD, which consists of preparation of catalysts and growth of CNTs. Catalysts used for CNTs nucleation are generally prepared by depositing thin metal films (such as Fe, Co and Ni) on silicon wafers using sputtering or electron beam evaporation. A buffer layer such as aluminum, alumina and silicon oxide is generally deposited or grown between the catalyst film and the Si wafer. The catalysts are then loaded into a tube furnace (Figure 2.13A) to synthesize CNTs following the process shown in Figure 2.13B. The growth process consists of four steps: S1 – S4. [106] Figure 2.13C shows the corresponding growth mechanism of CNT array. [107]

S1 is a ramping step, after loading catalysts into the tube, the furnace is heated up

Figure 2.12: Two models illustrating connection of MWCNTs during pulling process. (A) End-to-end model. [103] (B) Interconnection model. Blue and red bars represent small bundles of MWCNTs, and the distance between them is increased for clarity. Red arrows show the external force applied to the first bundle. [104]

from room temperature to setting temperature. S2 is a pretreatment step, where the furnace tube is held at the setting temperature. S1 and S2 are treated as pretreatment step together sometimes [109]. During S1 and S2, forming gases consisting of inert gas (*e.g.*, Ar, He and N_2) and reducing gas (*e.g.*, H_2) are flushed through the tube. Under the effect of heating and reducing gas, the metal film is broken into metal nanoparticles (Figure 2.13C). S3 is a growth step, carbon source (*e.g.*, C_2H_2 and C_2H_4) is introduced into the tube to trigger CNTs growth. Oxidizing agent (*e.g.*, water vapor) can be introduced to elongate the activity life of catalysts. The vapor-solid-solid model which originated from vapor-liquid-solid model [110], is generally accepted to explain the growth process. According to the vapor-solid-solid model, hydrocarbon gases are decomposed into carbon atoms at high temperature, carbon atoms diffuse to surface of catalysts and nucleate CNTs at its edges. Depending on strength of adhesion between catalysts and substrates, catalysts may be at the bottom or at the top of CNTs. The growth process is influenced by gas, temperature, pressure, and growth time. S4 is a cooling step, the furnace is cooled down to room temperature with protection of inert gases.

The process of synthesizing spinnable MWCNT arrays is very delicate. Minor changes

Figure 2.13: (A) Schematic of TCVD apparatus used to synthesize CNT arrays. [108] (B) Schematic of growth process of CNT arrays using TCVD. [106] (C) Schematic describing the growth mechanism of CNT arrays by TCVD. [107]

of the process may affect the spinnability of the arrays. Table 2.1 summarizes crucial parameters of synthesizing spinnable MWCNT arrays and corresponding physical properties of MWCNTs and MWCNT arrays. The effect of these parameters on the spinnability of MWCNT arrays are introduced in the following sections.

Si wafers are the most-frequently used substrate for growing spinnable MWCNT arrays. A buffering layer (*e.g.*, SiO₂ and Al₂O₃) between substrate and catalyst layer is usually needed to prevent reactions between them. Otherwise catalysts such as Fe can react with Si to produce non-catalytic silicides. However, the buffering layers may introduce impurity which disrupts the Si surface integrity and hence the fragmentation of catalysts. They can also change physical properties of the substrate such as thermal expansion, thermal and electrical conductivity. A SiO₂ layer with thickness ranging from 25 to 300 μm has been shown to be the best for growing spinnable MWCNT arrays. [111]

Catalysts are nucleating sites for synthesizing MWCNTs. Formation of catalysts with high density is important to synthesize spinnable MWCNT arrays. They are usually deposited as a thin metal film on buffer layers and then broken into nano-particles under

Table 2.1: Parameters used in growing spinnable MWCNT arrays by TCVD and corresponding physical properties of MWCNT arrays and MWCNTs.

No	Reference	Year	Furnace	Substrate	Buffer layer	Catalyst
1	Zhang <i>et al.</i> [103]	2006	1-in quartz tube 4-in quartz tube	Si, SiO ₂ and quartz		3.5 - 5.5 nm Fe EBE
2	Liu <i>et al.</i> [47]	2008	27 mm quartz tube	SiO ₂ /Si		0.2 nm Fe EBE 3.2 nm Fe EBE 5.0 nm Fe EBE
3	Li <i>et al.</i> [64]	2006	1-in quartz tube	1 μ m SiO ₂ /Si	10 nm Al ₂ O ₃ BAD	1 nm Fe sputter
4	Zhu <i>et al.</i> [105]	2011	2-in quartz tube	300 nm SiO ₂ /Si	10 nm Al ₂ O ₃ EBE	1 nm Fe sputter
5	Zhang <i>et al.</i> [106]	2009	1-in quartz tube	1 μ m SiO ₂ /Si	10 nm Al ₂ O ₃	1 nm Fe
6	Zhang <i>et al.</i> [62]	2004	45 mm quartz tube	Si		5 nm Fe EBE
7	Lepro <i>et al.</i> [115]	2010	65/72 mm quartz tube	stainless steel foil	100 nm SiO _x PECVD	2 nm Fe EBE
8	Cui <i>et al.</i> [116]	2013	5-in quartz tube	600 nm SiO ₂ /Si <100>		0.5 - 1 nm Fe EBE
9	Zhang <i>et al.</i> [117]	2008	38 mm quartz tube	500 nm SiO ₂ /Si <100>	15 nm Al ₂ O ₃ EBE	2 nm Fe EBE
10	Inoue <i>et al.</i> [118]	2008	40 mm quartz tube	SiO ₂ or quartz		FeCl ₂ powder
11	Kim <i>et al.</i> [113]	2010				4 - 6 nm Fe EBE
12	Kim <i>et al.</i> [119]	2010	quartz/stainless steel chamber	400 nm SiO ₂ /Si		3 - 4 nm Fe EBE
13	Lee <i>et al.</i> [109]	2012				5 nm Fe EBE
14	Huynh <i>et al.</i> [111]	2010				2.3 nm Fe thermal evaporation
15	Huynh <i>et al.</i> [114]	2011	ATM 44 mm quartz tube	50 nm SiO ₂ /Si N <100> type		2.5 nm Fe EBE

No	Growth step				Properties			
	Gas (sccm)	Temperature (°C)	Pressure (atm)	Duration (min)	Outer diameter (nm)	Wall number	Length (μ m)	Areal density (10 ¹⁰ /cm ²)
1	Ar/C ₂ H ₂ =12/425 H ₂ /C ₂ H ₂ =500/50	620 - 700 680 - 720	1 0.0026		15			
2	Ar/H ₂ /C ₂ H ₂ = 200/100/30 Ar/H ₂ /C ₂ H ₂ = 300/100/30 Ar/H ₂ /C ₂ H ₂ = 200/100/30	680 680 620	1	3 - 15 3 - 12.5	6.2 6.8 9.2	3 - 4 4 - 5 > 5	175 - 900 106 - 357	5 10 2.5
3	Ar/H ₂ /C ₂ H ₄ = 94/6/100	750	1	10 - 15	10	6	500 - 1500	
4	Ar/H ₂ /C ₂ H ₄ = 650/50/150	740	1	10 - 20	10		200 - 600	
5	Ar/H ₂ /C ₂ H ₄ = 131.6/8.4/30	750	1	10				
6	Ar/C ₂ H ₂ = 20/560	680	1	10	10		70 - 300	
7	Ar/H ₂ /C ₂ H ₂ = 504/240/56	700	1	10	11		150	
8	H ₂ /C ₂ H ₂ = 500/60	750	0.0013	10	10	8	630	
9	Ar/H ₂ /C ₂ H ₂ = 350/180/150 775 ppm water vapor	750	1	20	10	5 - 7	1000	
10	C ₂ H ₂	835	0.01	20	30 - 50	20	2000	
11	He/H ₂ /C ₂ H ₂ = 20000/100/700				12.5 - 13		380 - 420	1.7 - 2.8
12	He/C ₂ H ₂ = 20000/400	780	1	5			360	2.1 - 2.4
13	He/H ₂ /C ₂ H ₂ = 2000/100/400				12.5			1.2
14	He/C ₂ H ₂ = 650/34	670		20	10 $\pm$ 3	7 $\pm$ 2	400	
15	He/C ₂ H ₂ = 1000/25 wo/w 25 sccm H ₂	680	1	10	10.5/8.7	7 / 5 - 6	255/380	2.17/3.43

the effect of heating and reducing gas. Generally, by increasing film thickness, catalyst size, MWCNT diameter, and wall number increase, while areal density and spinnability would not increase monotonically [112–114]. Table 2.1 shows that Fe catalyst films with thickness ranging from 0.2 nm to 5 nm have been used to grow spinnable MWCNT arrays successfully. A suitable thickness is affected by buffering layer, deposition method and growth process. The reducing gas can revert metal oxide in the as-deposited films and facilitates formation of nano-particles under a wide range of annealing temperature and duration. [113] Under effect of heating, the nano-particles diffuse to meet with other particles and become coarsen. This coarsen process reduces the available nuclei and areal density, and eventually results in waved MWCNTs as there is not enough steric resistance. By introducing carbon source at the beginning, the growth of MWCNTs can occur as soon as the temperature is suitable and prevents coarsen of catalysts. [106, 109]

During growth step, both carbon sources (*e.g.*, C_2H_2 and C_2H_4) and agent gases (*e.g.*, water vapor and H_2) affect spinnability of MWCNT arrays. Carbon sources are decomposed into carbon atoms at high temperature. Their concentration, flow rate, and growth temperature determine availability of carbon atoms for synthesizing MWCNTs, and eventually affect the spinnability. [109, 111, 116]. As shown in Figure 2.14, by varying concentration of C_2H_2 from 0.25% to 6.94%, height and growth rate of MWCNT arrays are increased and then reduced, and MWCNTs are changed from waving morphology to aligned morphology and back to waving morphology. A low concentration C_2H_2 results in shortage of carbon atoms approaching to catalyst surface. While a high concentration C_2H_2 generates too much carbon byproduct such as amorphous carbon, which may cover catalysts surfaces and deactivate catalysts. [109] Both of these two conditions reduces the growth rate and height of CNT arrays. Even worse, part of catalysts are wasted as they can't obtain carbon or are deactivated, which subsequently increase inter-distance between CNTs and results in waving morphology. Only super-aligned MWCNT arrays with clean MWCNT surface are spinnable. The agent gases are generally used to reduce amorphous carbon, which extends activity of catalyst and maintains cleanliness of MWCNT surface. [64, 116, 120, 121]

Growth temperature affects decomposition rate of carbon sources, and subsequently determines availability of carbon atoms to catalysts and generation of amorphous carbon. It has similar effect as concentration of carbon source on the spinnability. [111, 116] Growth duration also affect the spinnability. A long growth duration increases height of arrays but intends to generate amorphous carbon. While a short duration produces short MWCNT arrays, which may not have enough interaction between MWCNTs [109, 111, 116].

Figure 2.14: SEM images showing morphology of CNT arrays grown at different C_2H_2 concentration: (A) 0.25, (B) 0.5, (C) 1.47, (D) 2.43, (E) 3.37, (F) 4.74, and (G) 6.94 vol.%. (H) Dependence of array height and growth rate on C_2H_2 concentration. [109]

2.4 Carbon nanotubes electrodes for electrochemical sensors

Carbon nanotubes electrodes have been used in electrochemical sensors to detect a wide range of species. [6–8, 122, 123] The CNT-based electrodes possess numerous distinct features such as excellent electron transfer ability, wide potential window, low surface fouling, high mechanical strength, high electrical conductivity, and high biocompatibility. The detection performance of electrodes is not only affected by intrinsic properties of electrode material, but also by electrode configuration. In this section, I introduces several configurations of CNT-based electrodes, and their corresponding advantages and disadvantages.

2.4.1 Individual carbon nanotube electrodes

Both individual MWCNT [16–19] and SWCNT [20, 70, 71] electrodes have been fabricated and demonstrated for electrochemical detection. Individual MWCNT electrodes (Figure 2.15A) are prepared by connecting a MWCNT to tip of a metal wire. The connection between them is fulfilled by using silver epoxy or electrical breakdown. The

Figure 2.15: (A) TEM image of a individual MWCNT electrode. A MWCNT is connected to a gold tip. [19] (B) SEM image of a individual SWCNT electrode. A SWCNT is grown on Si/SiO₂ substrate, and covered by palladium metal contact pad at one end. [70]

MWCNTs have diameter < 100 nm and length about few to tens of micrometers. They are synthesized by arc-discharge method [18] or CVD [16, 18, 19]. Individual SWCNT electrodes (Figure 2.15B) are generally prepared by selectively depositing metal film on individual SWCNTs, which are grown on insulating Si substrate by CVD. [20, 70, 71] The exposed area of SWCNTs to electrolyte can be defined by photolithography [20] or using scanning electrochemical cell microscopy [70, 71].

Individual CNT electrodes can be used to investigate intrinsic electrochemical properties of CNTs as they remain pristine structure of CNTs and prevent effect from catalyst. [70, 71] By using individual SWCNT electrodes, it has been proved recently that defect-free sidewalls of SWCNTs have high electrochemical activity, *e.g.*, comparable with gold for reduction of oxygen. [70] The nano-sized diameter of CNTs facilitates radial diffusion of analytes at individual CNT electrodes, which achieves high mass transfer rates and yields high current densities, coupled with small capacitances and small Ohmic drops. Combining with high mechanical strength, high aspect ratio, and excellent electrochemical properties of CNTs, individual CNT electrodes can be used to measure the kinetics of fast electron transfer reactions, to detect single molecules, to probe neurochemical micro-environments and as scanning electrochemistry probes. However, the nano-sized dimension results in vanishingly small current and high difficulty of fabrication and manipulation.

2.4.2 Carbon nanotube film electrodes

Carbon nanotube film electrodes are the most widely used CNT electrodes, resulting from their easy preparation and modification. The CNT film electrodes are gen-

erally prepared by: dispersing CNTs in solvents to form CNT solutions, casting the CNT solutions on substrates, and evaporating the solvents. [21–26] To further improve CNTs dispersion in the film electrodes, CNT films electrodes can be prepared by using vertically aligned CNT arrays [124–128], or assembling dispersed CNTs on conductive substrates by electrostatic forces [129]. The dispersion solvents include ethanol [22], N,N-dimethylformamide [22], chloroform [130], Dimethylformamide [131, 132], mixture of water and Nafion [131], and so on. The substrates include glassy carbons [21], highly order pyrolytic graphites [133] and insulate substrates [22]. Glassy carbons are the most frequently used substrates with advantages of electrochemical inertness in a wide potential window, easy regeneration, high robustness and low cost. [134] To improve sensitivity and selectivity of CNT films electrodes towards special species, CNTs can be functionalized with oxygen-containing functional groups [25, 26], metal oxides [127, 135], organic compounds [126, 136], and so on [123, 137].

The CNT film electrodes have several disadvantages. The hydrophobic nature of CNTs result in aggregation and non-uniform dispersion of CNTs in solvents. It is necessary to use long time acid treatment to change their wettability or strong ultrasonic to break long CNTs into short CNTs. The weak adhesion between CNT films and substrates may result in leached-off and high contact resistance between them. The CNT films are porous ensembles, which have high physical surface area and cause high electrical double layer charging current. [1, 124] The mass transfer of species towards the porous CNT films can't be explained simply by semi-finite diffusion mode, and instead by thin film diffusion mode, which is affected by both the inter-distance of CNTs and the film thickness. [23, 130, 133] Generally, inter-distance between CNTs in the porous films is small, which results in overlapping of CNT diffusion layers and low mass transfer coefficient. This limitation can be overcome by introducing forced convection across the electrodes. [125, 138] Impurities, *i.e.*, residual metals, amorphous carbons, and nanographite, affect electrochemical properties of CNT films electrodes seriously, and may cause serious discrepancy in detection performance of different electrodes. [24, 131, 139]

2.4.3 Carbon nanotube paste and composite electrodes

Carbon nanotube paste and composite electrodes are similar to CNT film electrodes and further use binders to increase their mechanical stability. They are generally prepared by dispersing CNTs in binders to form pastes or composites, which is followed by casting into cavities or on glassy carbon electrodes. The binders include insulating materials such as mineral oil [27], Teflon [28], epoxy [30], chitosan [29] and polysulfone [140], and conductive material such as polyaniline [141] and polypyrrole [142]. The insulating

Figure 2.16: SEM images of (A) a high-density VCA, (B) the VCA encapsulated in SiO₂ matrix, and (C) a high density VCN after polished. [37]

binders can cover sidewalls of CNTs and subsequently reduce electrical double layer charging current. [30–32] The conducting binders can improve electrical conductivity while reduce chemical stability. [32] Usage of binder materials improves the mechanical stability of the electrodes, and provides the possibility to renew the electrodes by simply polishing. [28, 30] Besides, the binder materials can affect electronic states of CNTs and increase electrochemical activity, sensitivity, selectivity, and anti-fouling towards special species. [29–31, 141, 143] To further improve those advantages, CNTs can be functionalized with oxygen-containing functional groups [144] and metal nanopartilces [145]; binder materials can be mixed with biomolecules [146], and redox mediators [29].

The CNT paste and composite electrodes have several limitations similar to CNT film electrodes, such as unpredictable effects from impurities [144] and difficulty of CNTs dispersion [140]. Infiltration of insulating materials reduces direct contacts between CNTs and subsequently reduces electrical conductivity of the CNT pastes and composites. [32]

2.4.4 Vertically aligned carbon nanotube nanoelectrode arrays

Vertically aligned carbon nanotube nanoelectrode arrays (VCNs) are the most promising CNT-based electrodes in electrochemical detections. VCNs are generally prepared by: synthesizing vertically aligned carbon nanotube arrays (VCAs), encapsulating VCAs in dielectric material, removing excess dielectric material and exposing one ends of CNTs by grinding and polishing. Figure 2.16 shows morphologies of VCNs are each steps. Although fabrication of VCNs is time-consuming and material-consuming, their supreme advantages for electrochemical detections attract lots of attention.

In VCNs, CNTs are encapsulated in dielectric material with tips exposing only. The sidewalls of CNTs are covered by dielectric material, which prevents them from contacting with electrolytes and reduces electrical double layer charging currents significantly. [33–35] The opened ends of CNTs are exposed to provides high electrochemical activity of VCNs towards a variety of species. Electrons generated at tips of CNTs can be

transferred directly from the tips through individual CNTs to current collectors. [33, 46] This configuration avoids contact resistance between CNTs, and makes use of high electrical conductivity of CNTs. The potential drop on VCNs is negligible. The covalent bonding functional groups such as -COOH and -OH at the ends of CNTs facilitate further covalent bonding of CNTs with other molecules. [36–38] Encapsulation in dielectric material provides VCNs highly mechanical stability and possibility to be renewed by simple polishing. [33–35] Besides, impurities such as residual catalysts and amorphous carbons are covered by dielectric material and won't affect performance of VCNs.

VCNs are generally fabricated from VCAs with site density $\approx 10^9 \text{ cm}^{-2}$, and the inter-distance between CNTs is few hundred nanometers. At conventional experimental timescale, *e.g.*, tens of seconds, this inter-distance is much smaller than diffusion layer thickness, thus the diffusion layers of CNTs overlap and the VCNs behave as single electrodes. [37, 46] This reduces mass transfer towards individual CNTs. Compared to solid electrodes with same dimensions, on the fast electron transfer condition, both VCNs and solid electrodes have same faradaic currents. However, VCNs are only partially covered by CNTs, thus they have much lower electrical double layer charging currents, and subsequent higher signal to noise ratios. [57] The VCNs behave as planar electrodes rather than porous electrodes, the current response is quick and can be predicted easily.

