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Hydrogen storage in pt/carbon nanotube sheets

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ABSTRACT

HYDROGEN STORAGE IN Pt/CARBON NANOTUBE SHEETS

by
An-Yu Ma

Three types of self-assembled carbon nanotube (CNT) sheets, for example, carboxylic functionalized multi-walled CNTs (MWNTs-COOH), pure multi-walled CNTs (MWNTs), and pure single-walled CNTs (SWNTs), were prepared as substrates by ambient environment vacuum filtration of suspensions of the nanotubes. To enhance hydrogen storage on the CNTs, platinum particles were deposited on the three types of CNT sheets using two processes: electrodeposition (ED) using a DC power source and electrochemical deposition under cyclic voltammetry (CV). To verify platinum deposition on the surface of the CNT sheets, a Scanning Electron Microscope (SEM) was used to obtain images, and Energy Dispersive X-ray (EDX) spectroscopy was used to determine the percentage of platinum particles coated on the CNT sheets. Hydrogen was produced and stored on the surface-modified CNT and pristine CNT sheets by cyclic voltammetry in alkaline electrolytic solution (6 N KOH). The hydrogen storage capacity in the electrochemically treated samples was evaluated using temperature-programmed desorption (TPD) measurement.

HYDROGEN STORAGE IN Pt/CARBON NANOTUBE SHEETS

by
An-Yu Ma

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APPROVAL PAGE

HYDROGEN STORAGE IN Pt/CARBON NANOTUBE SHEETS

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I dedicate this thesis to my beloved parents

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CHAPTER 1

INTRODUCTION

Hydrogen is a promising energy carrier, clean and renewable, which can be used for fuel cell applications. To produce large amounts of pure hydrogen remains a significant challenge for building a full hydrogen economy. A more critical problem to surmount is how to safely and efficiently store this hydrogen [1]. Carbon nanotubes are potentially a good candidate material for reversibly storing hydrogen via adsorption or absorption (see Figure 1.1) on the tube walls. To enhance the storage capacity, dispersed catalytic metals (for example, platinum) on the adsorption medium such as, carbon nanotubes have also been used in order to optimize the loading capacity [2].

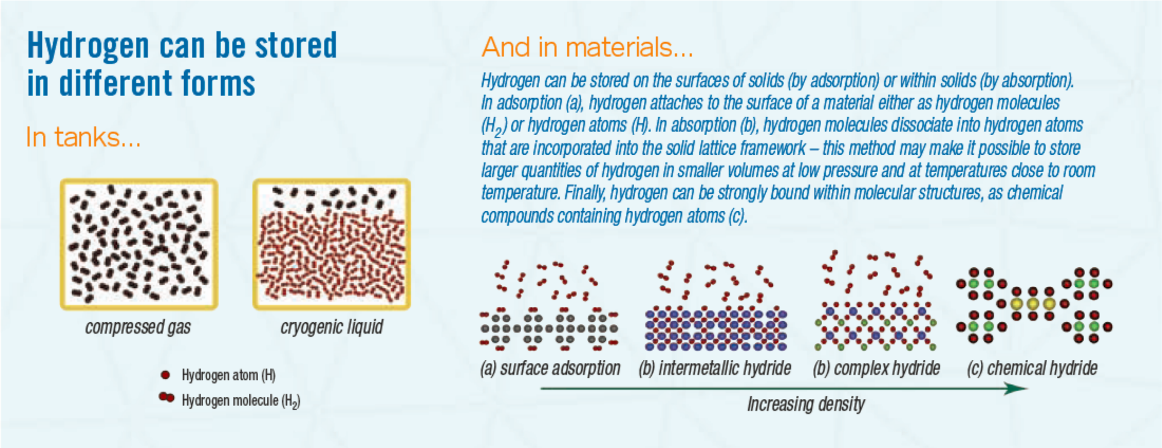
In this chapter, three sections are presented. Section 1.1 describes the basic concepts of hydrogen storage. Section 1.2 describes the process of using carbon nanotubes as the absorption medium, and the method used to coat a selected catalytic transition metal, platinum, onto the carbon nanotubes. Chemical binding of hydrogen to the transition metal by the Kubas interaction mechanism will also be elaborated on in this section. The mechanism of hydrogen “spillover” via metal particles and migration onto adjacent surface of the adsorption medium is also explained. Section 1.3 describes the experimental outline of the whole thesis.

1.1 Concepts Involved in Hydrogen Storage

Developing sustainable energy sources is one of the current challenges facing the world because fossil fuels widely used today generate energy economically, but are responsible for environmental pollution as well as global warming. Therefore, finding an alternative energy source is now a worldwide goal for researchers [3, 4].

Currently, hydrogen is the most attractive energy source because of its relative ease of production, light mass, and high energy conversion efficiency [5, 6]. Hydrogen can be produced from coal, natural gas and water. The latter is the most environmentally friendly source, which meets almost all the requirements to substitute fossil fuels [7]. Water contains both elements or components of a power source because when the hydrogen and oxygen produced from water are efficiently recombined in an electrochemical fuel cell, electrical power is generated. Actually, using hydrogen as an energy carrier is not a new idea. In 1874, Jules Verne, the well-known French author wrote that “Water will be the coal of the future.” in his book: “The Mysterious Island” [8].

Therefore, one of the key technological challenges for fuel cells is how to design a safe, reliable, compact, cost-effective and efficient medium for hydrogen storage [9]. Hydrogen is the lightest of all elements. That means to store enough hydrogen (for reference, the US Department of Energy goal is 5.5 wt % of gravimetric capacity, namely the usable hydrogen weight over the total weight of the storage medium) requires either large volumes or high pressures. Generally speaking, hydrogen can be stored in three different forms (Figure 1.1): pressurized gas in high pressure tanks, cryogenic liquid in insulated tanks, and in advanced materials where it is either physically (by van der Waals interactions of the order of 5 kJ/mol) or chemically (direct chemical interaction of greater than 100 kJ/mol) absorbed in a porous medium (e.g., carbon nanostructures or metal-organic frameworks) or chemically bonded in intermetallic, complex and chemical hydrides from which it can be obtained by dissociation at relatively low temperatures [9]. In an ideal hydrogen storage medium, adsorption energies should be in the 30-80 kJ/mol range. Storage of hydrogen as compressed gas or as liquid hydrogen is not safe and not practical, particularly for transportation and mobile applications. Solid-state storage materials are therefore the focus of current research and development. Among advanced materials, metal hydrides and porous carbon are the most attractive for hydrogen storage [10]. However, a suitable medium that meets all the criteria for hydrogen storage remains elusive.



Hydrogen can be stored on the surfaces of solids (by adsorption) or within solids (by absorption). In adsorption (a), hydrogen attaches to the surface of a material either as hydrogen molecules (H_2) or hydrogen atoms (H). In absorption (b), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework – this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms (c).

Figure 1.1 Hydrogen storage approaches.