The dimension, position and density of VCNs can be controlled by patterning catalyst layers. This approach not only facilitates miniature of VCNs and combination of VCNs with micro-fluidic system to do real-time detection [147, 148], but also increases mass transfer coefficient towards VCNs [47–50]. VCNs in the form of array have been fabricated. The VCNs have diameter as small as $2 \mu\text{m}$ to achieve radial diffusion and subsequent high mass transfer coefficient. The arrays have inter-distance of $50 \mu\text{m}$ to avoid overlapping of diffusion layers of each VCNs and amplify response current. [47] To further increase mass transfer coefficient and make use of nano-size of CNTs, VCNs with few micrometers inter-distance between CNTs have been fabricated. [37, 46, 149] However, CNTs in such VCNs have diameter of $\approx 100 \text{ nm}$, which are generally defined as carbon nanofibers and may have different properties compared with CNTs with $\approx 10 \text{ nm}$ diameter. The fabrication process becomes delicate. It generally requires to use nano-lithography to pattern catalysts, and plasma-enhanced CVD with the assistant of electrical field to synthesize low density VCAs. [55, 148–152]

Figure 2.17: (Left) Schematic of a SWCNT network electrode; (right) AFM profile of a typical SWCNT network. [53]

2.4.5 Single-walled carbon nanotube network electrodes

SWCNT network electrodes are a layer of randomly distributed and multiply connected SWCNTs (Figure 2.17). They are generally prepared by: growing 2D SWCNT networks on Si/SiO₂ substrates using catalytic CVD; patterning metal contacting pads at the edge of the 2D networks; defining exposed area of SWCNTs to electrolytes by photolithography. The density of SWCNTs can be controlled by varying the methane flow rate and growth temperature. [42, 153]

SWCNTs have excellent electrochemical properties such as high electrochemical activities towards various species and low intrinsic capacitance. [39–42, 70, 71] These facilitate the SWCNT network electrodes to obtain high faradaic current and low background current at the same time. Besides, low surface coverage ($< 1\%$) of SWCNTs on insulating substrates reduces the background current further. It has been reported that the background currents of SWCNT networks are about one and two order of magnitudes smaller than that of boron doped diamonds and glassy carbons, respectively. [154] The electrochemical properties of SWCNT networks can be further modified by varying SWCNT density, inducing oxygen-containing functional groups, and decorating metal nano-particles. [155, 156]

Similar to other CNT ensembles, inter-distances between SWCNTs in the network electrodes are much smaller than diffusion layer thickness of SWCNTs, and the mass transfer towards SWCNT network electrodes is dominated by planar diffusion. [40, 41] The SWCNT network electrodes have been assembled with flow-injection systems to introduce forced convection across the electrode surfaces. [51, 53] The forced convection significantly increases mass transfer towards electrodes and subsequently increases faradaic current, sensitivity, and low limit of detection. Besides, continuous flow of supporting electrolytes washes away reaction product, reduces exposed time of electrodes to the reaction product, and reduces electrodes fouling.

2.4.6 Summary

In section 2.4, I reviews current existing configurations of CNT-based electrodes for electrochemical sensors. These electrodes are generally composed of thousand of CNTs in order to increase response current. However, the averaged inter-distance between neighboring CNTs in these electrodes is much smaller than their diffusion thickness, which results in overlapping of diffusion fields of neighboring CNTs, and therefore significantly reduces mass transfer towards CNTs. Fabrication of these CNT-based electrodes generally requires lengthy preparation time (few hours) to obtain well dispersing CNT solution by acid treatment or strong ultrasonic, or encapsulate CNTs in dielectric materials to reduce background current. The current existing CNT-based electrodes also need binder materials to increase mechanical strength and stability. Overall, utilization of CNT-based electrodes in electrochemical sensors is limited by low mass transfer coefficient as well as high time and material consumption during electrode fabrication processes.

2.5 Carbon nanotube electrodes for thermocells

Energy is an essential constituent of all economic activities. The constant increase of energy consumption has caused several energy crises and led to requirement of developing sustainable energy and recycling waste energy. As one of sustainable energy, low-grade heat (temperature $< 130^{\circ}\text{C}$) has a wide range of sources, *e.g.*, industrial water streams, solar heating, heat engines, and geothermal activities. [9, 157, 158] For many years, low-grade heat is generally collected by using solid-state thermoelectrics [159] and Stirling engines [160]. However, current solid-state thermoelectrics are not cost-effective for collecting energy and are also constrained by physical and material limitations; Stirling engines are limited by high initial cost and low long-term reliability. Besides, they are inflexible and can't be used in heat sources with curved surfaces. Thermocells may become an attractive alternative for harvesting low-grade heat. They convert the low-grade heat energy into electrical energy by using the temperature dependence of electrochemical redox potentials. They have advantages such as simple cell structure, direct thermal-to-electric energy conversion, continuous operation, low maintenance, low cost, and zero carbon emission. [4, 5]

Thermocells are generally composed of two electrodes which contact with hot and cold sources, and electrolyte between them. Thermal separator is placed in electrolyte sometimes. Figure 2.18A shows schematic for a thermocell using $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ as electrolyte. In this thermocell, $\text{Fe}(\text{CN})_6^{3-}$ is reduced to $\text{Fe}(\text{CN})_6^{4-}$ at the cold side, and

Figure 2.18: (A) Schematic of a thermocell using $\text{K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6$ solution as electrolyte. [13] (B) Schematic of over potential represented as resistances. R_{lc} is leading wire and contacting resistance, R_{ct} is charge transfer resistance, R_{mt} is mass transfer resistance, and R_{so} is Ohmic solution resistance. [161]

Fe(CN)_6^{4-} is oxidized to Fe(CN)_6^{3-} at the hot side. The consumption and conversion of both species cause concentration gradient and subsequently cause diffusion. The temperature difference causes density difference and subsequently causes natural convection. Both mass transfer processes maintain concentration equilibrium of these two species in the whole cell and allow the thermocell to work in a continuous way. [13, 162]

The reaction entropy of the redox couple $\text{K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6$ generates a thermoelectrochemical force, which is defined as Seebeck effect. [5, 9, 161] The Seebeck coefficient Se can be expressed as

$$Se = \frac{\partial V}{\partial T} = \frac{\Delta S}{nF}, \quad (2.14)$$

where V is the electrode potential, and ΔS is the reaction entropy for the redox couple $\text{K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6$. At a given temperature difference, the thermocell generally has constant equilibrium potential (open circuit voltage). In order to generate power and energy, the thermocell has to overcome several kinds of over-potentials. These over-potentials are represented as resistances in the circuit (as shown in Figure 2.18B), which are the leading wire and contacting resistance R_{lc} , the solution resistance R_{so} , the electron transfer resistance R_{ct} , and the mass transfer resistance R_{mt} . [161] The sum up of them is internal resistance R_{in} of the thermocell. Both R_{lc} and R_{so} are Ohmic resistances, while R_{ct} and R_{mt} are the resistances from electrode process.

In a thermocell, the performance includes the maximum output power P_{max} and power

conversion efficiency η . [5, 9] They can be respectively estimated by

$$P_{\max} = \frac{V_{\text{oc}}^2}{4R_{\text{in}}}, \quad (2.15)$$

$$\eta = \frac{P_{\max}}{P_{\text{i}}} = \frac{P_{\max}}{A_{\text{c}}\kappa(\Delta T/d_{\text{e}})}, \quad (2.16)$$

with

$$V_{\text{oc}} = Se\Delta T, \quad (2.17)$$

where V_{oc} is the open circuit voltage, P_{i} is the input thermal power, A_{c} is the cross-section area of thermocells, κ is the thermal conductivity of electrolytes, d_{e} is the closest distance between two electrodes, and ΔT is the temperature difference between two electrodes. By combining Equations 2.15–2.17, I can obtain

$$\eta = \frac{\Delta T Se^2 d_{\text{e}}}{4R_{\text{in}} A_{\text{c}} \kappa}. \quad (2.18)$$

It can be observed from Equations 2.15 and 2.18 that $P_{\max}$ and η are affected by type of electrolyte (Se and κ), dimension of thermocell (A_{c} and d_{e}), and internal resistance R_{in} . The aqueous $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ electrolyte are widely used because this redox couple has Seebeck coefficient ($> 1 \text{ mV} \cdot \text{K}^{-1}$) and can yield high exchange current. [5, 9] The thermal conductivity can be further reduced by using thermal separator to reduce the heat exchange between hot and cold sides. [15] The inter-distance between two electrodes affects the mass transfer path, the solution resistance, and heat exchange between hot and cold electrodes. Generally, reducing d_{e} can increase $P_{\max}$ and reduce η . [9, 10] The internal resistance R_{in} is a complex item and affected by several factors such as the the electrolyte type, the thermocell geometry dimension, electrode material, and so on.

In order to increase $P_{\max}$ and η , many efforts have been contributed to reduce R_{in} by designing electrodes. Generally, platinum with high electrochemical activity is used as electrode material to obtain reasonable efficiency. However, due to its high price and limited efficiency, platinum electrodes are gradually replaced by CNTs electrodes. CNTs electrodes have advantages of high electrochemical activity, low price, high surface area, and ability to carry high current density. In the following section, I introduces thermocells using CNT-based electrodes, and emphasizes factors that may affect R_{in} .

The leading wire and contacting resistance R_{lc} consists of resistance of leading wire and CNTs, and resistance between leading wire and CNTs. This resistance is negligible for metal electrodes. However, it may not be the case for CNT electrodes. CNT bucky papers, which are prepared by vacuum infiltration, have laminate structure. In the case

that CNT bucky papers are clamped against current collectors, there is noncontinuous interface between them. Both of these two structures result in high R_{lc} . [9,14] The contact resistance can be reduced by growing CNTs array or coating CNT-PVDF solution on stainless steel substrate directly. [9,14] CNT aerogel electrodes are prepared by spinning CNT sheets on metal frames. Electrons generated at CNTs have to transfer through interconnects between CNTs to be collected by the metal frames. Compressing the electrodes can reduce pore size and porosity, and subsequently reduce R_{lc} and increase R_{mt} . [12]

The electron transfer resistance R_{ct} is the resistance of electron transfer across the interface between electrodes and electrolytes. It can be reduced by both increasing electrochemical activity and effective surface area of electrodes. The electrochemical activity of CNTs towards $K_3Fe(CN)_6/K_4Fe(CN)_6$ have been improved by removing amorphous carbons, inducing defects and doping, and decorating platinum nano-particles. Besides, these methods increase wettability of CNTs, facilitate infiltration of electrolytes into CNT electrodes, and increase effective surface area of the electrodes. [11,12,14] The effective surface area of electrodes can be increased by creating porous structure. For example, using CNT bucky papers [9], aerogel CNT sheets [12], CNT foams [15], and CNT graphene composites [13]. For these porous electrodes, it is crucial to control pore size and alignment of CNTs to facilitate mass transfer into the electrodes. Otherwise, inner parts of the electrodes can't be supplied with fresh electrolyte and may stop participating in reactions. [9,12,13,15]

The mass transfer resistance R_{mt} is the resistance of moving species from bulk solutions to electrode surfaces. It can be reduced by increasing both effective surface area and mass transfer coefficient. The effective surface area can be increased by the same method introduced in the previous paragraph. [9,12,13,15] The mass transfer coefficient can be increased by introducing forced convection across the electrodes. [9,12] By assembling two CNT electrodes on opposite walls of a channel, and pumping hot and cold electrolytes through the channel, fresh electrolytes are provided to the electrodes and reaction products are swept away. However, this method increases energy input and makes the design of thermocells complicated.

In section 2.5, I reviews CNT-based electrodes used in thermocells. Fabrication of CNT-based electrodes for thermocells follow the similar processes of fabricating CNT-based electrodes for electrochemical sensors. They therefore suffer from the problem of high time and material consumption during the electrode fabrication processes. The porous CNT-based electrodes are generally used to increase expose surface area and mass transfer coefficient, and subsequently reduce R_{mt} . However, the porosity inevitably

increases R_{ic} . Utilization of CNT-based electrodes in thermocells is limited by high time and material consumption during electrode fabrication processes, low mass transfer coefficient and low electrical conductivity.

Chapter 3

Experimental Details

In this chapter, I presents experimental details: growth of multi-walled carbon nanotube arrays; fabrication of multi-walled carbon nanotube electrodes, which are vertically aligned multi-walled carbon nanotube nanoelectrode arrays (VCNs), multi-walled carbon nanotube band electrodes (CBEs), and multi-walled carbon nanotube sheet electrodes on insulating polyimide-glass substrates (CSEs), stainless steel sheets (CSSEs), and stainless steel meshes (CSMEs); fabrication of Polydimethylsiloxane (PDMS) Y-channel; electrochemical experiments, including experimental setups and electrochemical methods; thermocells, including fabrication and measurement; and characterization techniques.

3.1 Growth of multi-walled carbon nanotube arrays

There are two kinds of multi-walled carbon nanotube (MWCNT) arrays used in this thesis: MWCNT arrays with controlled pattern and dimension, and spinnable MWCNT arrays. The growth of MWCNT arrays includes two stages.

Preparation of catalysts. Same kinds of catalyst is used to grow patterned MWCNT arrays and spinnable MWCNT arrays, while the former one require the usage of photolithography to pattern the catalyst layer, which includes several steps.

In step 1, a Si/SiO₂ wafer goes through several processes: cleaned by rinsing with acetone, isopropanol, and deionized water, dried by blowing N₂ gas, and baked at 110°C for 15 minutes on a hot plate.

In step 2, the wafer is coated with a layer of hexamethyldisilazane (HMDS) to increase its adhesion with the photoresist (AZ-7220, MicroChemicals). The Si atoms in HMDS are bonded to oxygen atoms on the wafer, then the methyl groups in HMDS form a hydrophobic layer, which improves the wettability of the non-polar photoresist.

In step 3, the photoresist is spin-coated at a speed of 5000 rpm for 30 s on the wafer to obtain a thickness of $1.4 \sim 1.5 \mu\text{m}$.

In step 4, the photoresist is soft-baked at 110°C for 90 s on a hot plate. This step reduces the remaining solvent content to avoid mask contamination and improve adhesion. The photoresist is further left at room temperature for ≈ 5 minutes to allow rehydration.

In step 5, the photoresist is selectively exposed to UV light (352 nm) with a power of $10.2 \text{ mW} \cdot \text{cm}^{-2}$ for 3.3 s using a mask aligner (Suss MA6, Karl Suss). The exposed photoresist contains indene carboxylic acids, which make them soluble in aqueous alkaline solutions. During this step, the UV light is selectively blocked by the mask and the pattern on the mask is transferred to the photoresist.

In step 6, the photoresist is baked at 110°C for 60 s on a hot plate. The post exposure baking near the softening point of the photoresist reduces the mechanical stress formed in the previous two steps.

In step 7, the photoresist is developed in a aqueous developer (AZ 300 MIF, Mico-Chemicals). Here, the exposed photoresist is washed away while the un-exposed photoresist remains on the wafer. The patterned photoresist is then rinsed with deionized water and dried by blowing N_2 gas.

In step 8, the patterned wafer is deposited by a buffering layer of 25 nm thick Al_2O_3 , followed by a catalyst layer of 0.8 nm thick Fe using magnetic sputtering. The thickness of the metal layers is varied by controlling sputtering power and duration. The photoresist and the catalyst on top are washed away by acetone in an ultrasonic bath for 5 minutes, leaving here patterned catalyst layer. The un-patterned catalyst is obtained by depositing Al_2O_3 and Fe layers on plane wafers using the same deposition procedure.

Thermal chemical vapor deposition. The wafer with catalyst is cut into multiple small pieces ($\approx 1 \times 1 \text{ cm}$), which are loaded into a quartz tube furnace at room temperature. The quartz tube is flushed with Argon gas with a flow rate of 180 sccm (standard cubic centimeters per minute) to evacuate the residue air and check the leakage of the whole system. After that, thermal chemical vapor deposition (TCVD) is used to grow MWCNT arrays. The schematics of TCVD process and growth of MWCNT arrays are illustrated in Figure 3.1A and B, respectively. The TCVD process consists of four steps: ramping, annealing, growth and cooling.

In the ramping step, the tube furnace is heated from 20 to 750°C in ≈ 10 minutes with flushing of buffering gas including Ar (180 sccm) and H_2 (20 sccm) through the tube.

Figure 3.1: (A) Schematic of growth process of CNT arrays using TCVD with four steps. (B) Schematic of growth of MWCNT array.

In the annealing step, the Fe catalyst layer is broken to form Fe nanoparticles (Figure 3.1B) under the effect of high temperature (750 °C) and reducing gas (20 sccm H_2 in 180 sccm Ar). As H_2 is introduced at the ramping step, the Fe nanoparticles are formed when the temperature is suitable. This is to facilitate formation of dense Fe nanoparticles. The size and density of the Fe nanoparticles are also affected by the gas flow rate, the temperature and the treating duration.

In the growth step, the buffering gas is stopped, and the carbon source gas consisting of C_2H_4 (58 sccm) and Ar (142 sccm) is introduced into the quartz tube. In the temperature of 750 °C, C_2H_4 is decomposed to carbon atoms, which are then deposited on Fe nanoparticles to form MWCNTs (Figure 3.1B). The height of the array can be controlled by adjusting the growth time. However, the growth speed of MWCNTs reduced with time due to the loss of catalytic activity of Fe nanoparticles and the difficulty of access

Figure 3.2: Schematic of fabricating VCNs. 1. A VCA is transferred to a copper wire. 2. The VCA is mounted in epoxy. 3. The VCA encapsulated in epoxy block is ground and polished. Part of VCN is zoomed in to observe structure of VCN. Black lines represent CNTs.

of carbon atoms to Fe nanoparticles. Generally, the height of the array is $\approx 400 \mu\text{m}$ for 7 minutes of growth step.

In the cooling step, the furnace tube is cooled down to 400°C with the protection of Ar (180 sccm). The tube is opened to take out the MWCNT arrays and finish the growth process.

3.2 Fabrication of multi-walled carbon nanotube electrodes

This section introduces fabrication of several kinds of MWCNT electrodes: vertically aligned MWCNT nanoelectrode arrays (VCNs), MWCNT band electrodes (CBEs), and MWCNT sheet electrodes (CSEs).

3.2.1 Vertically aligned multi-walled carbon nanotube nanoelectrode arrays

As shown in Figure 3.2, VCNs are fabricated by encapsulating vertically aligned multi-walled carbon nanotube arrays (VCAs) in epoxy and exposing tips of MWCNTs. The fabrication process includes three steps: transferring, mounting, and opening.

Transferring. In the transferring step, a VCA grown on the SiO_2/Si substrate is transferred to one end of a copper wire with silver epoxy (Chemtronics CW2460). The substrate including VCAs is fixed, while the copper wire is attached to a three dimension translational stage. The movement of the copper wire is observed using a microscope. After the VCA is transferred, the silver epoxy is left at room temperature for one day to cure. This curing process prevents silver epoxy from wetting through the whole VCAs.

Mounting. In the mounting step, the VCA is mounted in epoxy. The VCA to-

Table 3.1: Parameters of grinding and polishing.

Step	Cloth	Suspension	Force (N)	Speed (rpm)	Direction	Duration (minutes)
1	P800 SiC sand paper	no	15	300	same	depend
2	MD-Largo	DiaPro Allegro/Largo 9 μm	15	150	same	5
3	MD-Dac	DiaPro Mol R 3 μm	20	150	same	5
4	MD-Nap-T	DiaPro Nap 1 μm	10	150	same	1
5	MD-Dac	OP-S	5	150	counter	1
6	MD-Chem	OP-S	5	150	counter	0.5

gether with the copper wire are placed in a 30 mm diameter polypropylene mounting cup (Struers), which is subsequently filled with epoxy (Epolam 5015 resin and 5015 hardener, Axson Technologies) The Epolam 5015 resin is a mixture of Bisphenol F and Bisphenol A resins. The Epolam 5015 hardener consists of isophoronediamine and polyoxypropylene-diamine. The resin can react with hardener and become cross-linked, which is accelerated by heating. The mixture of 100 part resin and 30 part hardener by weight has low viscosity ($210 \text{ mPa} \cdot \text{s}$) and long pot life (135 minutes). The infiltration of epoxy into VCA is facilitated by degassing at a pressure of 3 torr for 2 hours. The epoxy is cured at room temperature for 24 hours, and then in an oven at 90°C for 16 hours.

Opening. In the opening step, the epoxy block is ground and polished to obtain a mirror surface at the VCNs. The epoxy block is detached from the mounting cup, and then is ground by P800 SiC sand papers (PRESI) to remove excessive epoxy to expose MWCNT tips. The exposure of MWCNT tips is confirmed by measuring the electrical resistance between the MWCNT tips and the copper wire. This method can also be used to check the electrical connection between the VCA and the copper wire. The epoxy block is further polished to obtain a mirror finish, which reduce the protrusion of MWCNTs above the epoxy. The grinding and polishing steps are carried out automatically on a grinding/polishing machine (Tegramin-25) to ensure reproducible surface finish. The parameters of the grinding and polishing process are shown in Table 3.1. The VCNs are then cleaned in isopropanol for 2 minutes and Milli-Q water for 3 minutes by an ultrasonic bath (Alstron), and treated with air plasma at 6.8 W, 300 mtorr for 5 minutes (Harrick Plasma). The used parameters are optimized already. The detail will be introduced in the next chapter.

3.2.2 Multi-walled carbon nanotube band electrodes

As shown in Figure 3.3, CBEs are fabricated by encapsulating MWCNT sheets in epoxy and exposing only tips of MWCNTs. Fabrication of CBEs is similar to that of VCNs except that CBEs are fabricated from MWCNT sheets while VCNs are from VCAs. The fabrication process includes two stages: fabrication of MWCNT-epoxy sheets and

Figure 3.3: Schematic of fabricating CBEs. (A) Fabrication of MWCNT-Epoxy sheets. 1. MWCNT sheet is drawn out from a spinnable MWCNT array and laid on a PTFE plate. 2. Epoxy is deposited on the MWCNT sheet. 3. The other PTFE is clamped against the MWCNT sheet to squeeze excessive epoxy and make MWCNT-Epoxy sheet. (B) Fabrication of CBEs from MWCNT-epoxy sheets. MWCNT-Epoxy sheets are mounted in epoxy and cut into slices to form CBEs.

fabrication of CBEs from the MWCNT-epoxy sheets.

Fabrication of MWCNT-epoxy sheets. As shown in Figure 3.3A, MWCNT-epoxy sheets are prepared by several steps.

In step 1, MWCNT sheet is drawn out from a spinnable MWCNT array and laid on PTFE plate 1. Subsequently, acetone is used to wet the MWCNT sheet and the substrate. Evaporation of acetone both reduces the distance and increases adhesion between MWCNT sheet and the substrate. Without wetting by acetone, the MWCNT sheet is lifted off easily and bundled together during infiltration of epoxy.

In step 2, epoxy (Epilam 5015 resin and 5015 hardener, Axson Technologies) is deposited on the MWCNT sheet and infiltrates into the sheet. The infiltration process is assisted by degassing in a vacuum oven for half an hour at 40 °C. A suitable temperature is crucial to reduce viscosity of the epoxy and avoid cross-link in the epoxy.

In step 3, PTFE plate 2 is clamped against the MWCNT sheet to squeeze excessive epoxy. Spacers with desired thickness are used between two plates to control the thickness of MWCNT-Epoxy sheet. The MWCNT-epoxy sheet is cured at room temperature for 24 hours and then at 80°C in an oven for 16 hours. After curing, the MWCNT-epoxy sheet is detached easily from the PTFE plates.

Fabrication of CBEs from the MWCNT-epoxy sheets. As shown in Figure 3.3B, CBEs are prepared from the MWCNT-epoxy sheets by several steps.

In step 1, single or multiple MWCNT-epoxy sheets are mounted vertically in epoxy to form a MWCNT-epoxy cylinder using a polypropylene mounting cup (Struers). The curing process is the same as that in the fabrication of MWCNT-epoxy sheet.

In step 2, the cured MWCNT-epoxy cylinder is cut into slices to expose MWCNT tips using a diamond cutter; each slice is a CBE.

In step 3, CBEs are ground and polished mechanically to obtain a mirror finish at one surface, which is the active side of the electrochemical sensor. The other site is connected with a leading wire using silver epoxy (Chemtronics, CW2460) after cleaning. The parameters for grinding and polishing CBEs are shown in Table 3.1.

In step 4, CBEs are cleaned in ethanol for 2 minutes and Milli-Q water for 3 minutes by an ultrasonic bath (Alstron), and treated with air plasma at 18 W, 300 mtorr for 5 minutes (Harrick Plasma).

3.2.3 Multi-walled carbon nanotube sheet electrodes

CSEs are prepared by laying pristine MWCNT sheets on polyimide-glass substrates. The polyimide is hydrophobic, insulating and chemically inert. The hydrophobicity increases adhesion between CNTs and substrates, while the insulating and chemically inert properties prevent background current from substrates during electrochemical detection. Figure 3.4 shows detail of fabrication process. A MWCNT sheet is drawn out from a spinnable MWCNT array and laid on polyimide-glass substrates, which are attached to a rotating wheel. The MWCNT sheet can be manually controlled to vary width and layer number. Acetone is then used to wet the MWCNT sheets. After acetone is evaporated, the MWCNT sheets attach firmly on the substrates, even after rinsing with water. Each substrate with MWCNT sheet on top is a electrode. For each electrode, one end of the MWCNT sheet is connected to a metal wire using silver epoxy (Chemtronics, CW2460), which is then connected to a potentiostat during electrochemical experiment, and the other end of the sheet is covered by the silver epoxy, which facilitates resistance measurement of the MWCNT sheets.

Figure 3.4: Schematic of fabricating CSEs. A MWCNT sheet is drawn out from a spinnable MWCNT array and laid on polyimide-glass substrates, which are attached to a rotating wheel.

Using the same setup and procedure, the MWCNT sheets are laid on stainless steel sheets (SSSs) and stainless steel meshes (SSMs) to respectively form electrodes, CSSEs and CSMEs, which are used in thermocells.

3.3 Fabrication of PDMS Y-channels

Photolithography is used to fabricate SU8 (SU8-3050, MicroChem) molds for casting PDMS Y-channels. SU8 is a negative photoresist composed of Bishpenol A Novolac epoxy, which is dissolvable in organic solvent. Unlike positive photoresist, negative photoresist becomes stable in organic solvent after exposing to UV light. The fabrication process includes several steps. The first two steps are the same as those used in patterning catalyst layer in Section 3.1.

In step 3, the negative photoresist is spin-coated on the wafer. In this step, photoresist is first spreaded at a speed of 500 rpm for 10 s, and followed by controlling thickness. The thickness of photoresist is controlled by varying rotation speed and duration. For example, I obtains a thickness of $62\text{ }\mu\text{m}$ by spin-coating at 1500 rpm for 30 s. The thickness is measured by a profilometer (Dektak 3st profilometer, Sitek).

In step 4, the photoresist is soft-baked at 95°C for 45 minutes on a hot plate for the solvent to be completely evaporated. The photoresist is then left at room temperature overnight to allow rehydration.

In step 5, the photoresist is exposed to 352 nm UV light on a Suss MA1006 mask aligner (Karl Suss) with a power of $10.2\text{ mW} \cdot \text{s}^{-1}$ for 25 s. The photoresist exposed to UV light becomes cross-linked and remains stable during subsequent developing step, while the remainders are soluble in developer.

In step 6, the photoresist is post baked at 65°C for 1 minutes, and at 95°C for 5 minutes. The post baked process helps to complete cross-linking of exposed SU8.

In step 7, the photoeresist un-exposed to UV light is washed away in developer with assistance of agitation. The developed SU8 is then rinsed with isopropanol to remove residue developer, with deionized water to remove residue isopropanol, and finally dried by N₂ gas to achieve SU8 mold.

In step 8, the wafer with SU8 mold is coated by silane to increase hydrophobicity and reduce adhesion between the mold and PDMS. The silane coating is achieved by leaving the wafer in a sealed petri-dish with few drops of silane, heating in an oven at 100°C for 30 minutes.

In step 9, the PDMS with 5:1 (base : curing agent) weight ratio is poured on the coated wafer, degassed to remove gas bubbles, and cured at 80°C for 3 hours in an oven. After soft-lithography, the PDMS Y-channels have the same size of the SU8 mold, which is 62 μm in depth, 500 μm in width, and 20 mm in length.

3.4 Electrochemical experiments

3.4.1 Experimental Setups

Electrochemical experiments are performed on a potentiostat (SP-200, Bio-Logic Science Instruments) with low current mode in a three electrode system: an Ag/AgCl (in saturated KCl aqueous solution) reference electrode, a platinum counter electrode, and a MWCNT-based electrode as working electrode. All the potential is quoted versus reference electrode if without further description. In order to reduce Ohmic resistance and subsequently potential drop between the reference electrode and the working electrode, supporting electrolyte is added in all solutions: 1 M KCl for K₃Fe(CN)₆ solution and 1× phosphate buffered saline (PBS) for dopamine solution.

Four kinds of electrochemical experiment care carried out under two conditions: cyclic voltammetry and electrochemical impedance spectroscopy (EIS) in stationary conditions, and linear sweep voltammetry and chronoamperometry in hydrodynamic conditions. Figure 3.5A shows the experimental setup used in stationary conditions. A PDMS well with a volume of 1 mL is used as electrochemical cell and clamped against a working electrode (*e.g.*, a VCN in this setup) using two acrylic plates. The reference and counter electrodes (not shown here) are placed in the cell to form a three electrode system with the VCN at the bottom. Figure 3.5B shows the experimental setup used in hydrodynamic conditions. The PDMS Y-channel is clamped against the working electrode (*e.g.*, a VCN

Figure 3.5: Schematic of experimental setups used (A) in stationary conditions and (B) in hydrodynamic conditions.

in this setup) between two acrylic plates. The VCN is positioned in the middle of the Y-channel to allow a fully developing laminar flow across the electrode. Two inlets of the channel are connected to two syringes (not shown here): one with supporting electrolytes, and the other with analyte solutions. These two syringes are driven individually by two syringe pumps (KD Scientific). The outlet is connected by a PTFE tubing (0.56 mm inner diameter) to a reservoir (not shown here), which is right on top of the acrylic plate. The reference and counter electrodes in the reservoir and the VCN in the channel form a three electrodes system. There is not any leakage in the microfluidic system with flow rate up to $3000 \mu\text{L} \cdot \text{min}^{-1}$.

3.4.2 Electrochemical methods

Cyclic voltammetry is generally to characterize electrochemical responses of CNT-based electrodes in stationary conditions. The scanning potential window is $[-0.2 \sim 0.6 \text{ V}]$ in KCl and $\text{K}_3\text{Fe}(\text{CN})_6$ solution, and $[-0.2 \sim 0.7 \text{ V}]$ in PBS and dopamine solution; the potential scan rate is generally $50 \text{ mV} \cdot \text{s}^{-1}$ if without further description. Each measurement is cycled for ≥ 4 runs. Cyclic voltammetry is also used to clean and activate working electrodes by running in supporting electrolytes for 20 cycles at a scan rate of $200 \text{ mV} \cdot \text{s}^{-1}$.

Linear sweep voltammetry is generally used to study effects of forced convection on electrochemical responses of CNT-based electrodes. The forced convection is controlled by varying flow rate. Linear sweep voltammetry is carried out and repeated at least

three times at each flow rate. The scanning potential windows are the same as these used in cyclic voltammetry. The scan rate is fixed at $50 \text{ mV} \cdot \text{s}^{-1}$. Based on study of linear sweep voltammetry, suitable flow rate and applied potential on working electrodes are chose and used in chronoamperometry.

Chronoamperometry is used in channel flow voltammetry to detect analytes with varying concentration. The flow rate is $1000 \mu\text{L} \cdot \text{min}^{-1}$ when using VCNs and CSEs as working electrodes, and $10 \mu\text{L} \cdot \text{min}^{-1}$ when using CBEs as working electrodes. The applied potential on the working electrode is 0 V for detecting $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.4 V for detecting dopamine. At the beginning of each experiment, the supporting electrolyte is pumped into the channel for 5 minutes to stabilize the background current. Subsequently, the supporting electrolyte and the analyte solution containing supporting electrolyte are pumped in from two inlets alternatively. The pumping is repeated ≥ 4 times for each concentration. The pumping volume is $400 \mu\text{L}$ when using VCNs and CSEs as working electrodes, and $4 \mu\text{L}$ when using CBEs as working electrodes.

Electrochemical impedance spectroscopy is generally used to characterize electrode processes in stationary conditions. EIS is recorded in 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl solution, at 300 mV dc potential with 10 mV ac potential, and at frequency ranging between 100 kHz and 0.1 Hz.

3.5 Thermocells

3.5.1 Fabrication

Figure 3.6 shows schematic of a home-made thermocell. The thermocell consists of two peltier units (55.6 W, Multicomp), two thermocouples (K Type, 0.075 mm diameter, RS), two electrodes, two sheets of rubber, and an acrylic chamber. They are mechanically clamped together. The configuration of thermocell is symmetric along the hole for filling electrolytes. The peltier units are used to heat up or cool down electrolytes. The thermocouples are clamped between the peltier units and the electrodes to measure the temperature of the electrodes. The rubber sheets are used to prevent leakage between electrodes and acrylic chamber, and their through holes define the exposed areas of electrodes to electrolytes. The acrylic chamber is used as cell for electrolytes.

Acrylic is used to fabricate the chamber as it is transparent, chemically inert and has low thermal conductivity ($0.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). The transparency is useful to observe the solution inside of the chamber and to remove bubbles as electrolyte is supplied to the chamber. The chemical stability upon exposing to $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ maintains

Figure 3.6: Schematic of a home-made thermocell.

stability of the thermocell and reduces experiment error. The low thermal conductivity prevents heat exchange between electrolyte and environment air. There are two kinds of acrylic chambers used in this thesis. One is a cylinder with 44 mm in length, 45 mm in diameter, and a 5.5 mm diameter through hole. The other one is a square plate with 13.5 mm in thickness, 45 mm in length, and a 11.5 mm diameter through hole.

3.5.2 Measurement

Temperature at both electrodes and discharging voltage of the thermocell are measured. Thermocouples are connected to a two-channel thermometer (RS-1314), which monitors the temperature of the electrodes continuously. After the temperature gradient is established for 10 minutes, the thermocell discharge at a variable resistor (TENMA 72-7270) continuously. A multimeter (DMM4050, Tektronix) is used to measure corresponding voltage on the variable resistor. Both the voltage and resistance are then used to calculate internal resistance and output power.

3.6 Characterization techniques

Scanning Electron Microscopy (SEM) is a microscopy technique which uses electron beam to interact with specimen surface to generate a number of different signals. For

example, secondary and backscattered electrons can provide information about surface morphology and element distribution in samples; x -radiation can yield both qualitative and quantitative elemental information. [163] Field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) is used to observe surface morphology of specimens.

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. Depending on composition or thickness of the specimen, absorption of electrons is different and subsequently generate different contrast on TEM images. [164] High resolution transmission electron microscopy (HRTEM, JEOL 2010) is used to observe structure of MWCNTs and measure their diameter.

Raman spectroscopy is a spectroscopic technique in which laser light interacts with molecular vibrations, photons or other excitations in the material, and resulting in the change of the laser photons energy. The change of energy provides information of defects and crystalline structure. [165] Raman spectroscopy is widely used to characterize carbon material. The most important feature of the spectrum for MWCNTs is the G band and D band, locating at around 1580 cm^{-1} and 1350 cm^{-1} , respectively. The G band is a doubly degenerated phonon Raman active mode for C-C bonds, while the D band is localized at imperfect lattice structures such as edges and defects. The intensity ratio between the D-band and the G-band I_D/I_G is used to quantify both the defects in MWCNTs and amorphous carbon. [166–170] Raman spectroscopy (Renishaw inVia Raman Microscope) with a 514 nm laser and a $50\times$ objective is used to characterize MWCNTs.

Chapter 4

Multi-walled Carbon Nanotube Epoxy Electrodes for Electrochemical Sensors

To address the challenge of achieving high mass transfer coefficient at CNT-based electrodes, this chapter presents development of two kinds of MWCNT-epoxy electrodes: vertically aligned multi-walled carbon nanotube nanoelectrode arrays (VCNs) and multi-walled carbon nanotube band electrodes (CBEs). VCNs are promising electrodes used for electrochemical detections, and their electrochemical responses are generally limited by the mass transfer process. I optimizes the fabrication process of VCNs, and systematically investigates effects of array diameter and forced convection on the electrochemical responses of VCNs. Based on the study of VCNs, I proposes a new configuration of MWCNT-epoxy electrodes, CBEs, and systematically investigates their electrochemical responses in both stationary and hydrodynamic conditions.

4.1 Vertically aligned multi-walled carbon nanotube nanoelectrode arrays

4.1.1 Optimization of fabrication process

The fabrication process is optimized to achieve VCNs with low background current, high electrochemical activity, and high repeatability. The fabrication process of VCNs is introduced in Chapter 3. Briefly, the VCNs is prepared by encapsulating VCAs in epoxy with the assistance of vacuum degassing, exposing tips of CNTs by grinding and

polishing, and cleaning by air plasma treatment. The optimized parameters include the degassing pressure P_d , the degassing duration t_d , the weight ratio of epoxy resin and hardener r_m , the curing temperature T_c , the curing process, and the plasma exposing duration t_p . As introduced in Chapter 2, cyclic voltammetry is performed in 1 M KCl and 1 mM $K_3Fe(CN)_6$ to respectively obtain background current I_b and peak potential difference ΔE_p . To compare electrodes with different surface area, I_b is divided by surface area A to obtain background current density i_b . Electrochemical activity is estimated from ΔE_p by using Nicholson's method. Repeatability is assessed based on standard deviation of i_b and ΔE_p obtained from ≥ 3 electrodes.