(Sourced from US Department of Energy site http://www.hydrogen.energy.gov/pdfs/doe_h2_storage.pdf)
(Accessed: Nov. 3rd, 2011)

1.2 Using Carbon Nanotubes as Media for Hydrogen Storage

Due to the large surface area to volume ratios nano-porosity, and light weight, carbon-based materials like carbon nanotubes (CNTs) have been considered to be an ideal medium for the reversible storage of hydrogen. [11, 12]. Since the early research by Dillon and co-workers [13] showed a possible 5 to 10 weight % hydrogen storage capacity for single-walled carbon nanotubes (SWNTs), a lot of attention was focused on CNTs as a safe hydrogen storage medium. Song et al. [14, 15] reported that multi-walled carbon nanotubes (MWNTs) have large electrochemical hydrogen storage capacity (above 200 mAh/g), and Dai et al. [16] also claimed that a purified single-walled carbon nanotube electrode has a maximal reversible electrochemical discharge capacity of 316 mAh/g. Lombardi et al. [17] also observed reversible hydrogen storage capacity of MWNTs both in alkaline (6 M KOH) and acidic (0.3 M H_2SO_4) electrolytic solutions.

However, hydrogen storage in carbon nanotubes remains well below the 10 weight % observed by Dillon et al. [18] because of weak binding energies of hydrogen on the CNT backbone and therefore still has a long way to go before it can be implemented in applications. In order to improve physisorption, catalytic metal particles (e.g., platinum) have been deposited on CNT substrates. Coating nanoparticles onto CNTs can form a new class of hybrid nanomaterials with unique properties that have potential applications both as a hydrogen storage medium and as a hydrogen fuel cell electrode [18]. Transition metals (e.g., palladium) can dissolve and dissociate hydrogen molecules which then spillover to the porous storage medium [20]. Hydrogen atoms adsorbed in metals can spillover to be absorbed on porous materials or frameworks. Zuettel et al. [19] showed that the electrochemical hydrogen storage capacities of an electrode containing 10-40%

MWNTs with Pd powder achieved a storage capacity of 110 mAh/g. The mechanism of the enhanced capability of hydrogen storage after metallic catalysts are decorated on surface of CNTs is because of two approaches shown in Figure 1.2.

First is the Kubas mechanism where hydrogen is adsorbed by a non-dissociative weak chemisorption by electron donation and back-donation processes, a reaction weaker than covalent bonds (strong chemisorption) but stronger than van der Waals forces (weak physisorption). The Kubas interaction provides just enough binding force to attract hydrogen molecules on metals, and can release hydrogen under the right conditions of heat and pressure. Preventing metal aggregation and finding a suitable receptor medium are challenges for hydrogen storage via the Kubas mechanism. Scientists from Rice University reported [20] that a single metal on the matrix of metallacarborane, a molecule that combines boron, carbon, and metal atoms in a cage-like structure, can bind up to 5 hydrogen molecules with a binding energy (ca. 0.4 eV/H_2) through the Kubas interaction.

Second is the spillover mechanism where hydrogen molecules dissociate to hydrogen atoms on the surface of metal particles and then spills over to the acceptor or support medium. However, spillover is controversial since it is still lacks of evidence for formation of C-H bonds through this mechanism [21]. A research group in the University of Michigan [22] has suggested two methods to induce hydrogen spillover. One is directly doping dissociation metals (Pt, Pd, Ru, and Ni) on the adsorbent carbon materials and metal-organic-framework (MOF) supports for preventing aggregation of metals. A second approach is by creating bridges (for example, by water molecules) between the dissociation metals and the adsorbent.

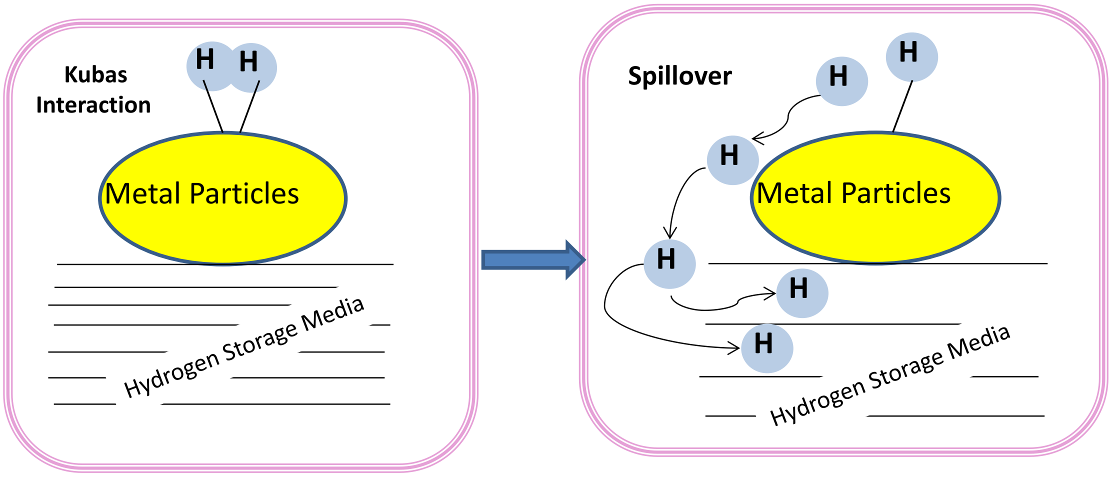


Figure 1.2 The hydrogenation mechanism of "spillover" where the hydrogen molecules are first absorbed and then dissociated from metal particles (e.g., Pt particles), then form covalent C-H bond by chemisorption or weak bonding through physisorption.

1.3 Contents of the Thesis

In this thesis, five chapters are presented. Chapter 1 introduces the basic concepts of this project. It briefly discusses the important issues of hydrogen storage, the trend to develop a better storage material for transportation of hydrogen and the role of carbon nanotubes as a potential medium for hydrogen storage. The important mechanisms of spillover and Kubas interaction to increase hydrogen storage by the addition of catalytic metals have been described. Chapter 2 explains the coating method by electrodeposition (ED) to deposit catalytic platinum particles on three different types of carbon nanotubes (MWNT sheets, MWNT-COOH sheets and SWNT sheets). The details of CNT sheet fabrication are also described in this section. Chapter 3 discusses the procedure to deposit platinum particles on the working electrode CNTs sheets using electrochemical cyclic voltammetry (CV). Chapter 4 describes the electrochemical hydrogen storage process using pristine and platinum-coated CNTs as substrates. In the last chapter, the results are briefly summarized and recommendations for future work are provided.

The experimental outline of this project is diagrammatically outlined in Figure 1.3. This flow chart covers the process from the starting raw materials - the CNTs powders, the fabrication of CNT sheets (Ch. 2), surface modification of the CNT sheets using electrodeposition (Ch. 2) and cyclic voltammetry (Ch. 3), to the use of pristine and Pt-coated-CNT sheets as hydrogen storage media or substrates (Ch. 4).