Firstly I investigate effect of degassing on performances of VCNs. Degassing is used to remove air bubble trapped in VCAs and facilitate infiltration of epoxy into VCAs. This step is necessary to completely cover sidewall of MWCNTs and fabricate repeatable VCNs. [34] The optimized parameters include the degassing pressure P_d , the degassing duration t_d , and the viscosity of epoxy. Here, the viscosity is changed by varying r_m . In order to investigate the effects of these three parameters, I use same grinding, polishing, and cleaning procedure (without air plasma treatment), varies P_d with conditions $r_m = 30\%$ and $t_d = 2$ h, varies t_d with conditions $r_m = 30\%$ and $P_d = 3$ torrs, and varies r_m with conditions $P_d = 20$ mtorrs and $t_d = 2$ h. However, $\Delta E_p > 400$ mV at all investigated conditions, suggesting low electrochemical activity. As a comparison, $\Delta E_p = 59$ mV in a reversible system. This result is consistent with that in Ref [34] while contradictory to that in Ref [33]. As $K_3Fe(CN)_6$ is surface-sensitive species [89], VCNs fabricated by using different kinds of epoxy and procedures may have different surface properties and subsequently generate different electrochemical activity towards $K_3Fe(CN)_6$.

Only two values of P_d are used: 20 mtorr, which is the lowest pressure of our pump can provide, and 3 torr, which is the vapor pressure of the epoxy. When $P_d < 3$ torr, volatile chemicals in the mixture evaporate and generate bubbles, which may change composition of the mixture and mechanical properties of the cured epoxy. However, P_d has a slight effect on i_b : while P_d is reduced from 3 torr to 20 mtorr, i_b varies from $0.22 \pm 0.07 \text{ mA} \cdot \text{m}^{-2}$ to $0.30 \pm 0.14 \text{ mA} \cdot \text{m}^{-2}$ correspondingly. Degassing at $P_d = 3$ torr provides a slightly better result. Figure 4.1A shows that t_p varying from 0.5 h to 3 h has a slight effect on i_b and repeatability, suggesting that degassing for half an hour is enough to completely remove air bubbles. Figure 4.1B shows the dependence of i_b on r_m . Using the mixture with $r_m = 40\%$ causes a tremendous increase in i_b and decrease of the repeatability compared with using other two mixtures ($r_m = 30\%$ and $r_m = 35\%$). Changing r_m affect both viscosity and mechanical properties of cured epoxy. The mechanical properties such as hardness affect grinding and polishing results, eventually

Figure 4.1: Dependence of background current density i_b on (A) degassing duration t_d and (B) mixing ratio of the epoxy resin and hardener r_m .

the protrusion of MWCNTs above epoxy. Based on this study, $P_d = 3$ torrs, $r_m = 30\%$, and $t_d = 2$ h are used for fabricating VCNs.

Both curing temperature and curing process affect the cross-link density of epoxy. At low curing temperature, the cross linking process occurs slowly resulting in a more expanded network structure. As the structure forms, the mobility of un-reacted group in the structure gradually decreases and they are impeded from migrating to the remaining open reactive sites. At sufficiently high curing temperature, sufficient kinetic energy is provided to initiate chemical reactions and move un-reacted groups to full network. However, curing at high temperature causes higher stress compared with that at low temperature. A good compromise is the stepped or staged curing process. In this method, epoxy is left at low temperature to slowly gel and build-up some structures, followed by curing at high temperature to achieve high density cross-links. The cross-link density affects mechanical and physical properties of the cured epoxy such as hardness, modulus, glass transition temperature and so on. As MWCNTs are harder and stronger than epoxy, MWCNTs always protrude out from the epoxy after polishing, and cause high i_b . Increasing hardness of epoxy may reduce the protrusion and subsequently reduce i_b . The curing temperature may affect the interaction between oxygen-containing functional groups on MWCNT sidewall and epoxy groups, and subsequently affect the density of electronic state and electrochemical properties of MWCNTs.

Secondly I investigates effects of curing temperature and curing process on performances of VCNs. The curing temperature T_c ranges from 80°C to 135°C. The curing processes include P1, P2, and P3. In process 1 (P1), the epoxy is left at room temperature for 24 hours, followed by curing in an oven at T_c for 16 hours. In process 2 (P2), the epoxy is cured in an oven at T_c for 16 hours. In process 3 (P3), the epoxy is left in an oven at 40°C for 24 hours, followed by curing at T_c for 16 hours. The recommended T_c

Figure 4.2: Dependence of (A) background current density i_b and (B) peak potential difference ΔE_p on curing temperature T_c and curing process. T_c is 80, 90, 100, 115, and 135 °C. The data obtained from P2 and P3 are offset respectively -5 °C and $+5$ °C for easy comparison.

Figure 4.3: Dependence of (A) background current density i_b and (B) potential difference ΔE_p on plasma exposing duration t_p .

and curing process from the manufacturing company (Axson Technologies) is 80 °C and P1, respectively. Figure 4.2A shows the variation of i_b on T_c and curing processes. The i_b has slight dependence on both T_c and curing process (except at 115 °C using P1), and has the lowest value at 90 °C using P1. Figure 4.2B shows the variation of ΔE_p on T_c and curing processes. The ΔE_p has the minimum value at 90 °C using P1. However, this value ($\Delta E_p = 224.7 \pm 50.5$ mV) is still much higher than the ideal value (59 mV). Based on this study, epoxy is cured at 90 °C using P1 during fabricating VCNs.

Finally I investigates the effect of surface properties on the performance of VCNs. The VCNs are cleaned in ethanol and isopropanol using an ultrasonic bath with duration up to 10 minutes. However, these procedures do not affect the performance of VCNs. The VCNs are then exposed to air plasma to: remove impurities induced during fabrication, induce oxygen-containing functional groups on MWCNTs, and create defects at the sidewall of MWCNTs. The air plasma is generated at power of 18 W and pressure of 300 mtorr. In Figure 4.3A and B, I shows the dependence of i_b and ΔE_p on plasma exposing duration t_p , respectively. The i_b increases sharply with t_p up to 3 min, then increases

Figure 4.4: (A) SEM image of several VCAs with 100 μm in diameter. Inset: TEM image of a MWCNT. (B) Optical image of a epoxy cylinder containing 3 VCN with diameter of 1 mm. (C) Optical image and (D) SEM image of a 100 μm diameter VCN after being polished from top-view. The dash line indicates the surface area A of the VCN.

slowly and becomes almost saturated at $t_p = 10$ min. The ΔE_p reduces gradually from 224.7 ± 50.5 mV at pristine VCNs to 119.5 ± 28.3 mV at $t_p = 10$ min. Estimating from Equation 2.7, standard heterogenous rate constant k_o increases from $6.0 \pm 3.7 \mu\text{m} \cdot \text{s}^{-1}$ to $28.3 \pm 15.9 \mu\text{m} \cdot \text{s}^{-1}$ correspondingly. Based on this study, air plasma treatment for 10 minutes is used as the last step of fabricating VCNs.

Based on these studies, VCNs are fabricated by the process using following optimized parameters: $P_d = 3$ torrs, $r_m = 30\%$, $t_d = 2$ h, $T_c = 90^\circ\text{C}$, P1, and $t_p = 10$ minutes.

4.1.2 Morphology and electrochemical characterization

Figure 4.4A shows a representative SEM image of several vertically-aligned carbon nanotube arrays (VCAs), each array has diameter $\approx 100 \mu\text{m}$ and length ≈ 1 mm. The MWCNTs in these arrays have outer diameter ≈ 10 nm (see inset of Figure 4.4A). Figure 4.4B shows an optical image of a epoxy cylinder containing 3 VCNs. Each VCN has a diameter of 1 mm. Figure 4.4C and D show a optical image and a SEM image of a VCN after polishing from top-view, respectively. From the optical image, I measures the diameter of VCN, which is indicated by a dash circle. Generally, the real diameters of

Figure 4.5: (A) Cyclic voltammograms of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl solution on a 400 μm diameter VCN, recorded at scan rate v 20-500 $\text{mV}\cdot\text{s}^{-1}$. (B) Dependence of peak currents $I_{s,p}$ on the square root of the scan rate $v^{1/2}$. The straight lines are fitted from experimental data.

VCNs are slightly smaller than the desired value due to condensation of the array during epoxy infiltration. For example, as the one shown in Figure 4.4C, the real value is 92 μm , while the desired value is 100 μm . In the SEM image (Figure 4.4D), the tips of MWCNTs appear as bright dots, and the dark areas indicate that the gaps between MWCNTs are effectively filled by epoxy. The inter-distance between MWCNTs ranges between tens to hundreds of nanometers. The tips of MWCNTs protrude above the epoxy because MWCNTs are more resistive to the polishing process compared to epoxy. This is one of reasons causing the background current to increase. [33].

A 400 μm diameter VCN is used as an example to study electrochemical properties of macro-sized VCNs by cyclic voltammetry. Figure 4.5A shows the voltammograms recorded at different scan rates v for the 400 μm diameter VCN in 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution. The peak shape of voltammograms suggests that planar diffusion under the total overlap regime happens at VCNs. Measuring from voltammograms, $\Delta E_p = 83 \text{ mV}$ at $v = 20 \text{ mV}\cdot\text{s}^{-1}$ and increases with v , suggesting that this system is quasi-reversible. [1,72] I further measures the anodic and cathodic peak currents $I_{s,p}$ from each voltammogram, and shows a plot of $I_{s,p}$ versus $v^{1/2}$ in Figure 4.5B. The linear relationship between $I_{s,p}$ and $v^{1/2}$ matches with Randles-Sevcik equation, suggesting that this system is close to reversible and electrochemical responses at VCNs are controlled by planar diffusion under the total overlap regime. [1,72]

The total overlap behavior at VCNs can be theoretically verified by comparing the inter-distance d_c between neighboring MWCNTs and the diffusion layer thickness δ . In cyclic voltammetry, δ at a reversible system is estimated by [72]

$$\delta \approx \left(\frac{\pi D \bar{R} T}{F v} \right)^{1/2}, \quad (4.1)$$

where $D = 7.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ is the diffusion coefficient of $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl at 25 °C [72], $\bar{R} = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the universal gas constant, $T = 298 \text{ K}$ is the solution temperature, and $F = 96485.3 \text{ C} \cdot \text{mol}^{-1}$ is the faradaic constant, and the scan rates used in our experiment is $20 \text{ mV} \cdot \text{s}^{-1} < v < 500 \text{ mV} \cdot \text{s}^{-1}$. The resulting estimation is $8.8 \mu\text{m} \leq \delta \leq 43.8 \mu\text{m}$, significantly larger than d_c (tens to hundreds of nanometers). Therefore, the diffusion layers of neighboring MWCNTs overlap completely and VCNs behave as single electrodes. For array electrodes under total overlap regime, the transition from planar diffusion to radial diffusion occurs when the characteristic dimension, *e.g.*, radius, is equal to diffusion layer thickness δ [49, 171]. Thus, 400 μm diameter VCNs experience planar diffusion under total overlap regime. It should be noted that because $\delta \propto v^{-1/2}$ (Equation 4.1), changing v causes variation in δ and eventually affects the array diameter at which radial diffusion transitions to planar diffusion.

From the experimental and theoretical analysis, I concludes that the mass transfer towards the 400 μm diameter VCNs is controlled planar diffusion under total overlap regime, and it is the limiting process of the electrochemical responses of VCNs. In the following subsections, I aims to enhance the mass transfer coefficient by reducing array diameter and introducing forced convection, and investigates their effects on the electrochemical responses of VCNs.

4.1.3 Effect of array diameter on electrochemical responses

At stationary conditions, mass transfer at nanoelectrode arrays under total overlap regime strongly depends on diffusion mode and measuring time. This, in turn, strongly correlates with the size of the arrays. On the one hand, planar diffusion is the dominant mode of mass transfer for macro-size arrays (diameter $d \geq 1 \text{ mm}$). In this case, the mass transfer coefficient reduces with experiment time as a result of the growing diffusion layer thickness. On the other hand, radial diffusion is dominant for micro-size arrays ($d \leq 100 \mu\text{m}$). Although the diffusion layer thickness increases with time, the diffusion area also becomes larger and subsequently leads to larger mass transfer coefficient compared to those in the planar diffusion mode. [1, 2, 72]

In order to investigate the dependence of the electrochemical responses of VCNs on the array diameter d , I use cyclic voltammetry to measure the current density $i = I/A$ for VCNs with different diameters in stationary solution. Here, I is the total response current, and A is the electrode surface area (see Figure 4.4C). Figure 4.6A shows several representative voltammograms for VCNs with d varying from 2000 μm to 50 μm . Correspondingly, the voltammogram's characteristics change from peak shape to sigmoidal

Figure 4.6: (A) Cyclic voltammograms of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl solution on VCNs with diameter d varying from 50 to 2000 μm , recorded at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. (B) Dependence of mass transfer coefficient m on array diameter d . The theoretical predictions of $m_{s,p}$ and $m_{s,l}$ are plotted in dash and solid line, respectively.

shape, suggesting a switch of the diffusion field from planar diffusion to radial diffusion, and the electrochemical responses at VCNs are limited by mass transfer processes.

I defines the maximum current density $i_{\text{max}} = I_{\text{max}}/A$, where I_{max} is either the peak current $I_{s,p}$ in planar diffusion, or the limiting current $I_{s,l}$ in radial diffusion (see inset of Figure 4.6A for the corresponding current density $i_{s,p}$ and $i_{s,l}$). Once i_{max} is obtained, the corresponding mass transfer coefficient m can be easily determined by [1]

$$m = \frac{i_{\text{max}}}{nFC}, \quad (4.2)$$

where $n = 1$ is the number of transferred electron to revert $\text{K}_3\text{Fe}(\text{CN})_6$, and $C = 1 \text{ mM}$ is the bulk concentration of $\text{K}_3\text{Fe}(\text{CN})_6$. In a reversible system, the mass transfer coefficient at the peak current position ($m_{s,p}$) in the planar diffusion mode and that at the limiting current position ($m_{s,l}$) in the radial diffusion mode can be respectively determined: [1]

$$m_{s,p} = 0.45 \left(\frac{nFDv}{RT} \right)^{1/2}, \quad (4.3)$$

$$m_{s,l} = 2.55 \frac{D}{d}. \quad (4.4)$$

Figure 4.6B shows a plot of m versus d and theoretical predictions for $m_{s,p}$ and $m_{s,l}$. The dependence of m on d exhibits three distinct characteristics. For $d < 150 \mu\text{m}$, m drops sharply with increasing d and is consistent with $m_{s,l}$ for the case of radial diffusion mode (Equation 4.4). The transition from radial diffusion to planar diffusion occurs in the range $150 \mu\text{m} < d < 500 \mu\text{m}$, in which m deviates significantly from the predictions of $m_{s,l}$ and $m_{s,p}$, and drops gradually with increasing d . For $d > 500 \mu\text{m}$, m depends weakly on d and is consistent with $m_{s,p}$ for the case of planar diffusion mode (Equation 4.3).

Here, I achieves an enhancement of m from $15.89 \pm 0.89 \mu\text{m} \cdot \text{s}^{-1}$ to $41.31 \pm 1.09 \mu\text{m} \cdot \text{s}^{-1}$ by reducing d from at $2000 \mu\text{m}$ to $50 \mu\text{m}$. The consistency between experimental data and Equations 4.3 and 4.4 further suggests that it is possible to obtain a 10-fold enhancement of m by reducing d from $\geq 1 \text{ mm}$ to $10 \mu\text{m}$.

4.1.4 Effect of forced convection on electrochemical responses

In electrochemical detection, forced convection is a frequently-used method to quickly form a steady state of mass transfer across electrodes with a high mass transfer coefficient. To introduce forced convection, I uses a VCN-embedded epoxy block as the base substrate of a PDMS Y-channel to form a channel electrode (Figure 3.5B). The diameter of the VCN is $400 \mu\text{m}$ and is exposed to the laminar flow in the channel.

Linear sweep voltammetry is used to investigate the effect of forced convection on the electrochemical responses of VCNs. Figure 4.7A shows representative voltammograms recorded at flow rate Q varying from $10 \mu\text{L} \cdot \text{min}^{-1}$ to $2000 \mu\text{L} \cdot \text{min}^{-1}$. The cyclic voltammogram recorded at the same system in stationary solution is inserted for comparison. By scanning the applied potential from 0.6 V to -0.2 V , the current density i at each value of Q increases and approaches the steady-state, suggesting that the electrochemical response is limited by the mass transfer of $\text{K}_3\text{Fe}(\text{CN})_6$. However, i has the tendency to arrive at the steady-state earlier at lower flow rates. For example, the steady-state of i starts from $\sim 0.1 \text{ V}$ at $Q = 100 \mu\text{L} \cdot \text{min}^{-1}$, while it starts from $\sim -0.1 \text{ V}$ at $Q = 1000 \mu\text{L} \cdot \text{min}^{-1}$. With increasing Q , m increases and becomes higher than the standard heterogeneous rate constant k_o , thus a higher over-potential is needed to increase the heterogeneous rate for reduction and achieve the steady-state. Figure 4.7C shows representative voltammograms for oxidation of $5 \mu\text{M}$ dopamine in the same system. As VCNs have higher electrochemical activity towards dopamine than that towards $\text{K}_3\text{Fe}(\text{CN})_6$, response current from detecting dopamine is easier to arrive at the steady-state than that from detecting $\text{K}_3\text{Fe}(\text{CN})_6$. From Figure 4.7A and C, I measures the limiting current density $i_{c,l}$ defined as i at -0.2 V (or 0.7 V), and uses it to calculate limiting mass transfer coefficient $m_{c,l}$ by using Equation 4.2.

To understand the dependence of $m_{c,l}$ on Q , I notes that for fully-developed laminar flows and shear Peclet number $\text{Pe}_s \gg 1$, the dependence of $m_{c,l}$ on Q can be estimated by [73, 74]

$$m_{c,l} = 1.57 \left(\frac{D^2 Q}{dw h^2} \right)^{1/3}, \quad (4.5)$$

where w and h respectively are the channel width and height. In this experiment, the smallest value of Pe_s is 2738 at the flow rate of $10 \mu\text{L} \cdot \text{min}^{-1}$ for detecting $\text{K}_3\text{Fe}(\text{CN})_6$.

Figure 4.7: Linear sweep voltammograms of (A) reduction of $5 \mu M$ $K_3Fe(CN)_6$ in 1 M KCl solution and (C) oxidation of $5 \mu M$ dopamine in $1 \times$ PBS solution on a $400 \mu m$ diameter VCN, recorded at a scan rate of $50 mV \cdot s^{-1}$, over the flow rate ranging from 10 to $2000 \mu L \cdot min^{-1}$. The limiting current density i_{lim} is measured at $-0.2 V$ or $0.7 V$. Inset shows the corresponding cyclic voltammogram recorded in the stationary condition. Dependence of the mass transfer coefficient m on the cube root of flow rate $Q^{1/3}$ for (B) $K_3Fe(CN)_6$ and (D) dopamine. The theoretical predictions of limiting mass transfer coefficient $m_{c,l}$ by Equation 4.5 are plotted in red dash lines. The linear fitting curves are plotted in black solid lines. $m_{s,l}$ at the $50 \mu m$ diameter VCNs and $m_{s,p}$ at the $400 \mu m$ diameter VCNs are added in the plot for comparing.

Thus Equation 4.5 can be used to describe the dependence of $m_{c,l}$ on Q in this experiment.

Figure 4.7B and D show a plot of $m_{c,l}$ versus $Q^{1/3}$ and theoretical prediction for detecting $K_3Fe(CN)_6$ and dopamine, respectively. Data of $m_{s,l}$ and $m_{s,p}$ in stationary conditions is added for comparison. Both $m_{c,l}$ increases linearly with $Q^{1/3}$, which follows the theory predicted by Equation 4.5, implying that the mass transfer coefficient can be enlarged by either using higher flow rates or reducing channel's dimensions. However, while values of $m_{c,l}$ from experimental and theoretical result are perfectly comparable for detecting $K_3Fe(CN)_6$ (deviation $< 13\%$), there is a difference for detecting dopamine (deviation $\leq 30\%$). The discrepancy may result from deformation of channels, contamination of VCNs by dopamine oxidants, and inaccurate estimation of diffusion coefficient.

A comparison between values of m at the $400 \mu m$ diameter VCN in the stationary condition and those in channel flow shows a substantial increase from $19.43 \pm 0.54 \mu m \cdot s^{-1}$

to $398.63 \pm 29.98 \mu\text{m} \cdot \text{s}^{-1}$ (at $Q = 2000 \mu\text{L} \cdot \text{min}^{-1}$) for detecting $\text{K}_3\text{Fe}(\text{CN})_6$, and from $18.46 \pm 2.32 \mu\text{m} \cdot \text{s}^{-1}$ to $249.41 \pm 1.56 \mu\text{m} \cdot \text{s}^{-1}$ for detecting dopamine. As a comparison, the maximum value of m that can be achieved by reducing d for detecting $\text{K}_3\text{Fe}(\text{CN})_6$ is $41.31 \pm 1.09 \mu\text{m} \cdot \text{s}^{-1}$ ($d = 50 \mu\text{m}$). It concludes that our microfluidic system is capable of producing a considerable and predictable increase in the mass transfer coefficient. Induced force convection is a much more efficient method to increase mass transfer coefficient compared to the method of reducing array diameter.

4.1.5 Summary

In Section 4.1, I optimize the fabrication process of VCNs and investigate the effect of array diameter and forced convection on the electrochemical responses of VCNs. In stationary conditions, by reducing array diameter from $2000 \mu\text{m}$ to $50 \mu\text{m}$, the diffusion mode at VCNs changes from planar diffusion to radial diffusion gradually, and the mass transfer coefficient increases roughly 3 folds. Estimated from theoretical analysis, the mass transfer coefficient can be further increased by reducing array diameter. However, this increases the difficulty of fabrication and may result in measurement of vanishingly small response current.

In hydrodynamic conditions, I assemble a VCN against a PDMS Y-channel to form a channel electrode, and increase the mass transfer coefficient by increasing flow rate. The mass transfer coefficient increases linearly with the cube root of the volumetric flow rate ranging from $10 \mu\text{L} \cdot \text{min}^{-1}$ to $2000 \mu\text{L} \cdot \text{min}^{-1}$. Compared with stationary conditions, the mass transfer coefficient increases about 20 folds at the flow rate of $2000 \mu\text{L} \cdot \text{min}^{-1}$. However, this causes high consumption of solution. It is anticipated a combined approach of reducing the array diameter and introducing forced convection can achieve high mass transfer coefficient and overcome their respective limitations at the same time.

4.2 Multi-walled carbon nanotube band electrodes

Based on the study of VCNs, I further propose a new configuration of MWCNT electrodes for electrochemical sensors, CBEs. CBEs are fabricated by encapsulating MWCNT sheets drawn from spinnable MWCNT arrays in epoxy and exposing only tips of MWCNTs. CBEs are designed to have micro-sized width to obtain high mass transfer coefficient, and macro-sized length to avoid measuring vanishingly small current.

4.2.1 Morphology

Figure 4.8A shows a side-view SEM image of a spinnable MWCNT array with height $\approx 393\ \mu\text{m}$. The CNTs are multi-walled with outer diameter $\approx 10\ \text{nm}$ (inset in Figure 4.8A). Figure 4.8B shows a MWCNT-epoxy sheet with $\approx 4\ \text{mm}$ in width and $\approx 75\ \text{mm}$ in length, and composed of single layer of MWCNT sheet. The thickness of MWCNT band can be controlled by using multiple layer of MWCNT sheets. CBEs fabricated from 1 layer (5 layer) MWCNT sheet are defined as 1-CBEs (5-CBEs). Figure 4.8C and D show a MWCNT-epoxy cylinder and a epoxy slice containing three 1-CBEs, respectively. Several MWCNT-epoxy sheets can be fabricated in one MWCNT-epoxy cylinder with height $\approx 25\ \text{mm}$, which can be cut into tens of slices with thickness $\approx 1\ \text{mm}$. Figure 4.8E shows an optical image of a 1-CBE ($\approx 3\ \text{mm}$) after gluing to silver epoxy (at the bottom). MWCNTs are well aligned and dispersed even after infiltration of epoxy. This morphology is important to achieve uniform width and shorten the pathes for electrons transfer. Figure 4.8F and G show top-view SEM images of a 1-CBE at low and high magnification, respectively. The tips of MWCNTs protrude about $300\ \text{nm}$ above epoxy. This is because MWCNTs are more resistance to both mechanical polishing and air plasma compared with cured epoxy. Measuring from high magnification SEM images, the width of 1-CBEs is $129.0 \pm 74.1\ \text{nm}$, and the width of 5-CBEs is $191.3 \pm 47.9\ \text{nm}$.

4.2.2 Electrochemical responses in stationary conditions

Cyclic voltammetry and electrochemical impedance spectroscopy are used to investigate and compare electrochemical responses of VCNs and CBEs in stationary conditions. Figure 4.9A, B and C show representative voltammograms at a VCN with $1\ \text{mm}$ diameter (1 mm-VCN), a 1-CBE, and a 5-CBE, respectively. The voltammogram's characteristics change from peak shape at the 1 mm-VCN to sigmoidal shape at the 5-CBE, suggesting that the diffusion field changes from planar diffusion to radial diffusion correspondingly, and the mass transfer is the limiting process of electrochemical responses at these two kinds of electrodes. [72] The shape of the voltammogram recorded at the 1-CBE is different from either peak shape or sigmoidal shape. The reduction current keeps increasing as the applied potential is lowered. This is because the significant enhancement on the mass transfer coefficient, and the electron transfer becomes the limiting process of the electrochemical response.

I further records the voltammograms with scan rate v varying from 20 to $500\ \text{mV} \cdot \text{s}^{-1}$ and measures the corresponding cathodic peak current $I_{s,p}$ or limiting current $I_{s,l}$. Figure 4.9D, E and F show the v -dependence of $I_{s,p}$ of the 1 mm-VCN, $I_{s,l}$ of the 1-CBE,

Figure 4.8: (A) Side-view SEM image of a spinnable MWCNT array. Inset: TEM image of a MWCNT. (B) Top-view image of a CNT-epoxy sheet. Images of (C) a MWCNT-epoxy cylinder, (D) a slice containing three 1-CBEs, and (E) a 1-CBE at 30° angle view. Top-view SEM images of a 1-CBE at (F) low and (G) high magnification.

and $I_{s,1}$ of the 5-CBE in log-log scale, respectively. I linearly fits these dependence and obtains the corresponding slopes: 0.423 ± 0.001 ($N = 2$), 0.029 ± 0.005 ($N = 6$), and 0.055 ± 0.004 ($N = 6$). The slope for the VCN is very close to 0.5, which is obtained at the condition of planar diffusion in a reversible system. [72] This suggests that the electrochemical responses of VCNs are limited by planar diffusion. As a comparison, slopes for both CBEs are very small, and $I_{s,1}$ is almost constant with v varying from 20 to $500 \text{ mV} \cdot \text{s}^{-1}$. This suggests that radial diffusion occurs at CBEs. [58–60, 72] These conclusions can be theoretically verified by the method introduced in Section 4.1.2 and won't be explained again in this section.

Figure 4.9G, H and I show Nyquist plot of 1 mm-VCN, 1-CBE, and 5-CBE, respectively. The plot of 1 mm-VCN is composed of a small semi-circle and a large straight-line, the plot of 1-CBE is composed of a large semi-circle, and the plot of 5-CBE is composed of a large semi-circle and a small straight-line. As the semi-circle represents a electron-transfer-limited process and the straight-line represents a mass-transfer-limited process (Figure 2.8), [31,37,172] I concludes that the limiting process of electrochemical responses is changed from mass-transfer-limited at the VCNs to electron-transfer-limited at the 1-CBEs. This conclusion is consistent with the results obtained from cyclic voltammetry.

The potential drops on the MWCNTs leading wires of VCNs and CBEs are estimated to assess the effect of electrode resistance on electrochemical responses. At the condition of detecting $1 \text{ mM } \text{K}_3\text{Fe}(\text{CN})_6$ using cyclic voltammetry (Figure 4.9A, B and C), the maximum current I_{max} is 1353 nA , 84 nA , and 89 nA for the 1 mm-VCN, 1-CBE, and 5-CBE, respectively. The corresponding resistance is $\approx 300 \Omega$, $\approx 5000 \Omega$, and $\approx 1000 \Omega$. By

Figure 4.9: Representative cyclic voltammograms on (A) a 1 mm-VCN, (B) a 1-CBE, and (C) a 5-CBE at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. Dependence of (D) cathodic peak current $I_{s,p}$ at the 1 mm-VCN and limiting current $I_{s,l}$ at (E) the 1-CBE and (F) the 5-CBE on the scan rate v in log-log scale. v is varied from 20 to $500 \text{ mV} \cdot \text{s}^{-1}$. The straight lines are fitted from experimental data. The dash line is plotted based on Equation 2.2. Representative Nyquist plots at (G) the 1 mm-VCN, (H) the 1-CBE, and (I) the 5-CBE. The electrolyte is $1 \text{ mM K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl solution. The spectra are recorded at 300 mV dc potential with 10 mV ac potential and frequency varying between 100 kHz and 0.1 Hz .

multiplying I_{max} with the resistance, the corresponding potential drop E_{pd} is 0.40 mV , 0.42 mV , and 0.09 mV . These potential drops are negligible compared with the applied potential ranging from 0.6 V to -0.2 V and won't have effects on electrochemical responses of the investigated electrodes.

The 5-CBEs are compared with both individual CNT electrodes [16,18,19] and 1 mm-VCNs based on maximum response current and mass transfer coefficient. The maximum response current is obtained from cyclic voltammograms, which are recorded in 1 mM analytes involving one-electron reactions at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. The mass transfer coefficient is calculated from the maximum response current by using Equation 4.2. The maximum response current is $\approx 0.3 \text{ nA}$ at individual CNT electrodes, $90.0 \pm 6.3 \text{ nA}$ at 5-CBEs, and $1161.0 \pm 114.6 \text{ nA}$ at 1 mm-VCNs. The corresponding mass transfer coefficient is $\approx 1347.4 \mu\text{m} \cdot \text{s}^{-1}$, $487.1 \pm 33.1 \mu\text{m} \cdot \text{s}^{-1}$, and $15.3 \pm 1.5 \mu\text{m} \cdot \text{s}^{-1}$. Compared

with individual CNT electrodes, 5-CBEs significantly enhance response current while maintain comparable mass transfer coefficient. Compared with 1 mm-VCNs, 5-CBEs achieve a 32-fold enhancement on mass transfer coefficient. The maximum response current at 5-CBEs can be further increased by elongating their length or fabricating in two-dimensional structures.

4.2.3 Electrochemical responses in hydrodynamic conditions

To introduce forced convection, I uses a 5-CBE-embedded epoxy block as the base substrate of a PDMS Y-channel to form a channel electrode (Figure 3.5B). The forced convection is controlled by varying flow rate Q from 1 to 1000 $\mu\text{L} \cdot \text{min}^{-1}$. Linear sweep voltammetry is used to investigate the electrochemical responses of 5-CBEs in hydrodynamic conditions.

Figure 4.10A and B show the representative voltammograms of detecting 10 μM $\text{K}_3\text{Fe}(\text{CN})_6$ and 10 μM dopamine at different flow rates, respectively. At the condition that $Q \leq 50 \mu\text{L} \cdot \text{min}^{-1}$, the response currents increase along the potential scan direction and approach steady-state starting from 0 V for $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.4 V for dopamine. The currents at the steady-state correspond to the mass transfer limiting currents, suggesting that the electrochemical responses are limited by mass transfer. At the condition $Q > 50 \mu\text{L} \cdot \text{min}^{-1}$, the response currents keep increasing along the potential scan direction, suggesting that the electrochemical responses are limited by electron transfer. From each voltammograms, I measures the limiting current $I_{c,l}$ at -0.2 V (or 0.7 V) and use it to calculate mass transfer coefficient m .

I further compares the effect of forced convection on the mass transfer coefficients of two kinds of electrodes: 5-CBEs and 400 μm -VCNs. Figure 4.10C shows the dependence of m on Q in log-log scale for 5-CBEs and 400 μm -VCNs. Data from stationary conditions is added for comparison. For detecting $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine, 5-CBE has respective slopes of 0.127 and 0.150, while 400 μm -VCN has respective slopes of 0.343 and 0.315, which are close to theoretical value (1/3) estimated by Equation 2.4. Equation 2.4 is not suitable to predict behavior of 5-CBEs in hydrodynamic conditions as diffusion become significant compared with forced convection. By introducing forced convection, 5-CBEs achieve a 3-fold enhancement of m for detecting $\text{K}_3\text{Fe}(\text{CN})_6$ from $487.1 \pm 33.1 \mu\text{m} \cdot \text{s}^{-1}$ at the stationary condition to $1450.2 \pm 31.4 \mu\text{m} \cdot \text{s}^{-1}$ at $Q = 1000 \mu\text{L} \cdot \text{min}^{-1}$; 400 μm -CBEs correspondingly achieve a 17-fold enhancement from $15.3 \pm 1.5 \mu\text{m} \cdot \text{s}^{-1}$ to $371.8 \pm 2.5 \mu\text{m} \cdot \text{s}^{-1}$. The forced convection has a slight effect on the mass transfer towards 5-CBEs, and this is beneficial for CBEs to achieve stable response currents in hydrodynamic conditions.

Figure 4.10: Linear sweep voltammograms of (A) reduction of $10 \mu\text{M K}_3\text{Fe(CN)}_6$ in 1 M KCl solution and (B) oxidation of $10 \mu\text{M}$ dopamine in $1 \times \text{PBS}$ solution on a 5-CBE, recorded at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, over flow rate Q ranging from 1 to $1000 \mu\text{L}\cdot\text{min}^{-1}$. The limiting current density i_{lim} is measured at -0.2 V or 0.7 V . (C) Dependence of mass transfer coefficient m at a 5-CBE and a $400 \mu\text{m}$ -VCN on flow rate Q in log-log scale. Data from stationary conditions for detecting $\text{K}_3\text{Fe(CN)}_6$, which is plotted in solid shape, is added for comparison. The straight lines are fitted from experimental data. The dash horizontal line is added for comparison between two kinds of electrodes.

However, that mass transfer coefficient of 5-CBEs obtained in stationary conditions is even higher than that of $400 \mu\text{m}$ -VCN obtained at a flow rate of $1000 \mu\text{L}\cdot\text{min}^{-1}$.

4.2.4 Summary

In Section 4.2, I have successfully fabricated CBEs by encapsulating MWCNT sheets in epoxy and exposing tips of CNTs. I shows that the in-house fabricated CBEs, which have macro-sized length and micro-sized width, respectively achieve high response currents and high mass transfer coefficients in electrochemical detections. Compared with individual CNT electrodes, CBEs significantly enhance response current while maintain comparable mass transfer coefficient. Compared with 1 mm -VCNs, CBEs achieve a 32-fold enhancement on mass transfer coefficient. The maximum response current at CBEs can be increased by elongating their length or fabricating in two-dimensional structures.

4.3 Summary

I presents the development of two kinds of MWCNT-epoxy electrodes: vertically aligned multi-walled carbon nanotube nanoelectrode arrays (VCNs) and multi-walled carbon nanotube band electrodes (CBEs). Utilization of VCNs and CBEs has successfully addressed a common challenge of CNT-based electrochemical sensors: achieving high mass transfer coefficient.

Electrochemical responses of macro-sized VCNs are limited by the mass transfer process. I investigates the effect of array diameter and forced convection on the mass transfer coefficient at VCNs. The mass transfer coefficient at VCNs is increased about 3 folds by reducing array diameter from 2000 μm to 50 μm . While it is increased about 20 folds at 400 μm VCNs by introducing forced convection at a flow rate of 2000 $\mu\text{L} \cdot \text{min}^{-1}$. Although induced forced convection is a much more efficient method compared to reducing array diameter, it causes high consumption of solution.

Based on the study of VCNs, I designs a new configuration of CNT-based electrodes, CBEs, to further reduce electrode size in one dimension. The CBEs have micro-sized width to obtain high mass transfer coefficient and macro-sized length to obtain high current response. Compared with individual MWCNT electrodes, CBEs obtain about few hundreds folds enhancement on current responses. Compared with macro-sized VCNs, CBEs achieve about 32-fold enhancement on mass transfer coefficient without assistance of forced convection.

Chapter 5

Single Layer Multi-walled Carbon Nanotube Sheet Electrodes for Electrochemical Sensors

To address the challenge of keeping time and material consumption during fabrication processes at the minimum, this chapter presents development of multi-walled carbon nanotube sheet electrodes (CSEs). CSEs are simply fabricated by drawing MWCNT sheets from spinnable MWCNT arrays and placing them on polyimide-glass substrates. The fabrication process is finished within few minutes, and does not require usage of any surfactant and binder materials. I systematically investigates the dependence of electrochemical responses of CSEs on the length of MWCNT leading wires, the layer number of MWCNT sheets, air plasma treatment, and forced convection. At the end, I implements three kinds of designed electrodes in channel flow voltammetry to detect both $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine, and compares their performances with literature results.

5.1 Characterization

CSEs are fabricated from spinnable MWCNT arrays. Figure 4.8A shows morphologies of the spinnable array. Figure 5.1A shows a top-view optical image of a 1-layer CSE (1-CSE) with 3.8 mm in width and 22.3 mm in length. The width and layer of number of CSEs can be varied between 2-5 mm, and 1-20, respectively. Figure 5.1B and C show top-view SEM images of a 1-CSE at low and high magnification, respectively. 1-CSE consists of well aligned and dispersed MWCNTs with occasional cross fibers. Figure 5.1D shows a side-view image of a 2 μL water droplet on a pristine 10-layer CSE (10-CSE) with

Figure 5.1: (A) Top-view optical image of a 1-CSE. Top-view SEM images of the 1-CSE at (B) low and (C) high magnification. (D) Side-view image of a 2 μL water droplet on a pristine 10-CSE. (E) A representative Raman spectrum of pristine MWCNT sheets on Si substrates.

contact angle $137.8 \pm 1.46^\circ$. The hydrophobicity of CSEs may prevent infiltration of electrolyte into CSEs and subsequently reduce effective surface area for electrochemical reactions. Figure 5.1E shows a typical Raman spectrum of pristine MWCNT sheets on Si substrates with normalizing intensity to the peak intensity at D-band. I fits the spectrum by using Lorentz function and extract exact position of three distinguish bands: D-band at 1350 cm^{-1} , G-band at 1580 cm^{-1} , and G'-band at 2697 cm^{-1} . The area intensity ratio of D-band and G-band I_D/I_G is 0.98 ± 0.07 , suggesting high quality of MWCNTs.