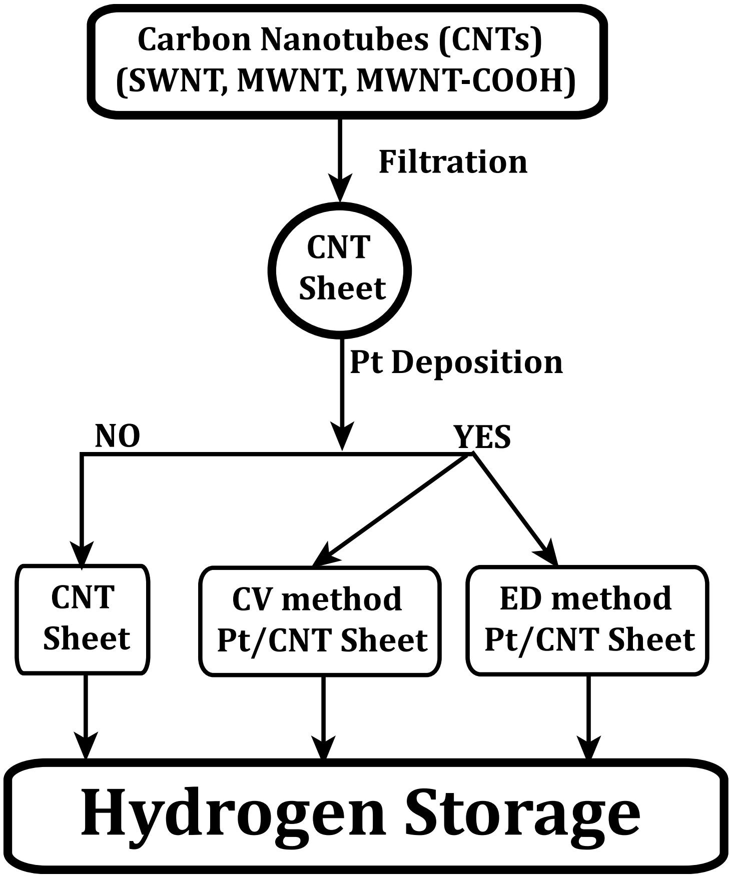


Figure 1.3 The experimental outline of hydrogen storage from raw materials to form CNT sheets and then use it as the medium, with and without platinum deposition, to store hydrogen.

CHAPTER 2

ELECTROCHEMICAL DEPOSITION OF PLATINUM PARTICLES ON CARBON NANOTUBE SHEETS

In order to decorate carbon nanotube (CNT) sheets with platinum particles, an electrodeposition process was used. In this chapter the technique employing a DC power source and a CNT sheet as the cathode is described. Three different types of CNT sheets made from SWNTs, MWNTs and MWNTs functionalized with –COOH groups, have been prepared and used as the cathode to form Pt-decorated nanocomposite substrates for hydrogen storage. Deposition of Pt on the CNT sheets was confirmed by field-emission scanning electron microscopy (FE-SEM), and confirmed and the weight percentages measured by Energy Dispersive X-ray (EDX) spectroscopy.

2.1 Overview

Ultrasonication employing a horn sonicator was used to disperse CNTs to form suspensions together with about 1% by weight of surfactants (e.g., Triton X-100) [23]. The CNT suspensions were then filtered under vacuum to produce films of nanotubes on polytetrafluoroethylene (PTFE) -coated filter paper from which they were peeled off to obtain free standing nanopaper [24, 25].

2.2 Experiments

2.2.1 Fabricating Carbon Nanotubes Sheets

Materials: SWNTs were purchased from Cheap Tubes (SKU# 0101), and MWNTs and MWNTs-COOH were purchased from NanoLab, Inc. Sodium dodecyl sulfate (SDS, Sigma Aldrich) was used as surfactant. A 45 mm diameter PTFE membrane from Millipore) was used as the filter paper during fabrication.

Equipment: The horn-sonicator (Ultrasonic processor, Cole-Parmer Instruments, Model CPX130) was used to obtain the CNTs suspension.

Procedure: The three different types of carbon nanotubes sheets have been prepared by procedures developed in our group based on those of Rinzler et al. and Baughman et al. These CNTs were used as-received without further purification. The protocol of fabrication of CNT sheets was as follows: For making the CNT papers or substrates used in this work, we first weighed 50 mg CNTs and then dispersed it in 50 ml of 0.5 wt% surfactant, sodium dodecyl sulfate (SDS) in aqueous solution. The horn-sonicator (Ultrasonic processor, Cole-Parmer Instruments, Model CPX130- Figure 2.1) was used to form the CNT suspensions. After ultrasonicating for 30 minutes with the power set at AMP50% of an ON/OFF pulse interval (30 seconds ON and 10 seconds OFF), the solution was then poured into the vacuum filtration system (Figure 2.1). In the stainless steel manifold filtration system, a 47 mm diameter of polytetrafluoroethylene (PTFE) membrane filter paper was pre-wetted in ethanol solution. During the filtration, 200mL warm water (ca. 90 °C) was added twice, and methanol was poured once to rinse away extra SDS surfactant. After thorough washing the CNT sheet was allowed to dry at room temperature for approximately 2 hours under vacuum. The CNT sheet was then peeled and ready to use as substrate for Pt deposition. Digital photographs of the CNT sheets are shown in Figure 2.3.

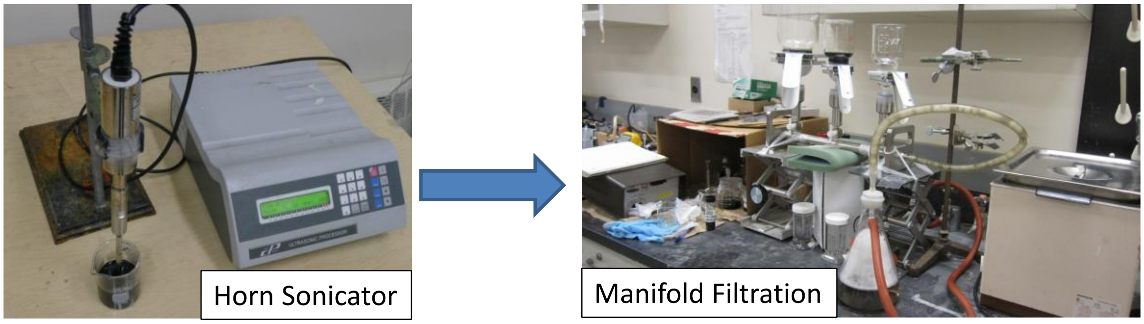


Figure 2.1 Fabrication of Carbon Nanotube sheets: horn sonicator to mix dispersed CNT in SDS aqueous solution (left) and filtration to harvest CNT sheets (right).

2.2.2 Electrochemical Deposition of Platinum on CNT sheets

Materials: Three as-prepared CNTs, SWNT, MWNT and MWNT-COOH sheets, were used as substrates. Platinum (IV) Chloride (>= 99.99% metals basis, Sigma-Aldrich) was used as- received. Platinum wire (CHI115) was purchased from CH Instrument, TX.

Instrument and apparatus: DC power supply HY1803D (Tekpower, Montclair CA). Scanning electron microscope (VP 1530 Zeiss LEO) equipped with an EDX analyzer was used to obtain the images of deposition and perform quantitative analyses, respectively.