5.2 Effect of geometrical dimensions on electrochemical responses

Figure 5.2A shows a schematic illustrating usage of CSEs in electrochemical sensors. The surface area A of CSE exposed to solution is defined by a PDMS well, which is also used as an electrochemical cell. Both counter electrodes and reference electrodes are inserted into this well to form a three-electrode system with the CSE as working electrode. Part of CSE is unavoidably used as leading wire of the working electrode. The

Figure 5.2: (A) Schematic of a CSE illustrating: the width w_w and length l_w of MWCNT leading wire (the 2nd length $l_{w,2}$ and 5th length $l_{w,5}$ are shown), the exposing area A of the CSE to solution. (B) Representative cyclic voltammograms in 1 mM $K_3Fe(CN)_6$ of a 1-CSE ($w_w = 2.9$ mm, $A = 13.0$ mm²) with varying l_w : (1), 6 mm; (2), 10 mm; (3), 19 mm; (4), 28 mm; (5), 40 mm; and (6), 50 mm. Scan rate is 50 mV $\cdot$ s⁻¹. Dependences of (C) peak potential difference ΔE_p and (D) specific peak current density $j_{s,p}$ on l_w .

length and width of the MWCNT leading wire are represented by l_w and w_w . Multiple metal wires are connected to the CSE to vary l_w from $l_{w,1}$ to $l_{w,6}$.

I firstly investigates effect of l_w on the electrochemical responses of 1-CSEs by using cyclic voltammetry. The voltammograms are recorded at a constant scan rate 50 mV $\cdot$ s⁻¹ in two kinds of solution: $5 \mu M$ and 1 mM $K_3Fe(CN)_6$. Figure 5.2B shows representative voltammograms in 1 mM $K_3Fe(CN)_6$. At each voltammogram, I measures the peak potential difference ΔE_p and the peak current density $i_{s,p}$. According to Nicholson's method, ΔE_p can be used to calculate the standard heterogeneous rate constant k_o . [1, 72, 75] To compare $i_{s,p}$ achieved at different concentration C , $i_{s,p}$ is normalized with C to obtain specific peak current density $j_{s,p}$. In this Chapter, to differentiate variables obtained at solutions with different concentration, concentration is showed in subscript. For example, peak potential difference obtained at $5 \mu M$ $K_3Fe(CN)_6$ is denoted as $\Delta E_{p,5\mu M}$.

Figure 5.2C shows the dependence of ΔE_p on l_w . By increasing l_w from 6 to 50 mm,

$\Delta E_{p,5\mu\text{M}}$ remains constant with a value of ≈ 100 mV, while $\Delta E_{p,1\text{mM}}$ increases gradually from 137 to 360 mV. This difference may be resulted from the drop in potential E_{pd} at MWCNT leading wires, which is estimated $E_{pd} = I_s R_w$. Here, I_s is the response current and R_w is the resistance of MWCNT leading wires. For example, the 1-CSE with $l_w = 50$ mm has $R_w = 23.7\text{ k}\Omega$, the total current at the cathodic position is ≈ 48.9 nA and ≈ 6.0 μA respectively for detecting 5 μM and 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, the corresponding estimated E_{pd} is 1.16 mV and 143.0 mV. I subtracts $\Delta E_{p,1\text{mM}}$ by E_{pd} at both peak positions to obtain the estimating potential difference $\Delta E_{p,e}$. As shown in Figure 5.2C, $\Delta E_{p,e}$ is close to $\Delta E_{p,5\mu\text{M}}$ with a maximum deviation of 16.9%.

Figure 5.2D shows the dependence of $j_{s,p}$ on l_w . By increasing l_w from 6 to 50 mm, $j_{s,p,5\mu\text{M}}$ remains constant at about $0.63\text{ A}\cdot\text{mM}^{-1}\cdot\text{m}^{-2}$, while $j_{s,p,1\text{mM}}$ reduces gradually from $0.57\text{ A}\cdot\text{mM}^{-1}\cdot\text{m}^{-2}$ to $0.33\text{ A}\cdot\text{mM}^{-1}\cdot\text{m}^{-2}$. The peak-shape voltammograms suggest that electrochemical responses of 1-CSEs are controlled by planar diffusion mode. I therefore expects that $j_{s,p} = nFm_{s,p}$, with $m_{s,p} \propto (D/t_d)^{1/2}$. [72] Here, t_d is the duration starting from diffusion layer formation to the cathodic peak. The increase of l_w results in increase of t_d , and eventually reduces $j_{s,p}$.

The drop in potential on MWCNT leading wires may result in serious underestimation of electrochemical activity, especially at high response current conditions. It is evident that E_{pd} can be reduced by using lower I_s and lower R_w . While I_s can be reduced by reducing A and C , R_w can be reduced by reducing l_w , and increasing w_w and layer number LN of MWCNT sheet. However, increasing LN also increase density of defect sites, which improve electrochemical activity, and physical surface area, which increases background current. I defines sheet resistance $R_s = R_w w_w / l_w$ to preclude effects from both w_w and l_w . The background current I_b is obtained by running cyclic voltammetry in supporting electrolyte as introducing in Section 2.2.1, and normalized to surface area A to obtain i_b . Figure 5.3A shows the variation of R_s and i_b with changing LN . By increasing LN from 1 to 20, R_s reduces proportionally from $1494.6 \pm 46.8\ \Omega$ to $71.5 \pm 2.8\ \Omega$, and i_b increases gradually from $0.97 \pm 0.08\text{ mA}\cdot\text{m}^{-2}$ to $4.95 \pm 0.87\text{ mA}\cdot\text{m}^{-2}$. According to Equation 2.6, i_b should increase proportionally with LN . However, I only observes a 5-fold increase of i_b at a 20-fold increase of LN . There are two possible reasons. One is that MWCNTs of neighboring layers bundle together and subsequently reduces surface area exposing to electrolytes. The other one is that the hydrophobicity of MWCNT sheets prevents infiltration of electrolyte into CSEs, and subsequently reduces exposing area of CSEs.

I further investigates effect of LN on electrochemical responses of CSEs by using cyclic voltammetry. The voltammograms are recorded at a constant scan rate $50\text{ mV}\cdot\text{s}^{-1}$ in

Figure 5.3: (A) Dependence of sheet resistance R_s and background current density i_b on layer number LN . (B) Representative cyclic voltammograms in $10\ \mu\text{M}$ $\text{K}_3\text{Fe}(\text{CN})_6$ at CSEs with LN varying from 1, 2, 5, 10, to 20. (C) Dependence of the peak potential difference ΔE_p and standard heterogeneous rate constant k_o on LN . (D) Dependence of specific peak current density $j_{s,p}$ and signal to noise ratio S/N on LN .

two kinds of solution: $10\ \mu\text{M}$ and $1\ \text{mM}$ $\text{K}_3\text{Fe}(\text{CN})_6$. The data obtained from detecting $10\ \mu\text{M}$ $\text{K}_3\text{Fe}(\text{CN})_6$ is only slightly affected by potential drop on MWCNT leading wire and is used as reference. Figure 5.3B shows the representative voltammograms of CSEs with LN varying from 1 to 20 in $10\ \mu\text{M}$ $\text{K}_3\text{Fe}(\text{CN})_6$.

Figure 5.3C shows the dependence of ΔE_p and k_o on LN . I observes that $\Delta E_{p,10\mu\text{M}}$ reduces sharply from 152.7 ± 43.3 to 77.7 ± 3.8 mV with LN increasing from 1 to 5, and becomes saturated at ≈ 72 mV with $LN \geq 10$; while $k_{o,10\mu\text{M}}$ increases gradually from 18.2 ± 11.0 to $144.5 \pm 34.4\ \mu\text{m}\cdot\text{s}^{-1}$ with LN increasing from 1 to 10, and approaches the maximum value $154.5 \pm 31.5\ \mu\text{m}\cdot\text{s}^{-1}$ at $LN = 20$. The difference between these two dependence is because that k_o increases gradually with ΔE_p reducing at $\Delta E_p \geq 80$ mV, while it increases sharply at $\Delta E_p < 80$ mV in Nicholson's method (as shown in Figure 2.5). Due to the substantial potential drop on the MWCNT leading wire $E_{pd,1\text{mM}}$, $\Delta E_{p,1\text{mM}}$ is larger than $\Delta E_{p,10\mu\text{M}}$ for all CSEs. By increasing LN from 1 to 20, R_w and subsequently $E_{pd,1\text{mM}}$ are reduced, and eventually the difference between $\Delta E_{p,1\text{mM}}$ and $\Delta E_{p,10\mu\text{M}}$ is reduced from 115 mV to 14 mV

Figure 5.3D shows the dependence of $j_{s,p}$ and signal to noise ratio S/N on LN . The signal to noise ratio is defined as $S/N = i_{s,p}/i_b$. I observes that $j_{s,p,10\mu M}$ increases sharply from 0.96 ± 0.19 to $1.33 \pm 0.10 \text{ A} \cdot \text{mM}^{-1} \cdot \text{s}^{-2}$ with doubling LN and then increases to $1.57 \pm 0.08 \text{ A} \cdot \text{mM}^{-1} \cdot \text{s}^{-2}$ slowly with LN increasing to 20. The same tendency is observed for $j_{s,p,1mM}$. Both $j_{s,p,10\mu M}$ and $j_{s,p,1mM}$ are limited by the Rnadle-Sevick equation (Equation 2.2), suggesting that CSEs are planar electrodes rather than porous electrodes. I uses degassing to facilitate infiltration of electrolyte into 10-CSEs. However, the electrochemical response is not changed. As the enhancement of $j_{s,p}$ is smaller than that of i_b with LN increasing from 1 to 20, S/N reduces from 12.7 ± 2.2 to 4.1 ± 0.7 correspondingly.

In this section, I implements CSEs for electrochemical detections and investigates effects of l_w and LN on electrochemical responses of CSEs. Part of CSE is unavoidably used as leading wire of working electrodes and may result in serious underestimation of electrochemical activity of CSEs. I experimentally minimizes this effect by reducing l_w and increasing LN . Increasing LN also significantly increases electrochemical activities of CSEs at the cost of high consumption of MWCNTs. However, CSEs behave as planar electrodes and their electrochemical responses are limited by mass transfer processes.

5.3 Effect of air plasma on electrochemical responses

CSEs are treated with air plasma to improve their wettability and electrochemical activity. Plasmas are generated by ionizing gas molecules under low pressure and high frequency oscillating electromagnetic field. These ionized gases can interact with MWCNTs to induce both oxygen-containing functional groups (-OH and -COOH), and defects on MWCNTs, which subsequently change wettability and electrochemical activity of MWCNTs. The contact angle measurement shows a significant reduction from $137.8 \pm 1.46^\circ$ at pristine CSEs (Figure 5.1D) to $< 10^\circ$ at CSEs with air plasma treatment duration $t_p \geq 30 \text{ s}$.

I investigates effect of t_p on the electrochemical responses of 1-CSEs and 10-CSEs by using cyclic voltammetry. The voltammograms are recorded at a constant scan rate $50 \text{ mV} \cdot \text{s}^{-1}$ in two kinds of solution: $10 \mu\text{M}$ and 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. Figure 5.4A show dependence of ΔE_p and k_o of 1-CSEs on t_p . By treating 1-CSEs with air plasma, $\Delta E_{p,10\mu M}$ reduces and k_o increases significantly with t_p increasing from 0 s to 60 s, and the both of them remain almost constant with $t_p \geq 60 \text{ s}$. Compared with pristine 1-CSEs, 1-CSEs treated with air plasma for 600 s obtain a reduction of $\Delta E_{p,10\mu M}$ from 202.2 ± 28.5 to $66.3 \pm 1.0 \text{ mV}$, and a corresponding enhancement of k_o from 7.8 ± 2.2 to

Figure 5.4: Dependence of (A) peak potential difference ΔE_p and standard heterogeneous rate constant k_o , (B) specific peak current density $j_{s,p}$ and background current density i_b of 1-CSEs on plasma time t_p . (C) and (D) is the corresponding dependence of 10-CSEs for detecting 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$.

$267.6 \pm 44.4 \mu\text{m}\cdot\text{s}^{-1}$. The 1-CSEs treated with air plasma for $t_p \geq 60$ s have larger k_o than the pristine 20-CSEs ($144.5 \pm 34.4 \mu\text{m}\cdot\text{s}^{-1}$). The dependence of $\Delta E_{p,1\text{mM}}$ on t_p follows the same relation as that of $\Delta E_{p,10\mu\text{M}}$ on t_p . The difference between $\Delta E_{p,1\text{mM}}$ and $\Delta E_{p,10\mu\text{M}}$ is ≈ 100 mV at different t_p .

Figure 5.4B, shows the dependence of $j_{s,p}$ and i_b of 1-CSEs on t_p . By treating 1-CSEs with air plasma, i_b increases significantly from $0.75 \pm 0.07 \text{ mA}\cdot\text{m}^{-2}$ at $t_p = 0$ s to $11.16 \pm 2.26 \text{ mA}\cdot\text{m}^{-2}$ at $t_p = 60$ s, and then increased gradually to $22.87 \pm 6.0 \text{ mA}\cdot\text{m}^{-2}$ at $t_p = 600$ s. There are two reasons for this enhancement. One is that hydrophilic CSEs facilitates infiltration of electrolyte into CSEs and subsequently increase surface area exposing to electrolyte. The other one is that the inducing functional groups cause pseudo-capacitance and then increase capacitance of CSEs. In contrast to the huge enhancement of i_b and k_o , there is only a 2-fold increase on $j_{s,p}$. The response current is limited by the Randle-Sevcik equation (Equation 2.2). The signal to noise S/N ratio for detecting 10 μM $\text{K}_3\text{Fe}(\text{CN})_6$ reduces from 17.0 ± 5.1 at pristine 1-CSEs to 1.0 ± 0.1 at 1-CSEs treated with air plasma for $t_p = 600$ s.

Figure 5.5: (A) Representative Raman spectra for 1-CSEs treated with air plasma for duration t_p varying from 0 s to 600 s. (B) Dependence of area intensity ratio I_D/I_G on t_p .

I carries out the same experiments on 10-CSEs. By treating 10-CSEs with air plasma, background current increases significantly and the signal current from 10 μM $\text{K}_3\text{Fe}(\text{CN})_6$ can't be distinguished. I shows the results of detecting 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in Figure 5.4C and D. These results are similar to that of 1-CSEs.

It is generally accepted that air plasma treatment induces defects on sidewalls of MWCNTs and subsequently improves their electrochemical activities. [69, 91, 93, 94] I uses Raman spectroscopy to investigate the effect of air plasma on the structure of MWCNTs. Figure 5.5A shows representative Raman spectra of MWCNTs with varying t_p . Figure 5.5B shows that I_D/I_G increases gradually from 0.98 ± 0.07 to 1.72 ± 0.06 upon increasing t_p from 0 to 300 s, and then remains almost constant with t_p up to 600 s. Comparison between Figure 5.4A and Figure 5.5B shows that k_o approaches the maximum value at $t_p = 120$ s while I_D/I_G approaches the maximum value at $t_p = 300$ s. There are two possible reasons. The first one is that k_o has arrived at the maximum value when CSEs are treated with air plasma for 120 s, and won't increase with increasing t_p . The other one is the inaccurate estimation of k_o resulted from potential drop on CNT leading wire. When $\Delta E_p \leq 75$ mV, small variation of ΔE_p can cause substantial change of k_o .

Air plasma treatment has been shown as an efficient method to significantly increase wettability and electrochemical activity of CSEs. However, air plasma treated CSEs still behave as planar electrodes rather than porous electrodes, and their electrochemical responses are limited by the mass transfer process.

5.4 Effect of forced convection on electrochemical responses

To introduce forced convection, I uses a CSE as the base substrate of a PDMS Y-channel to form a channel electrode (Figure 3.5B). The forced convection is controlled by varying flow rate Q from 100 to 2000 $\mu\text{L} \cdot \text{min}^{-1}$. Linear sweep voltammetry is used to investigate the effect of forced convection on electrochemical responses of 1-CSEs, 10-CSEs, and 1 layer CSEs treating with air plasma for 2 minutes (AP-1-CSEs). Those electrodes have variation in dimensions, which affect the limiting current $I_{c,l}$ according to Equation 2.4. To exclude the dimension effect, I defines specific peak current density $j_c = I/Cw_e x_e^{2/3}$, and limiting specific peak current density $j_{c,l} = I_{c,l}/Cw_e x_e^{2/3}$.

Figure 5.6A shows representative voltammograms of detecting 10 μM $\text{K}_3\text{Fe}(\text{CN})_6$. For AP-1-CSEs, j_c increases along the potential scan direction and approaches a steady-state at all value of Q , suggesting that the electrochemical response is limited by mass transfer. For both 1-CSEs and 10-CSEs, j_c keeps increasing along the potential scan direction at all value of Q , suggesting that the electrochemical response is limited by electron transfer. The steady-state of response current is crucial for measurement and quantitative analysis. By introducing forced convection, an AP-1-MCSE ($x_e = 2.59 \text{ mm}$, $w_e = 0.5 \text{ mm}$) achieves a 19-fold enhancement of the maximum specific response current from $1.51 \pm 0.08 \text{ mA} \cdot \text{mM}^{-1} \cdot \text{m}^{-2}$ at stationary conditions to $28.96 \pm 0.97 \text{ mA} \cdot \text{mM}^{-1} \cdot \text{m}^{-2}$ at $Q = 2000 \mu\text{L} \cdot \text{min}^{-1}$.

Figure 5.6B shows representative voltammograms for detecting 10 μM dopamine. As these three kinds of CSEs have high electrochemical activity towards dopamine, their response currents approach steady-states with increasing applied potential. Compared with 1-CSEs and 10-CSEs, AP-1-CSEs achieve the steady-state response currents at the lowest potential, *e.g.*, 0.4 V at $Q = 1000 \mu\text{L} \cdot \text{min}^{-1}$.

I further compares experimental results of $j_{c,l}$ of AP-1-CSEs with theoretical results. As shown in Figure 5.6A and B, the experimental values of $j_{c,l}$ are obtained by measuring j_c at -0.2 V and 0.7 V in the voltammograms from detecting $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine, respectively. The theoretical value of $j_{c,l}$ is estimated by using Equation 2.4. Figure 5.6C shows plots of experimental and theoretical values of $j_{c,l}$ versus Q in log-log scale. In the log-log scale, $j_{c,l}$ increases linearly with Q at a slope of 0.296 and 0.283 for detecting $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine, respectively. These values are comparable with the value (1/3) estimated from Equation 2.4. The comparability between the experimental results and theoretical results suggests that $j_{c,l}$ can be further increased by increasing Q or reducing the dimensions of Y-channel. However, I notes that the deviation of experimental results from theoretical results may be because the deformation of the channel and the

Figure 5.6: Linear sweep voltammograms for (A) reduction of 10 μM $\text{K}_3\text{Fe}(\text{CN})_6$ and (B) oxidation of 10 μM dopamine at a 1-CSE, a 10-CSE, and a AP-1-CSE. The voltammograms are recorded at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, over flow rate Q ranging from 100 to 2000 $\mu\text{L}\cdot\text{min}^{-1}$. The specific limiting current density $j_{c,l}$ of detecting $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine is measured at -0.2 V and 0.7 V , respectively. (C) Dependence of $j_{c,l}$ of AP-1-CSEs on flow rate Q in log-log scale. The straight lines are fitted from experimental data. The function plot based on Equation 2.4 is in dash line for $\text{K}_3\text{Fe}(\text{CN})_6$ and dot line for dopamine.

inaccurate estimation of exposing area of CSEs to solution.