Procedure: The source of platinum particles was using as received platinum (IV) chloride (PtCl4, Sigma-Aldrich) without further modification. A home-made CNT sheet (ca. 5.1 cm^2) was connected to the negative side of the DC power supply while platinum wire was connected as counter electrode to the positive side of the power supply. The power of potential voltage was setup at 5 volts and then applied charging for 2 hours. The electrolytes solution was prepared using 1mM $PtCl_4$ aqueous solution. In order to remove extra platinum particles tangling on the surface of the CNT sheet after electrodeposition process, The Pt/CNT substrate was gently washed by de-ionized water several times. The CNT sheet was then dried under ambient environment before further used for hydrogen storage. The setup for electrodeposition of platinum particles on the CNT sheet is shown in Figure 2.2.

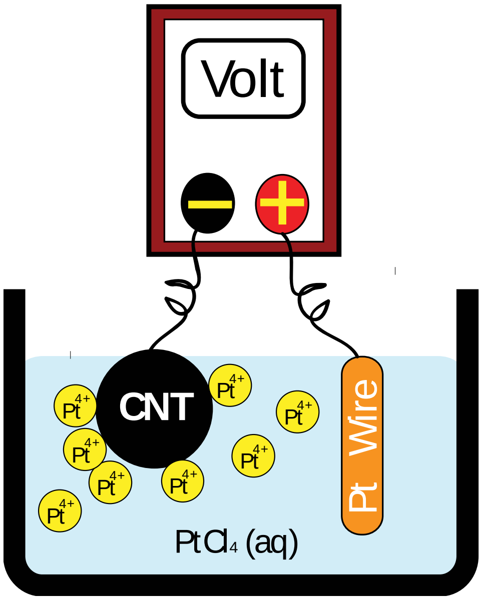


Figure 2.2 A schematic diagram showing the set up for electrochemical deposition of Pt on a CNT sheet.

2.3 Results

After the deposition process, the Pt/MWNT-COOH sheets were cut into small pieces for SEM (scanning electron microscope) imaging and EDX (energy dispersive x-ray) spectroscopy. Figure 2.4 is a high resolution SEM image of a Pt/MWNT-COOH sheet. A lower resolution SEM image is shown on Figure 2.5. The presence of Pt is confirmed by the EDX spectrum from the sample shown in Figure 2.6. Besides showing the presence of C and Pt in the sampling area, the EDX spectrum also displayed relatively strong signals from K and O [26]. The oxygen peak is likely to be from the –COOH functional groups on the CNTs and K peak is due to the presence of K_2PtCl_6 impurity in $PtCl_4$. The quantitative data shown in Table 2.1 indicate the presence of 1.7 at wt% of Pt in the sample.

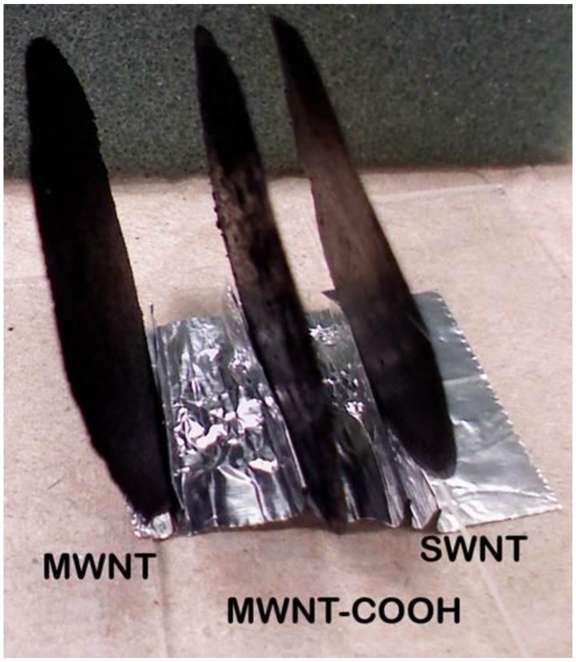


Figure 2.3 Digital photographs of cut pieces of as-prepared MWNT, MWNT-COOH and SWNT sheets.

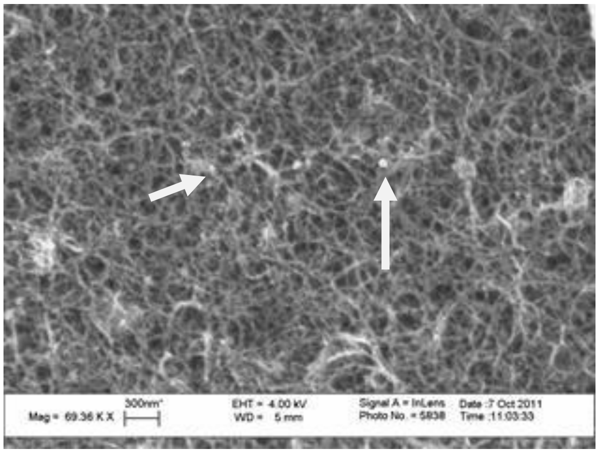


Figure 2.4 High resolution SEM image of MWNT-COOH sheet after Pt electrodeposition. Arrows point to some of the Pt nanoparticles with about 20-50 nm diameter.

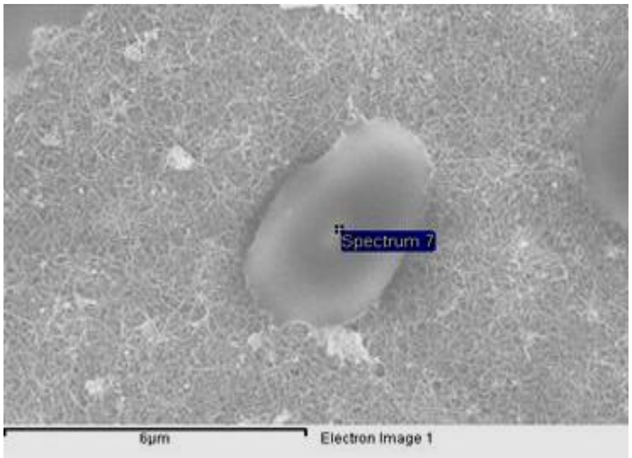


Figure 2.5 Lower resolution SEM image of Pt-decorated MWNT-COOH sheet showing a large Pt from which EDX data shown in Table 2.1 were obtained.

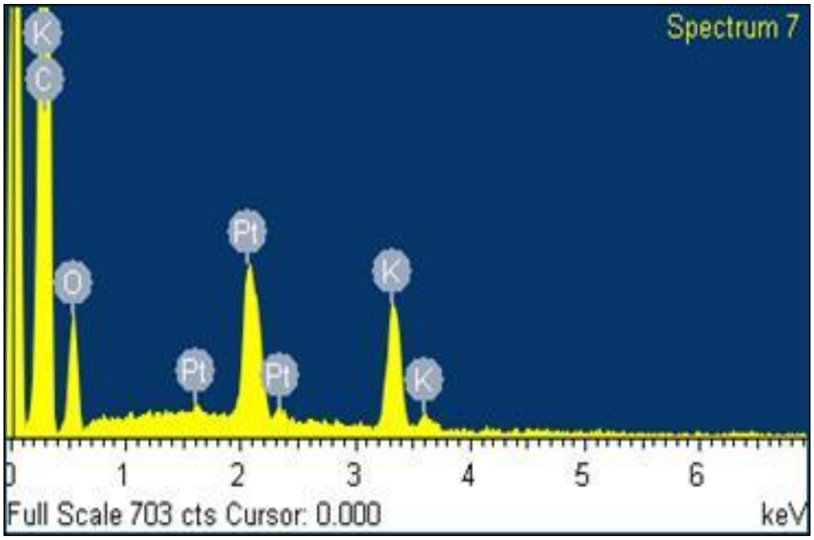


Figure 2.6 EDX spectrum from Pt-decorated MWNT-COOH sheet.

Table 2.1 EDX results in wt% and atomic wt% of the elements.

Element	Weight%	Atomic wt %
C	67.36	86.16
O	10.06	9.66
K	7.66	3.01
Pt	14.92	1.71

CHAPTER 3

ELECTROCHEMICAL DEPOSITION OF PLATINUM PARTICLES ON CARBON NANOTUBE SHEETS BY CYCLIC VOLTAMMETRY

This chapter describes a different approach for electrodeposition of platinum particles on the surface of carbon nanotube sheets. This technique involves using a potentiostat under cyclic voltammetric conditions. Through cyclic voltammetry (CV), the experimental setup was used to evaluate the efficiency of coating platinum particles on carbon nanotube (CNT) substrates compared with electrodeposition (ED) using a power source discussed in the previous chapter. These surface modified CNT substrates are used to run the experiments of electrochemical hydrogen storage of hydrogen, which will be described in next chapter entitled “Hydrogen Storage Application”. Scanning electron microscope (SEM) images were taken to examine the existence, morphology, and homogeneity of platinum particles on the CNT sheets. Energy-dispersive X-ray (EDX) spectroscopy measurements were used to analyze the elements on the modified substrates.

3.1 Overview

3.1.1 Applications of Carbon Nanotube Sheets

Porous carbon materials have attracted interest for applications in many different areas, such as gas sensor, gas storage, catalyst-support, and electrochemical devices [27]. Different methods to synthesize and form macroscopic sizes of CNT paper or thin films (sometimes called buckypapers) are continuing to be developed to produce a larger area (e.g., d = 10 cm) and more flexible to fold in desirable shapes [28]. Multi-walled carbon nanotube (MWNT) papers or thin films of CNTs have been reported for making gas sensors (e.g., H_2 sensor) using Pd-decorated-MWNT paper [29].

To reach the ability to transfer electrons for applications, the supporting substrate should be highly electrically conductive; hence, the highly conductive CNTs can be a good candidate to act as a new substrate for metal catalysts to from new metal/CNT composites [30]. There are many new developments that suggest using carbon materials as supporting backbone for catalysts as electrodes, either in anode or cathode, to improve fuel cell performance. For anodic material in lithium-ion batteries, metal-oxide/CNTs nanocomposite (i.e., TiO_2/CNTs) has been investigated as potential anode materials through electrochemical procedure in a cyclic voltammetry experiment [31]. In one of the applications, direct methanol fuel cells (DMFCs) used CNT supports as Pt/CNT composites in order to solve the slow reaction rate of the cathodic oxygen reduction reaction (ORR) [32]. Many investigations have focused on fabrication of novel metal (e.g., Ag, Au, Pt)-decorated-CNTs [33]. However, it is a challenge to produce metal/CNT working electrodes by depositing metals on CNTs substrates [34]. Hussein et al. reported using multi-walled carbon nanotubes to fabricate buckypapers, and then using the buckypaper as substrate to deposit platinum nanoparticles catalysts as biocathodes for glucose biofuel cells [35]. The goal was to reduce expensive platinum consumption, and still maintain catalytic activities. Using CNTs as supporting substrate can also reduce the occurrence of catalyst agglomeration that improves the effectiveness of biofuel cells. Nanocomposites of Pt/CNTs were used as oxygen reduction reaction (ORR) cathodes, and the conductivity was measured in a three-electrode electrochemical cell using a potentiostat/galvanostat apparatus and cyclic voltammetry techniques.

3.1.2 Electrochemical Deposition Using Cyclic Voltammetry

Electrodepositon is a process that is widely used. Electrodeposition can be performed by different techniques, such as electrolytic deposition, electrophoretic deposition, etc. In this study electrochemical deposition was carried out by cyclic voltammetry using a potentiostat-galvanostat.

Electrochemical cyclic voltammetry is a standard method for characterization of solution-based metal deposition [36]. Electrochemical deposition can also be performed using cyclic voltammetry. Schilling and co-workers demonstrated electrochemical deposition preparation of a composite of multi-walled carbon nanotubes and iron-nitrogen compounds on a glassy carbon electrode through a potential deposition technique by running controlled cyclic voltammograms in a defined potential range [37].

Cyclic voltammetry (CV) is a potentiodynamic electrochemical method to investigate redox (reduction and oxidation) reactions. A cyclic voltammetry experiment comprises of three electrodes: a working electrode, a counter electrode, and a reference electrode. The working electrode potential varies linearly with time while the reference electrode maintains a constant potential. The current from the signal source to the working electrode is conducted by the counter electrode. The electrolytic solution plays the role of providing ions to the electrodes during the redox reactions [38, 39]. The cyclic voltammetry cycle starts by adding potential voltages to the working electrode. Cyclic voltammetry then scans from the initial potential to the set one by using a chosen scan rate [40]. When a set potential is reached, the working electrode potential is reversed [41, 42]. Cyclic voltammetry is now widely used in obtaining qualitative information about electrochemical processes. For example, the presence of intermediates in oxidation reactions and reduction reactions as well as the reversibility of a reaction can be determined by CV measurements. Furthermore, a system’s electron stoichiometry, an analyte’s diffusion coefficient, and the formal reduction potential can be determined by using CV technique.

Cyclic voltammetry can also be used for electrochemical deposition (ECD). Electrochemical deposition is a valuable method to create nanostructures. Stroeve’s group in UC Davis reported fabrication of a nanocable using ECD to grow Te on the surfaces of Au nanotubes for 14 hours approaching layer-by-layer deposition [43]. Cyclic voltammetry can be used to perform both deposited under direct potential control and monitor/characterized the electrochemical responses of Au nanoparticles on SWNT/SiO_2 surface [44]. Nowadays, there are many evolutions in nanomaterials to find new carbon materials (such as, carbon nanotubes and graphene) for better applications. Composition of polypyrrole, one of the comducting polymers with widely attention for many applications, on single-layer of sulfonated graphene sheets was achieved using a potentialstat-galvanost and the evaluation of the ECD performance was also using the same electrochemical workstation by the cyclic voltammetry technique [45]. Hence, electrochemical deposition is a very useful procedure to deposit metals on a highly conducting substrate, and cyclic voltammetric technique can help achieve ECD.