5.5 Stability

Passivating analytes may contaminate electrodes and affect stability of their current response. [173] I investigates the stability of three kinds of CSEs (1-CSE, 10-CSE, and AP-1-CSE) in channel flow voltammetry. Figure 5.7 A and B show the variation of j_c of CSEs under continuous exposure to 100 μM $\text{K}_3\text{Fe}(\text{CN})_6$ and 50 μM dopamine, respectively. At the condition of continuous exposure to 100 μM $\text{K}_3\text{Fe}(\text{CN})_6$ for an hour, there is no j_c reduction happening at these three kinds of CSEs. At the condition of continuous exposure to 50 μM dopamine for 2000 s, j_c reduces $27.9 \pm 9.0\%$ at 1-CSEs, $22.0 \pm 3.3\%$ at 10-CSEs, and $5.7 \pm 3.0\%$ at AP-1-CSEs. The dopamine oxidation products form an insulating film on the electrode surface. This film blocks the active sites and prevents

Figure 5.7: Current response at a 1-CSE, a 10-CSE, and a AP-1-CSE for continuous exposing to (A) $100 \mu\text{M K}_3\text{Fe(CN)}_6$ and (B) $50 \mu\text{M}$ dopamine in channel flow voltammetry. The applied potentials at the electrodes are -0.2 V and 0.7 V , respectively. The flow rate is $1000 \mu\text{L} \cdot \text{min}^{-1}$.

them from participating in electrochemical reaction. [174] The comparison indicates that AP-1-CSEs can withstand fouling and prevent adsorption of the oxidation products, respectively due to their high degree of defects and their oxygen-containing function groups. [174]

5.6 Implementation of multi-walled carbon nanotube electrodes for electrochemical sensors

In this section, I demonstrates utilization of three kinds of MWCNT-based electrodes in channel flow voltammetry to detect $\text{K}_3\text{Fe(CN)}_6$ and dopamine, and compares their performances with literature results. The used electrodes are: a VCN with diameter of $400 \mu\text{m}$, a 5-CBE with length of 2.42 mm , a AP-1-CSE with width of 2.15 mm used for detecting $\text{K}_3\text{Fe(CN)}_6$, and a AP-1-CSE with width of 2.34 mm used for detecting dopamine. Experimental details can be found in Section 3.4.2.

Figure 5.8A, C, and E shows respective current responses of the VCN, the CBE, and the CSEs at detecting $\text{K}_3\text{Fe(CN)}_6$ (top panel) and dopamine (bottom panel) with three different concentrations. The response current from the analytes with concentration $C = 10 \text{ nM}$ can be well differentiated from the baseline current. The difference between the total response current and the baseline current is defined as signal current I_h . The signal current I_h at each concentration C is highly reproducible with a maximum relative standard deviation of 7%.

Figure 5.8B, D, and F shows the corresponding dependence of I_h on C in log-log scales. From this dependence, I obtains the linear range, at where I_h increases linearly with increasing C . I further estimates sensitivity S and the limit of detection LOD

Figure 5.8: Current responses in channel flow voltammetry of (A) a VCN to 400 μ L $K_3Fe(CN)_6$ solution with concentration 10 nM, 1 μ M and 1 mM (top panel) and 400 μ L dopamine solution with concentration 10 nM, 1 μ M and 100 μ M (bottom panel); (C) a 5-CBE to 4 μ L $K_3Fe(CN)_6$ solution with concentration 10 nM, 1 μ M and 1 mM (top panel) and 4 μ L dopamine solution with concentration 10 nM, 1 μ M and 200 μ M (bottom panel); and (E) AP-1-CSEs to 400 μ L $K_3Fe(CN)_6$ solution with concentration 10 nM, 1 μ M and 1 mM (top panel) and 400 μ L dopamine solution with concentration 10 nM, 1 μ M and 50 μ M (bottom panel). The flow rate is 1000 μ L $\cdot$ min $^{-1}$ when using the VCN and the CSE as working electrodes, and it is 10 μ L $\cdot$ min $^{-1}$ when using the CBEs as working electrodes. (B), (D), and (F) show the dependence of baseline-corrected peak height current I_h on concentration C of $K_3Fe(CN)_6$ (top panel) and dopamine (bottom panel) for the VCN, the 5-CBE, and the AP-1-CSEs, respectively. The graph is plot on log-log scale. The straight line was fitted from experimental data.

Table 5.1: Comparison between performance of a VCN, a 5-CBE, and two AP-1-CSEs in channel flow voltammetry

Electrode	A (mm^2)		Linear range		S ($\times 10^4 \text{ A} \cdot \text{M}^{-1} \cdot \text{m}^{-2}$)		LOD (nM)	
	$\text{K}_3\text{Fe}(\text{CN})_6$	Dopamine	$\text{K}_3\text{Fe}(\text{CN})_6$	Dopamine	$\text{K}_3\text{Fe}(\text{CN})_6$	Dopamine	$\text{K}_3\text{Fe}(\text{CN})_6$	Dopamine
VCN	1.257×10^{-1}		10 nM – 1 mM	10 nM – 100 μM	2.46	2.58	4.23	3.03
CBE	1.194×10^{-3}		10 nM – 1 mM	10 nM – 200 μM	6.87	9.93	3.35	0.29
CSE	1.075	1.170	10 nM – 1 mM	10 nM – 50 μM	1.99	2.71	3.15	0.54

by [53, 175]

$$S = k/A, \quad (5.1)$$

$$\text{LOD} = 3\sigma_b/k, \quad (5.2)$$

where k is the slope obtained from the dependence of I_h on C in the linear range, and σ_b is the standard deviation of the baseline current ($N = 10$). The surface area A is the projecting area of the electrodes for both VCNs and CSEs, while it is the surface area of the protruding band for CBEs.

Table 5.1 summarizes A , the linear range, S , and LOD. The CBE has the most supreme performance including the widest linear range, the highest S , and the lowest LOD. Beside, the flow rate and pumping volume used in the channel flow voltammetry for the CBE is only 1% of these for the VCN and the CSEs. However, due to small A , the response current of the CBE is about 2 – 3 order of magnitude smaller than that of the VCN and the CSEs. The measurement of response current of the CBE requires high accuracy potentiostat. While the maximum concentration in the linear range is 1 mM for detecting $\text{K}_3\text{Fe}(\text{CN})_6$ using these three kinds of electrodes, it is 100, 200, and 50 μM for detecting dopamine using the VCN, the CBE, and the CSE, respectively. The saturation for detecting dopamine may result from fouling of the electrode by dopamine oxidation products. [174] The slightly higher detecting limit on CBEs may because high density of defect sites. I notes that LOD is highly dependent on σ_b , which is seriously affected by the setting of the potentiostat, the vibration from environment, and the cleanliness and concentration of the supporting electrolytes.

I further compares these three kinds of MWCNT-based electrodes with other reported CNT-based electrodes based on the linear range, S and LOD. Only the CNT-based electrodes with $\text{LOD} \leq 100 \text{ nM}$ are included. Figure 5.9A and B show the comparison for detecting $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and dopamine, respectively. I notes that numerous studies aiming to reduce the LOD, increase S and widen the linear range of detection have either used complex functionalized processes [142, 173, 176–178], or SWCNTs [51, 53, 179, 180], both of which require lengthy and dedicated fabrication processes. Compared

Figure 5.9: Comparison of the linear range, sensitivity S and the limit of detection LOD between VCNs, 5-CBEs, AP-1-CSEs with other CNT-based electrodes for detecting (A) $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, and (B) dopamine. The linear range is plotted in line. The sensitivity S is plotted in solid circle.

to those in which such processes are not employed, our electrodes offers both the lowest LOD, highest sensitivity and widest linear range for detecting both analytes.

5.7 Summary

I successfully fabricates multi-walled carbon nanotube sheet electrodes (CSEs) with the minimum time and material consumption. I systematically investigates the dependence of electrochemical responses of CSEs on the length of MWCNT leading wires, the layer number of MWCNT sheets, air plasma treatment, and forced convection. The potential drop at the MWCNT leading wires may reduce applied potential at the electrodes significantly and subsequently result in serious underestimation of electrochemical activity of CSEs. Both increasing the layer number and air plasma treatment can significantly improve electrochemical activity of CSEs, while air plasma treatment is a more efficient method. Introducing forced convection can significantly increase the mass transfer coefficient and subsequently the response current. On the contrary to the current literature report, this study shows that single layer CSEs can obtain high electrochemical activity and high mass transfer coefficient, and have a promising potential for electrochemical detection.

At the end, I demonstrates the utilization of a VCN, a 5-CBE, and AP-1-CSEs in channel flow voltammetry to detect both $\text{K}_3\text{Fe}(\text{CN})_6$ and dopamine. Among these three kinds of electrodes, the 5-CBE demonstrates the most supreme detection performance including the widest linear range, the highest sensitivity, and the lowest limit of detection. I further compares these three electrodes with other CNTs-based electrodes in

electrochemical detection. The comparison shows that the performance of these three kinds of electrodes exceed most of the reported CNT-based electrodes. These three kinds of electrodes can used on the lab-on-a-chip systems for analytical applications with the advantages of wide linear range, high sensitivity and low limit of detection.

Chapter 6

Multi-walled Carbon Nanotube Sheet Stainless Steel Electrodes for Thermocells

To address the challenges of achieving high mass transfer coefficient and high electrical conductivity, and keeping the time and material consumption during fabrication processes at the minimum, this chapter presents the design and implementation of MWCNT sheet stainless steel electrodes for thermocells. MWCNT sheets are drawn out from spinnable MWCNT arrays and placed on stainless steel sheets (SSS) and stainless steel meshes (SSM) to form CSSEs and CSMEs, respectively. Similar to the fabrication process of CSEs, fabrication of CSSEs and CSMEs requires minimum time and material consumption. MWCNTs are attached firmly and directly to stainless steels by Van der Waals force. The direct contact between MWCNTs and the substrates reduces thermal and electrical resistance across the interface. Moreover, the well aligned and dispersed MWCNT sheets facilitate diffusion of electrolytes into the electrodes. I investigate the effect of layer number of MWCNT sheets, air plasma treatment, and substrate type on the output power of thermocells. At the end, I compare performance of thermocells using CSSEs with literature results.

6.1 Characterization

Figure 6.1A and B show representative images of CSSEs with the layer number LN of MWCNT sheets varying from 1 to 20, and CSMEs with LN varying from 1 to 10, respectively. CSSEs (CSMEs) with $LN = N$ are denoted as N-CSSEs (N-CSMEs). As

Figure 6.1: Images of (A) CSSEs and (B) CSMEs with varying layer number LN of CNT sheets. Numbers on top of electrodes indicate LN . Images of (C) a 10-CSSE and (D) a 10-CSME immersed in water, and (E) and (F) taken out from water. SEM images of (G) a 10-CSSE and (H) a 10-CSME.

MWCNT sheets attached firmly to stainless steel substrates due to Van der Waals forces, they did not detach from the substrates when being immersed in water (Figure 6.1C and D), taken out from water (Figure 6.1E and F), or rinsed with water. The strong adhesion therefore excludes usage of binder materials, which may increase thermal and electrical resistance between MWCNTs and the conductive substrates. I measures the electrical resistance between a SSS and a 10-CSSE, which are clamped together with the MWCNT sheet in the middle. The typical value of the resistance is $< 1 \Omega$, suggesting that the electrical resistance R_{lc} between MWCNTs and the conductive substrates is $< 1 \Omega$. Figure 6.1G and H show SEM images of a 10-CSSE and a 10-CSMEs, respectively. MWCNTs in these electrodes are well aligned and distributed with occasional across MWCNT bundles.

6.2 Calibration of Thermocells

Thermocell with a long acrylic chamber (44 mm in length, 5.5 mm in inner diameter) is calibrated by measuring the Seebeck coefficient Se of $K_3Fe(CN)_6/K_4Fe(CN)_6$ and investigating the effect of concentration and temperature on the output power of thermocell. The design of the thermocell is shown in Section 3.5, and the corresponding schematic is illustrated in Figure 3.6.

Figure 6.2: (A) Dependence of open circuit voltage V_{oc} on temperature difference ΔT for thermocell using platinum wires. Dependence of (B) V_{oc} , (C) short circuit current I_{sc} , and (D) internal resistance R_{in} and maximum output power P_{max} on ΔT for thermocell using 10-CSSEs. Concentration of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution is varied from 0.05 M to 0.4 M.

Firstly, I measures Se of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution with concentration C varying from 0.05 M to 0.4 M in a thermocell using platinum wires as electrodes. The corresponding Se is denoted as Se_{Pt} . The temperature T_c at the cold side electrode is maintained at 20°C, while the temperature T_h at the hot side electrode is adjusted to vary the temperature difference ΔT from 10 to 50 K. The open circuit voltage V_{oc} is measured at each value of ΔT . Figure 6.2A shows the dependence of V_{oc} on ΔT with varying C . At each concentration, V_{oc} increases linearly with increasing ΔT , suggesting that Se is not effected by temperature. I linearly fits the dependence of V_{oc} on ΔT to obtain Se_{Pt} , which are 1.60, 1.66, 1.52, and 1.33 $mV \cdot K^{-1}$ for $K_3Fe(CN)_6/K_4Fe(CN)_6$ solutions with concentration of 0.05, 0.1, 0.2, and 0.4 M, respectively. The slight increase in Se_{Pt} with reducing C could be resulted from the variation of effective redox species concentration and activity with changing solution concentration and ionic strength. [9, 158] The value of Se_{Pt} of 0.4 M $K_3Fe(CN)_6/K_4Fe(CN)_6$ has a 7% deviation from the literature value (1.43 $mV \cdot K^{-1}$) [9, 10, 12], ensuring the reliability of the home-made thermocell.

I replaces the platinum electrodes by 10-CSSEs and repeats the experiment. Figure 6.2B shows the dependence of V_{oc} on ΔT with varying C . For $K_3Fe(CN)_6/K_4Fe(CN)_6$

Figure 6.3: Dependence of electrical conductivity σ of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution and estimated solution resistance R_{so} of thermocells on (A) solution temperature T_s at 0.4 M $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution and (B) concentration C at $T_s = 25^\circ C$.

solutions with concentration of 0.05, 0.1, 0.2, and 0.4 M, Se_{CSSE} is 1.76, 1.75, 1.65, and 1.55 mV · K⁻¹, respectively. Similar to Se_{Pt} , Se_{CSSE} at low concentration is slightly higher than that at high concentration. The value of Se_{CSSE} at 0.4 M $K_3Fe(CN)_6/K_4Fe(CN)_6$ has a 8.4% deviation from the literature value (1.43 mV · K⁻¹). The deviation may be resulted from the measurement of temperature: the thermocouples are not sufficiently closed to CSSEs, thus may not reflect the temperature at CSSEs accurately. I will use $Se = 1.43 \text{ mV} \cdot \text{K}^{-1}$ in the following sections to avoid experimental error from measuring temperature.

Secondly, I investigate the effect of concentration and temperature on the output power of thermocell using 10-CSSEs. Figure 6.2C shows the dependence of short circuit current I_{sc} on ΔT with varying C . Figure 6.2D shows the dependence of internal resistance R_{in} and maximum output power P_{max} on ΔT with varying C . In contrast to the slight dependence of V_{oc} on C , I_{sc} and P_{max} are affected significantly by C . For example, at $\Delta T = 50^\circ C$, I_{sc} increases from 0.08 mA at $C = 0.05 \text{ M}$ to 0.29 mA at $C = 0.4 \text{ M}$. Correspondingly, P_{max} increases about 3-fold from 1.74 μW to 5.20 μW. At each concentration, P_{max} increases with increasing ΔT at a gradient higher than a linear relationship, which can be confirmed by Equations 2.15 and 2.17. It is therefore preferred to use high ΔT . Figure 6.3A and B show the dependence of electrical conductivity σ of $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution and solution resistance R_{so} on solution temperature T_s and concentration C , respectively. It can be observed that σ increases linearly with T_s from 25°C to 83°C and C from 0.05 M to 0.4 M. Correspondingly, R_{so} reduces with increasing T_s and C . Comparison between R_{in} (Figure 6.2D) and R_{so} (Figure 6.3) shows that R_{so} dominates roughly half of R_{in} , indicating C and T_s affect not only R_{so} but also R_{ct} and R_{int} . The enhancement of P_{max} is resulted from the enhanced electrical conductivity and enhanced concentration of redox ions available at the electrodes. In the

following sections, I uses 0.4 M $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ solution as electrolyte and sets $\Delta T = 50^\circ\text{C}$ with $T_c = 20^\circ\text{C}$.

6.3 Effect of layer number on the output power of thermocells

Effects of layer number of MWCNT sheets on the output power of thermocells are investigated. As shown in Equations 2.10 and 2.12, the mass transfer resistance R_{mt} and the electron transfer resistance R_{ct} reduce with increasing surface area A . In porous structures, A is the area exposing to electrolytes and participating in electrochemical reactions. Increasing layer number LN in CSSEs may increase A , reduce R_{mt} and R_{ct} , and therefore increase output power. To avoid interference from R_{so} , I uses a short acrylic chamber (13.5 mm in length, 11.5 mm in inner diameter) in thermocells to obtain small value of R_{so} , which is estimated to be $9.77\ \Omega$ at $T_s = 25^\circ\text{C}$.

After establishing a stable temperature difference, thermocell discharges on a variable resistor with R_{lo} . The voltage E_d on R_{lo} is measured and used to calculate discharging current I_d . To avoid interfere of using electrodes with different area, I_d is normalized with A to obtain discharging current density i_d . Figure 6.4A shows the dependence of i_d on E_d . I linearly fits the dependence to achieve specific internal resistance $R_{\text{in,s}} = R_{\text{in}}/A$, and calculates the output power $P_o = E_d I_d$, which is further used to calculate specific power density $P_s = P_o/A\Delta T^2$. Figure 6.4B shows the dependence of P_s on E_d . I quadratically fits the dependence to obtain the maximum value $P_{\text{s,max}}$.

Figure 6.4C and D show the dependences of $R_{\text{in,s}}$ and $P_{\text{s,max}}$ on LN , respectively. It can be observed that $R_{\text{in,s}}$ reduces significantly, from $72805\ \Omega \cdot \text{mm}^2$ at SSSs to $2636 \pm 398.5\ \Omega \cdot \text{mm}^2$ at 1-CSSEs, and $P_{\text{s,max}}$ increases correspondingly from $0.0067\ \text{mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$ to $0.189 \pm 0.031\ \text{mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$. I therefore neglects power generated from SSSs. By increasing LN to 5, $R_{\text{in,s}}$ reduces to $1155 \pm 91.2\ \Omega \cdot \text{mm}^2$ and $P_{\text{s,max}}$ increases to $0.427 \pm 0.034\ \text{mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$. However, further enhancement of LN (up to 20) has slight effect on $R_{\text{in,s}}$ and $P_{\text{s,max}}$.

Figure 6.5 shows SEM images of CSSEs with LN varying from 1 to 20. For 1-CSSEs and 2-CSSEs, there are parts of SSS not covered by MWCNTs, while for CSSEs with $LN \geq 5$, no SSS is exposed. Both $P_{\text{s,max}}$ and MWCNT surface coverage are saturated at $LN = 5$. I speculates that electrolytes can not diffuse into CSSEs and only interact with MWCNTs at the top surface. The hydrophobic nature of MWCNTs and small inter-distance between MWCNTs may hinder the diffusion of electrolytes into CSSEs. CSSEs

Figure 6.4: Plots of (A) discharging current density i_d and (B) specific power density P_s versus discharging voltage E_d . (C) Dependence of specific internal resistance $R_{in,s}$ and (D) maximum specific power density $P_{s,max}$ on layer number LN for thermocells using CSSEs.

behave as planar electrodes rather than porous electrodes.