In this chapter, three types of carbon nanotubes sheets fabricated as described in the previous chapter, were used as the supporting substrate to electrochemically deposit platinum particles on the nanotube surface.

3.2 Experiments

Materials: Three types of CNT sheets, SWNTs, MWNTs and MWNTs-COOH, were used as substrates. Platinum (IV) Chloride ($PtCl_4$, >= 99.99% metals basis, Sigma-Aldrich) was used as received as the electrolyte for platinum deposition. Platinum wire (CHI115) counter electrode and Ag/AgCl standard electrode were purchased from CH Instruments, Austin, TX.

Equipment: Electrochemical processes were performed with a computer-controlled CHI 832C analyzer/workstation detector system (CH Instruments, Austin TX) using cyclic voltammetry technique. Images and analysis of percentage elements were obtained from a Field Emission Scanning Electron Microscope Energy Dispersive X-ray spectroscopy - LEO 1530 VP FE-SEM/EDX at NJIT and Hitachi S-4800 FE-SEM at Rutgers University, Newark.

Procedure: Experiment was performed using a three-electrode setup carried out by cyclic voltammetry using a CHI 832C workstation. As-prepared CNTs (SWNT, MWNT and MWNT-COOH) sheets cut into half (ca. semi-circle, 5.1 cm^2) were used as the working electrode. A platinum wire served as the counter electrode. Silver chloride electrode

(Ag/AgCl), a silver wire coated with silver chloride thin layer, was used as the reference electrode. The electrolyte was 1mM $PtCl_4$ aqueous solution prepared by dissolving 10 mg $PtCl_4$ in 30 mL de-ionized water. Figure 3.1 illustrates the setup of the cyclic voltammetry experiment.

In the analyzer (CHI 832C workstation), a scan rate of 10 millivolt per second was selected for two hours duration of cyclic voltammetry to deposit platinum particles on the CNTs, SWNT, MWNT, and MWNT-COOH, substrates. The Pt/CNT paper was then washed with de-ionized water several times to thoroughly remove additional platinum particles dangling on the surface. After washing, the Pt/CNT substrate was dried at ambient temperature overnight.

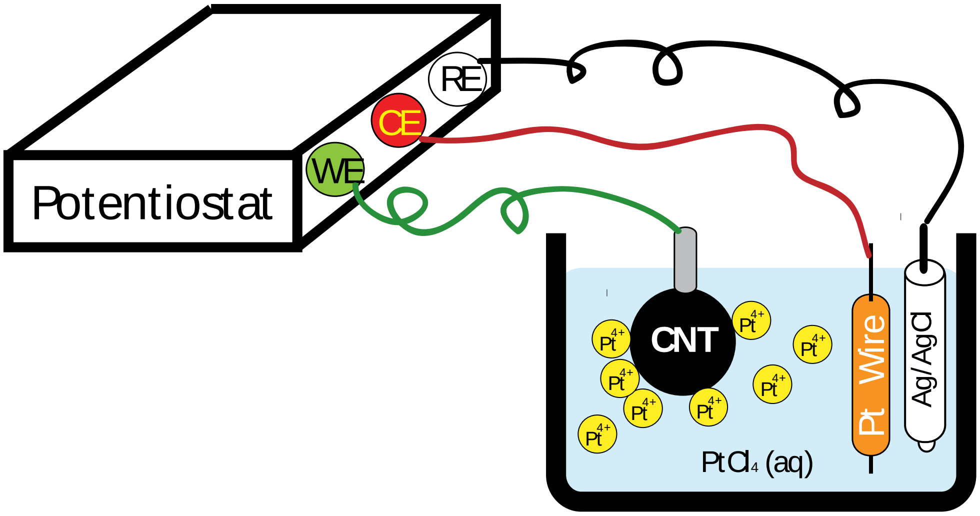


Figure 3.1 Schematic showing the three-electrode method of electrochemical deposition of Pt on the CNT sheet working electrode using cyclic voltammetry. A Pt wire is the counter-electrode and Ag/AgCl is the reference electrode.

3.3 Results

Figure 3.2 shows the cyclic voltammetry data during Pt deposition on different types of carbon nanotubes. After cyclic voltammetry, the morphology and compositions of the three different Pt/CNT substrates were evaluated using scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX or EDS). The nanocomposite sheets were cut into small pieces (ca. 0.04 cm^2) to investigate the distribution and homogeneity of platinum particles attached to the surface of three different types of CNTs sheets using SEM imaging and EDX analysis. The image and quantitative EDX analysis of the Pt/MWNT-COOH sheet shown in Figure 3.3 were obtained using a LEO 1530 VP FE-SEM microscope with EDX. In comparison for different types of nanocomposite on CNT-sheets, the SEM images were obtained using a Hitachi SEM microscope in Figure 3.4. The images for Pt/SWNT (Fig 3.4a) and Pt/MWNT-COOH (Fig 3.4b) display the cluster form of platinum particle aggregating on the surface of the carbon nanotubes, but the images in Fig 3.4c and 3.4d (in different magnitude) display a well dispersion homogeneous structure of particles distribute well on the top of the MWNT sheet.

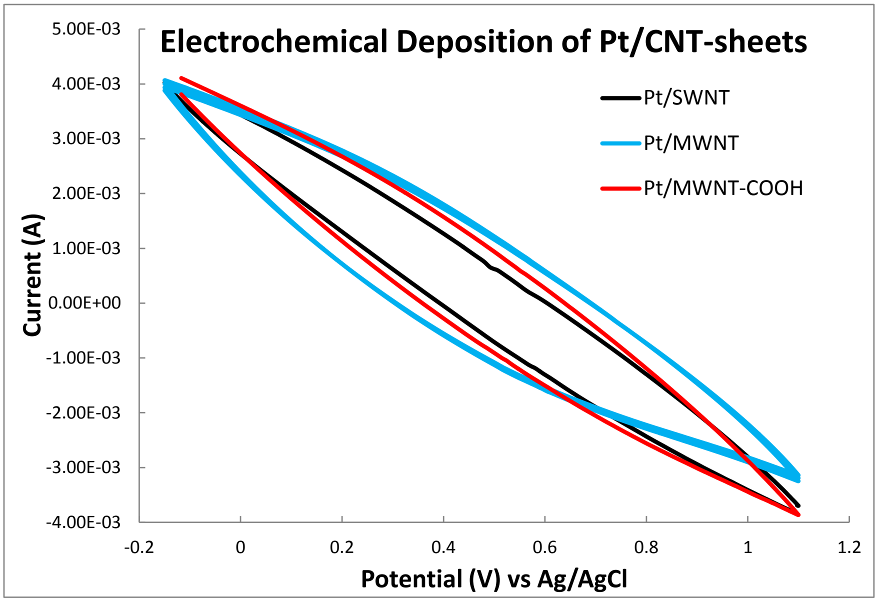


Figure 3.2 Cyclic voltammetry scans for Pt deposition on three types of CNT-sheets shown in the figure.

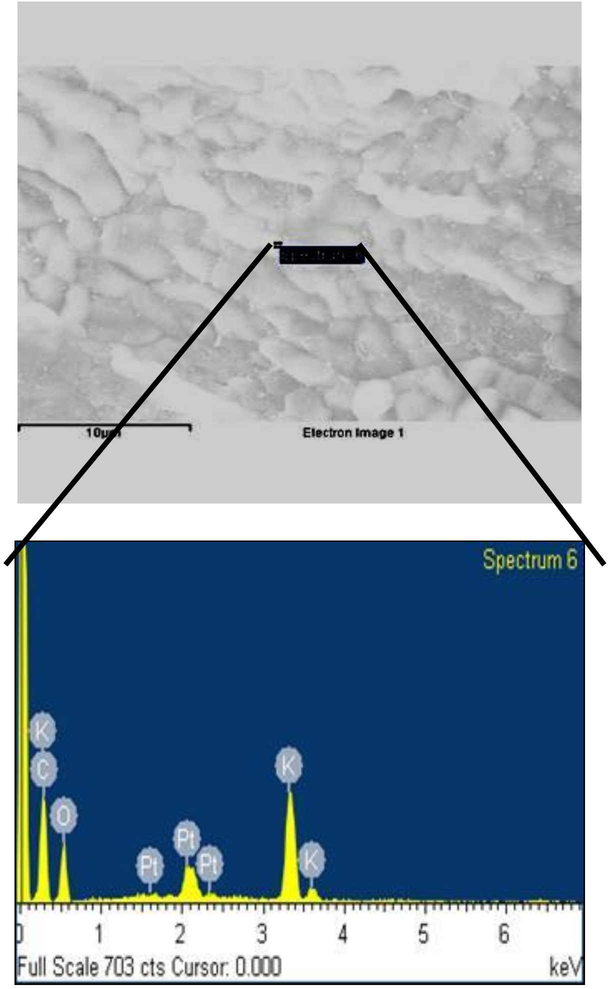


Figure 3.3 Low resolution SEM image of Pt/MWNT sheet (top), and the EDX spectrum (bottom) from the indicated location on the SEM image.

Table 3.1 Weight% and atomic weight % of the elements from the EDX spectrum.

Element	Weight%	Atomic%
C	27.04	47.70
O	25.03	33.15
K	32.18	17.44
Pt	15.75	1.71

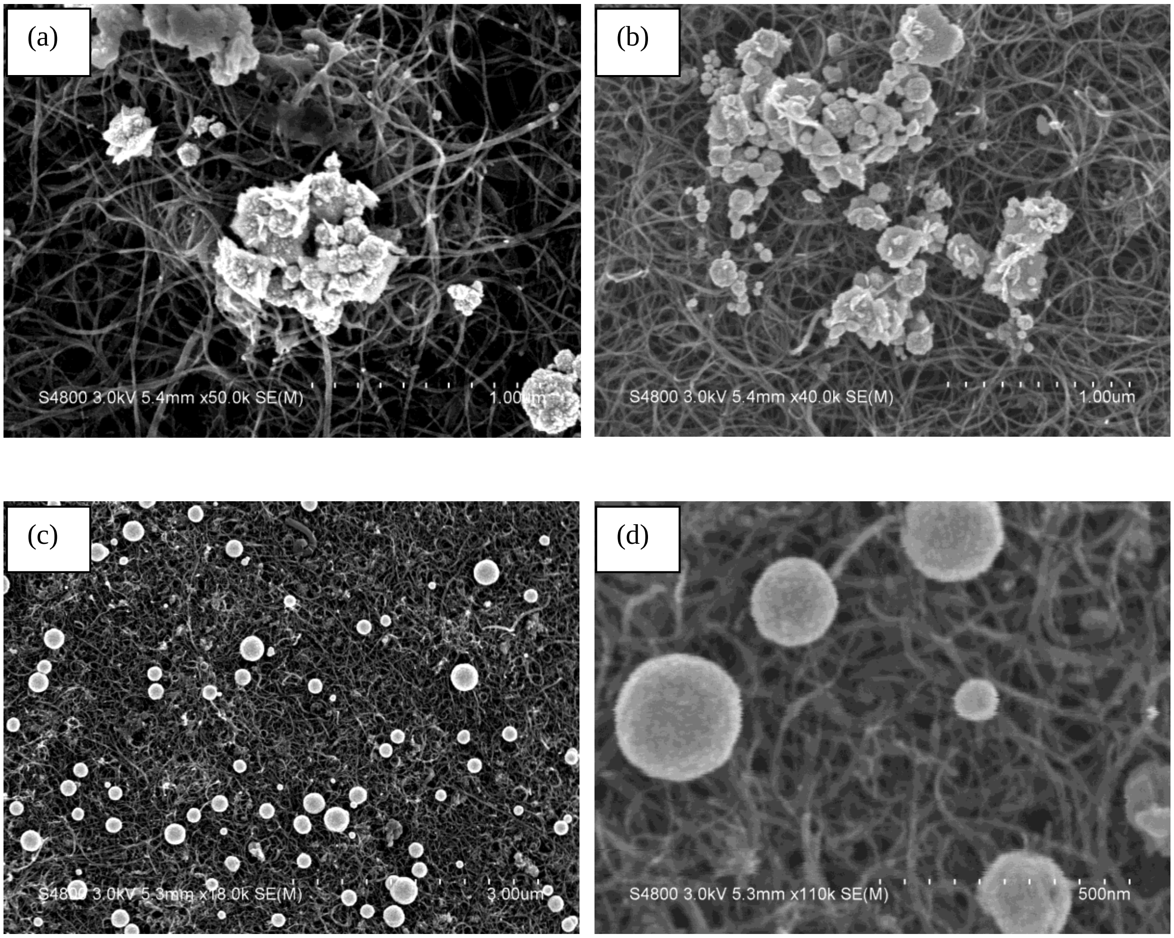


Figure 3.4 SEM images of electrochemically deposited Pt on SWNTs (a), Pt on MWNT-COOH (b), and Pt on MWNTs(c) and (d).

CHAPTER 4

INVESTIGATION OF HYDROGEN STORAGE

The ultimate goal of this project was to develop suitable materials for hydrogen storage. In this chapter, as-prepared pristine and modified CNT-sheets were used to evaluate their potential as hydrogen storage materials.

Carbon nanotubes sheets were prepared using single-walled, multi-walled, and carboxyl functionalized multi-walled nanotubes (Chapter 2). CNT sheets prepared were modified by deposition of platinum particles using electrodeposition employing a power source and by cyclic voltammetry, as discussed in previous chapters. In order to determine electrochemical hydrogen adsorption cyclic voltammetry (CV) was conducted on both surface-modified CNTs substrates as well as pristine ones in an alkaline 6 N KOH(aq) solution. Tested samples were then examined by temperature-programmed desorption (TPD) to determine whether or not hydrogen was stored on catalyst-modified and pristine CNT-sheets during cyclic voltammetry.