6.4 Effect of air plasma treatment on the output power of thermocells

Effects of air plasma treatment on the output power of thermocells are investigated. CSSEs are treated with air plasma to increase their wettability and electrochemical activity. The transition from hydrophobic to hydrophilic facilitates infiltration of aqueous electrolyte into CSSEs, which may increase effective surface area. The improvement of electrochemical activity can reduce the electron transfer resistance R_{ct} . I denotes 1-CSSEs (10-CSSEs) treated with air plasma for 5 minutes as AP-1-CSSEs (AP-10-CSSEs).

Figure 6.6A and B show plots of i_d and P_s versus E_d , respectively. Figure 6.6C and D compare effect of air plasma treatment on $R_{in,s}$ and $P_{s,max}$, respectively. Comparison between pristine electrodes and air plasma treated electrodes shows that air plasma treatment only slightly increases $R_{in,s}$ and reduces $P_{s,max}$. I estimates $R_{ct}A$ by using Equation 2.10. The following parameters are used: $A = 25 \text{ mm}^2$; k_o is $7.8 \mu\text{m} \cdot \text{s}^{-1}$ for

Figure 6.5: SEM images of CSSEs with varying layer number of MWCNT sheets: (A) and (B) 1 layer, (C) and (D) 2 layers, (E) and (F) 5 layers, (G) and (H) 10 layers, and (I) and (J) 20 layers.

Figure 6.6: Plots of (A) discharging current density i_d and (B) specific power density P_s versus discharging voltage E_d . Comparisons of (C) specific internal resistance $R_{in,s}$ and (D) maximum specific power density $P_{s,max}$ of thermocells using different kinds of electrodes.

1-CSSEs, $144.5 \mu\text{m} \cdot \text{s}^{-1}$ for 10-CSSEs, and $240.9 \mu\text{m} \cdot \text{s}^{-1}$ for both AP-1-CSSEs and AP-10-CSSEs; and $C = 0.4 \text{ M}$. The estimated $R_{ct}A$ is $85 \Omega \cdot \text{mm}^2$ for 1-CSSEs, $4.5 \Omega \cdot \text{mm}^2$ for 10-CSSEs, and $2.75 \Omega \cdot \text{mm}^2$ for both AP-1-CSSEs and AP-10-CSSEs. Compared with $R_{in,s}$ shown in Figure 6.6C, $R_{ct}A$ is negligible. For thermocells using CSSEs, due to the high electrochemical activity of pristine MWCNTs towards $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ and the utilization of high concentration $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$, electron transfer resistance is a negligible component of the internal resistance of thermocells.

6.5 Effect of substrate type on the output power of thermocells

Effects of substrate type on the output power of thermocells are investigated. MWCNTs sheets are adhered on two kinds of substrates, stainless steel sheets and stainless steel meshes, to form two kinds of electrodes, CSSEs and CSMEs. The meshes are composed of $30 \mu\text{m}$ diameter stainless steel wires with $60 \mu\text{m}$ inter-distance. Figure 6.7 shows SEM images of CSMEs with LN varying from 1 to 10. For 1-CSMEs and 2-CSMEs, MWCNTs

Figure 6.7: SEM images of CSMEs with varying layer number of MWCNT sheets: (A) and (B) 1 layer, (C) and (D) 2 layers, (E) and (F) 5 layers, and (G) and (H) 10 layers.

attach to stainless steel wires and do not block the holes of SSMs. While for 5-CSMEs or 10-CSMEs, MWCNTs arrange in sheet morphology and block the holes of SSMs.

Figure 6.8A and B show plots of i_d and P_s versus E_d , respectively. Figure 6.8C and D compare $R_{in,s}$ and $P_{s,max}$, respectively. Thermocells using SSMs have the lowest $R_{in,s}$, $1358 \pm 81.4 \Omega \cdot \text{mm}^2$, which is even smaller than thermocells using 1-CSSEs and 2-CSSEs. It can be observed that $R_{in,s}$ ($P_{s,max}$) increases (reduces) with LN increasing from 0 to 5, and then reduces (increases) with further increasing LN . Coverage of SSMs with MWCNTs deteriorates output power. It happens to find that SSMs may be a good

Figure 6.8: Plots of (A) discharging current density i_d and (B) specific power density P_s versus discharging voltage E_d . (C) Dependence of specific internal resistance $R_{in,s}$ and (D) maximum specific power density $P_{s,max}$ on layer number LN for thermocell using CSMEs.

candidate of electrodes used in thermocells and will explore reasons in the future. By further cleaning SSMs in 1 M NaOH, $R_{in,s}$ is reduced to $1012.8 \pm 36.9 \Omega \cdot mm^2$, which is comparable to the thermocells using N-CSSEs ($N \geq 5$).

6.6 Comparison between performance of thermocells

In this section, I compares performances of thermocells using four kinds of electrodes (SSSs, 10-CSSEs, SSMs, and SSM-scrolls) based on two parameters: the maximum specific power density $P_{s,max}$, and the relative power conversion efficiency η_c . I obtains $P_{s,max}$ at the condition of $A_c = A$, and η_c from the power conversion efficiency η (Equation 2.18) by $\eta_c = \eta T_h / \Delta T$. Here, T_h is the temperature of hot side electrode in thermocells. A long acrylic chamber (44 mm in length, 5.5 mm in inner diameter) is used in thermocells. SSM-scrolls are fabricated by rolling SSMs with length of 240 mm and width of 11 mm into scrolls with diameter of 5.5 mm and length of 11 mm. SSM-scrolls are inserted into the acrylic chamber, and heated and cooled from the bottom. The closed distance between these two electrodes is 22 mm.

Figure 6.9A and B show plots of i_d and P_s versus E_d , respectively. Due to the

Figure 6.9: Plots of (A) discharging current density i_d and (B) specific power density P_s versus discharging voltage E_d . Comparisons of (C) specific internal resistance $R_{in,s}$ and (D) maximum specific power density $P_{s,max}$ of thermocells using different kinds of electrodes.

limit power of peltier coolers, thermocells using SSM-scrolls only achieve $V_{oc} \approx 36.5$ mV. Figure 6.9C and D compare different electrodes based on $R_{in,s}$ and $P_{s,max}$, respectively. It can be observed that $R_{in,s}$ reduces significantly from $72805.5 \Omega \cdot \text{mm}^2$ at SSSs to $3997.3 \pm 281.5 \Omega \cdot \text{mm}^2$ at 10-CSSEs, $P_{s,max}$ increases correspondingly from $0.007 \text{ mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$ to $0.123 \pm 0.009 \text{ mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$. Thermocells using SSMs have similar performances as that using 10-CSSEs. By using SSM-scrolls, $R_{in,s}$ further reduces to $994.6 \Omega \cdot \text{mm}^2$, and $P_{s,max}$ increases correspondingly to $0.492 \text{ mW} \cdot \text{m}^{-2} \cdot \text{K}^{-2}$. SSM-scrolls have highly porous three-dimensional structures, which reduce cross-sectional area normal to the direction of heat flow and allow a high degree of electrolyte exposure to the electrode surface for redox reactions. The enhancement of $P_{s,max}$ by using SSM-scrolls is partially resulted from reducing d_e , which reduces the solution resistance and the mass transfer resistance.

I further compares thermocells designed in this thesis with literature results based on $P_{s,max}$ and η_c in Table 6.1. As $P_{s,max}$ and η_c are affected by both T_h and d_e , which can't be simply excluded, they are included in Table 6.1 for reference. Thermocells designed in this thesis have comparable performances as thermocells using MWCNT-PVDF-SSS electrodes [14]. PVDF denotes polyvinylidene fluoride. In order to achieve performance

Table 6.1: Comparison between performance of thermocells

Reference	Electrode	T_h (°C)	d_e cm	$P_{s,max}$ (mW · m ⁻² · K ⁻²)	η_c
Hu et al. (2010)	Bucky paper scroll	65	5	0.5	1.40%
Romano et al. (2013)	SWCNT-RGO 10 stacks	97	2	1.9	2.63%
	SWCNT-RGO 1 stack			0.46	0.65%
Holubowitch et al. (2016)	MWCNT-PVDF	80	3.3	0.14	0.29%
Im et al. (2016)	MWCNT sheet scroll	91	2.5	2.5	3.95%
	Activated carbon cloth			1.8	0.40%
Zhnag et al. (2017)	MWCNT foam	100	0.26	1.35	NA
	C-cork (pressed)			1.15	
	Graphene sheet			0.78	
	MWCNT sheet			0.59	
	Platinum foil			1.38	
This thesis	SSS	70	4.4	0.008	0.02%
	10-CSSE	70	4.4	0.12	0.33%
	SSM	70	4.4	0.16	0.43%
	SSM-scroll	46 (estimated)	2.2	0.49	0.67%

as other thermocells shown in Table 6.1, it is necessary to fabricate highly porous CNT electrodes.

6.7 Summary

I successfully fabricates multi-walled carbon nanotube sheet on stainless steel sheets (CSSEs) and stainless steel meshes (CSMEs) for thermocells. The fabrication processes require minimum time and material consumption. I have investigated the effect of layer number of MWCNT sheets, air plasma treatment, and substrate type on the output power of thermocells. For thermocells using CSSEs, their internal resistances reduce with increasing layer number and become saturated at five layers. The CSSEs behave as planar electrodes rather than porous electrodes. Air plasma treatment significantly improves wettability and electrochemical activity of CSSEs, and subsequently reduces electron transfer resistance. However, it has slightly effect on reducing the internal resistance as the electron transfer resistance is a negligible component of internal resistance in these thermocells. By changing substrates from SSSs to SSMs, thermocells using SSMs have comparable output power with that using N-CSSEs ($N \geq 5$), and MWCNTs coverage on SSMs deteriorates output power. SSMs are a good candidate to be used in thermocells, which requires further investigation. Thermocells using 10-CSSEs achieve comparable performance as that using MWCNT-PVDF-SSSs, attesting the success of utilizing CSSEs in thermocells. Finally, I notes that efforts to fabricate CNT electrodes with highly porous structures should be taken to further improve performance of thermocells.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

The utilization of CNT-based electrodes in both electrochemical sensors and thermocells is generally limited by challenges: achieving high mass transfer coefficient, as well as keeping time and material consumption in fabrication processes at the minimum. To address these challenges in electrochemical sensors, this thesis presents several designs of multi-walled carbon nanotube (MWCNT) based electrodes: vertically aligned MWCNT nanoelectrode arrays (VCNs), MWCNT band electrodes (CBEs), and MWCNT sheet electrodes (CSEs). Based on the study of CSEs, this thesis further presents designs of electrodes for thermocells, *i.e.*, MWCNT sheets on stainless steel sheets (CSSEs) and stainless steel meshes (CSMEs). The main conclusions and contributions are listed as follows.

Electrochemical responses of macro-sized (diameter ≥ 1 mm) VCNs are limited by the mass transfer processes. This thesis investigates the effect of array diameter and forced convection on the mass transfer towards VCNs. In stationary conditions, by reducing array diameter from 2 mm to 50 μm , the diffusion field on the electrode surface gradually transfers from the planar diffusion to the radial diffusion, and the mass transfer coefficient increases roughly 3-fold. The mass transfer coefficient, as estimated from theoretical analysis, can be further increased by reducing the array diameter. However, reducing array diameter increases the difficulty of fabrication and results in measurement of vanishingly small response current. In hydrodynamic conditions, a channel electrode is formed by using a VCN and a PDMS Y-channel to introduce forced convection across the electrode surface. Compared to detection conducted at stationary conditions, the mass transfer coefficient increases about 20-fold at the maximum tested flow rate of 2000 $\mu\text{L} \cdot \text{min}^{-1}$. By introducing forced convection at high flow rates, VCNs are capable

of obtaining both high response current and high mass transfer coefficient.

Based on the study of VCNs, this thesis proposes a new configuration of CNT-based electrodes, CBEs, which is fabricated by encapsulating MWCNT sheets in epoxy and exposing the tips of MWCNTs. CBEs have micro-sized width (≈ 200 nm) and macro-sized length (≥ 3 mm), which respectively achieves high mass transfer coefficient and high response current. Compared to macro-sized VCNs, the diffusion mode changes from planar diffusion mode to radial diffusion mode, and the mass transfer coefficient at CBEs increases ≈ 32 folds. Compared to individual CNT electrodes, the response current at CBEs increases about few hundred folds. CBEs can achieve higher response current by elongating their length or being fabricated in two-dimensional structures. CBEs are also assembled with PDMS Y-channels to introduce forced convection across electrode surface. In this hydrodynamic condition, the mass transfer at CBEs is affected slightly by forced convection because the mass transfer has been significantly enhanced by using micro-sized width. Forced convection is not required, making CBEs the CNT-based electrodes capable of obtaining high response current and high response current density without causing high consumption of solution.

This thesis successfully fabricates CSEs by drawing out MWCNT sheets directly from spinnable MWCNT arrays and placing them on insulating polyimide-glass substrates. The fabrication process only takes few minutes and does not require usage of surfactant or binder material. This thesis also investigates the dependence of the electrochemical responses of CSEs on the length of MWCNT leading wires, the layer number of MWCNT sheets, air plasma treatment, and forced convection. The potential drop at the MWCNT leading wires may seriously reduces the applied potential at CSEs, and subsequently results in serious underestimation of electrochemical activity of CSEs. This problem can be overcome by reducing length of MWCNT leading wires, increasing width and layer number of MWCNT sheets, reducing exposing surface area of CSEs to electrolyte, and usage of low concentration analytes. Both increasing the layer number and treating with air plasma can significantly improve electrochemical activity of CSEs, while the later one is a more efficient method. As the electrochemical responses of CSEs are limited by mass transfer processes, introducing forced convection effectively increases the mass transfer coefficient and subsequently the response current (17-fold enhancement compared to stationary conditions). Single layer CSEs with air plasma treatment can achieve high electrochemical activity and high mass transfer coefficient.

This thesis further demonstrates the utilization of 400 μ m diameter VCNs (400 μ m-VCNs), five layers CBEs (5-CBEs), and single layer CSEs treated with air plasma (AP-1-CSEs) in channel flow voltammetry to detect both $K_3Fe(CN)_6$ and dopamine. These

three kinds of electrodes demonstrate excellent performances with wide linear range, high sensitivity, and low limit of detection, which exceed most of CNT-based electrodes reported in literature. Among these three kinds of electrodes, 5-CBEs exhibit the best performances including the widest linear range, the highest sensitivity, and the lowest limit of detection.

Both electrochemical sensors and thermocells rely on electrochemical reactions to realize their functions. The successful application of CSEs on electrochemical sensors inspires the utilization of MWCNT sheets on thermocells. Using the same method of fabricating CSEs, this thesis successfully fabricates MWCNT sheets on stainless steel sheets and stainless steel meshes to form CSSEs and CSMEs, respectively. The strong adhesion between MWCNTs and the substrates ensures the electrodes with high mechanical stability, and high electrical and thermal conductivity. This thesis investigates the dependence of thermocell output power on the layer number of MWCNT sheets, air plasma treatment, and substrate type. For thermocells using CSSEs, their internal resistance reduces with increasing layer number and becomes saturated at five layers. As the small inter-distance between MWCNTs prevents diffusion of electrolyte into electrodes, CSSEs behave as planar electrodes rather than porous electrodes. Air plasma treatment significantly improves wettability and electrochemical activity of CSSEs, and subsequently reduces electron transfer resistance. However, this resistance is a negligible component and has slightly effect on the internal resistance. By changing substrates from SSSs to SSMs, it is found that thermocells using SSMs have comparable output power with that using N-CSSEs ($N \geq 5$), and MWCNTs coverage on SSMs deteriorates their output power. SSMs are a good candidate of electrodes for thermocells, which will be investigated in the future. At the end, this thesis shows that thermocells using 10-CSSEs can achieve comparable performance with those using MWCNT-PVDF-SSSs, attesting the success of utilizing CSSEs in thermocells.

This PhD thesis presents detailed studies on designing and implementing VCNs, CBEs, and CSEs for electrochemical sensors, and CSSEs and CSMEs for thermocells. These electrodes successfully achieve high mass transfer coefficient while keeps the time and material consumption in fabrication processes at the minimum. The excellent performances of these electrodes used in electrochemical sensors and thermocells demonstrate the successful design of these electrodes, and provide guidelines for designing next generation of CNT-based electrodes.

7.2 Future work

This thesis recommends the following directions and opportunities for future work:

1. *Design recessed CNT nano-ring and nano-disc arrays for electrochemical sensors.*

Even though CBEs have demonstrated the ability of achieving both high response current and high mass transfer coefficient, the response current from analytes with low concentrations, *e.g.*, 10 nM, is only a few pico-amperes. The measurement of such vanishingly small current highly depends on potentiostats with high accuracy. It is obvious that the response current can be increased by increasing exposing edges of CBEs by fabricating them in the form of two-dimensional structure, *e.g.*, recessed nano-ring arrays [181, 182].

For CSEs, due to small inter-distance between CNTs, the mass transfer is dominated by planar diffusion. Even though the mass transfer can be significantly improved by introducing forced convection, it consumes a large amount of solution. In order to improve mass transfer without consuming high volume of solution, CSEs can be patterned in the form of nano-disc arrays to achieve radial diffusion mode. [182]

Both CNT nano-ring and nano-disc arrays can be fabricated by using the same procedure. MWCNT sheets can be patterned by using a thin layer of insulating epoxy to selectively exposing CNTs and subsequently form recessed nano-disc arrays. By controlling the diameters and inter-distances of nano-discs, each CNT discs behave as independent nano-sized electrodes, at where radial diffusion occurs. The recessed CNT nano-disc arrays can be further treated with strong plasma to remove exposed MWCNTs and subsequently form recessed CNT nano-disc arrays.

2. *Design CNT electrodes with hierarchical structures for thermocells.*

To achieve high performances of thermocells, it is crucial to use highly porous CNT-based electrodes with high mass transfer coefficient and high electrical conductivity. CNT-based electrodes with hierarchical structures may fulfill this requirement. They can be fabricated by growing [183] or coating [184] CNTs on stainless steel meshes. These electrodes have micro-sized holes to facilitate diffusion of electrolytes, and nano-sized CNTs covered on the meshes to significantly increase surface area. Besides, growing or coating CNTs on the meshes reduces contact resistance. Electrons generated at CNTs are transferred through individual CNTs or thin CNTs sheets, and collected by the adjacent stainless steel. These electrodes may reduce internal resistance and subsequently improve performance

of thermocells.

3. *Investigate electrochemical properties of MWCNTs.*

It is generally accepted that electrochemical properties of MWCNTs are similar to highly oriented pyrolytic graphite (HOPG): the electrochemical activity of MWCNTs and HOPG are contributed from defects and edges, while sidewalls of MWCNTs are same as basal planes of HOPG, which are electrochemically inert. However, recent reports show a contradictory statement that the basal planes of the fresh prepared HOPG have comparable electrochemical activities as platinum electrodes towards several kinds of outer spherical species. The environment contamination deteriorates the electrochemical activities of HOPG and results in the misunderstanding of their real properties. [92, 96, 97] This misunderstanding may happen at MWCNTs. The fundamental studies on electrochemical activities of MWCNTs can guide the design of MWCNT-based electrodes for electrochemical application.

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