4.1 Overview

The potential of carbon nanotubes to store hydrogen has been investigated for almost two decades. In this section, the hydrogen storage capacities of different materials besides CNTs are briefly discussed in sect. 4.1.1, the cyclic voltammetry method to electrochemically store hydrogen in CNTs is discussed in sect. 4.1.2, and TPD measurements on electrochemically charged CNT sheets are discussed in sect. 4.1.3. A summary listing hydrogen storage experimental and theoretical results on different types of CNTs and graphene is provided in Table 4.1.

4.1.1 Candidate materials for hydrogen storage

Scientists and researchers have continued to search for new hydrogen storage materials since the best source has not been found yet. Different materials besides CNTs have been investigated for hydrogen storage. For example, Luzan et al. reported a 0.75 wt% for the maximal hydrogen storage capacity of a zinc-based metal-organic framework (MOF) [46], and Sakintuna et al. reported a competitive hydrogen storage capacity up to 7.6 wt% for a group of magnesium-based hydrides [47].

Carbon-based materials, such as carbon nanotubes (CNTs) and graphene, are also popular materials in many studies. Guo et al. investigated different thicknesses of single-walled carbon nanotube (SWNT) substrates for electrochemical hydrogen storage [48]. Zhang et al. investigated electrochemical hydrogen storage in pure multi-walled carbon nanotubes (MWNTs) with different diameters [49]. Lee et al. theoretically showed that the gravimetric capacity of hydrogen for a calcium-decorated zigzag graphene nanoribbon (ZGNR) is 5 wt% [50].

To enhance hydrogen storage capacity in CNTs, extra steps were taken to modify the surface of hydrogen storage media. As mentioned in Ch. 1, transition metals are now deposited on either CNTs or other substrates in order to enhance the hydrogen storage capacity. Yildirim and Ciraci reported 8 wt% of hydrogen adsorption in titanium-deposited single-walled carbon nanotubes in their theoretical work [51]. Yang et al. reported an electrochemical discharge capacity of 1404 mAh/g for a SWNT electrode with a coating of 8 wt.% Ni nanoparticles, which corresponded to 5.27 wt% hydrogen storage [52]. Some research group deposited alkali metals (e.g., potassium) rather than transition metals (e.g., platinum, palladium and titanium) onto the surface of CNTs. Chen et al. claimed hydrogen adsorption of lithium-and potassium-doped carbon nanotubes ranging from 14 wt% to 20 wt% when the temperature was raised from room temperature to 400℃ at ambient pressure [53]. Later work [54, 63] however showed only 2.5 wt%. of hydrogen storage in these materials.

4.1.2 Hydrogen storage measurement methods

Liu et al. reported mixing purified MWNT with KOH powder in order to deposit potassium on the nanotubes [54]. Most common electrochemical method to store hydrogen in CNTs is putting the CNT substrate as the working electrode in KOH aqueous solution followed by electrochemical reaction using cyclic voltammetry [55]. Nilsson's group from Stanford University exposed Pt/SWNT samples to hydrogen in a chamber and measured the hydrogen adsorption by changes in electrical conductivity of the SWNTs [56].

4.1.3 Measurement of hydrogen storage

When it comes to characterize the gas phase hydrogen sorption properties, three techniques, volumetric methods, gravimetric methods and temperature-programmed desorption (TPD), have been widely used [57].

In volumetric methods, also known as the Sieverts method, the hydrogen sorption or uptake is measured by monitoring the drop in hydrogen pressure in a system of a fixed, known volume, with desorption being monitored by an increase in pressure. Reilly et al.

were the early group using the volumetric technique to detect hydrogen adsorption in alloys [58]. Zacharia et al. used a Sieverts apparatus to explore hydrogen storage capacities of Pd- and V-doped CNTs [59].

In gravimetric methods, the hydrogen uptake is measured by monitoring the mass of the sample following a step change in the hydrogen pressure. Benham et al. used a fully computer-controlled gravimetric system to assess hydrogen adsorption [60].

Temperature-programmed desorption (TPD), the technique employed in this project in collaboration with the group of Prof X. Wang of Chem. Eng. NJIT, is used to determine the quantity of hydrogen desorbed following the application of a thermal ramp. The reason that research groups prefer TPD is the small sample sizes that can be used, typically in the region of a few mg. Panella et al. used thermal desorption spectroscopy (TDS, also known as TPD) in their study to investigate hydrogen physisorption and determine the quantitative amounts of hydrogen stored in SWNTs [61].

Table 4.1 Summary of different catalysts and media used for hydrogen storage together with corresponding wt% of hydrogen adsorbed theoretically and experimentally.

Catalyst	Media	H_2 adsorption	References
Ca	graphene nanoribbon	5.00 wt%*	[49]
Ti	graphene nanoribbon	8.00 wt%*	[50]
Ti	SWNT	8.00 wt%*	[51]
K	SWNT	1.80 wt%	[61]
Cu	SWNT	2.90 wt%	[62]
Li	SWNT	2.50 wt%	[63]

*****Theoretical estimates

4.2 Experiments

Materials: Carbon nanotube sheets prepared from SWNT, MWNT and MWNT-COOH were prepared by methods described in chapters 2 and 3. The following three sets of nanotube sheets for use as working electrodes were fabricated: Pristine CNT sheets, Pt-deposited-CNT sheets using cyclic voltammetry (abbr. Pt/CNT-CV), and Pt-deposited-CNT sheets using electrodeposition (abbr. Pt/CNT-ED). Ag/AgCl was used as the reference electrode and a platinum wire was used as the counter electrode in the cyclic voltammetry experiments. Potassium hydroxide pellets were purchased from Fisher Scientific (CAS# 1310-58-3) and dissolved in deionized water to prepare the electrolyte solution.

Procedures: Hydrogen storage experiments were performed using a three-electrode setup with three different types of CNTs sheets comprising of Pt-coated and uncoated SWNTs, MWNTs and MWNT-COOH's. The experimental setup was the same as that used in the previous chapter for Pt deposition except that the electrolyte used was 6 N KOH(aq) prepared by dissolving 10.099 g KOH in 30 mL de-ionized water. Figure 4.1 shows the CV setup used for carrying out electrochemical hydrogen storage.

The scan rate was set at 5 millivolt per second for two hours duration in the potentiostat-galvanostat workstation to investigate the capability of hydrogen storage of the nanotube sheets under cyclic voltammetry. The scan rates for three substrates, Pt/MWNT-COOH-ED, MWNT-COOH and MWNT, were variable under the set conditions and had to be adjusted so that the CV could be run smoothly. After the CV runs the substrates were washed with de-ionized water and dried at ambient temperature. Temperature-programmed desorption (TPD) measurements using an AutoChem 2920 II system (Figure 4.1c) were then carried out on the substrate to determine the hydrogen adsorbed on the samples. The sample weights were MWNT-COOH (0.0021g), MWNT-COOH in KOH (0.0116g), Pt/ MWNT-COOH by CV in KOH (0.0107g), and Pt/ MWNT-COOH by ED in KOH (0.0100g). After 10 mL/min He flow was introduced to purge the samples for 30 minutes, the samples were heated up to 550 °C at 10 °C /min under He flow to detect the hydrogen released.

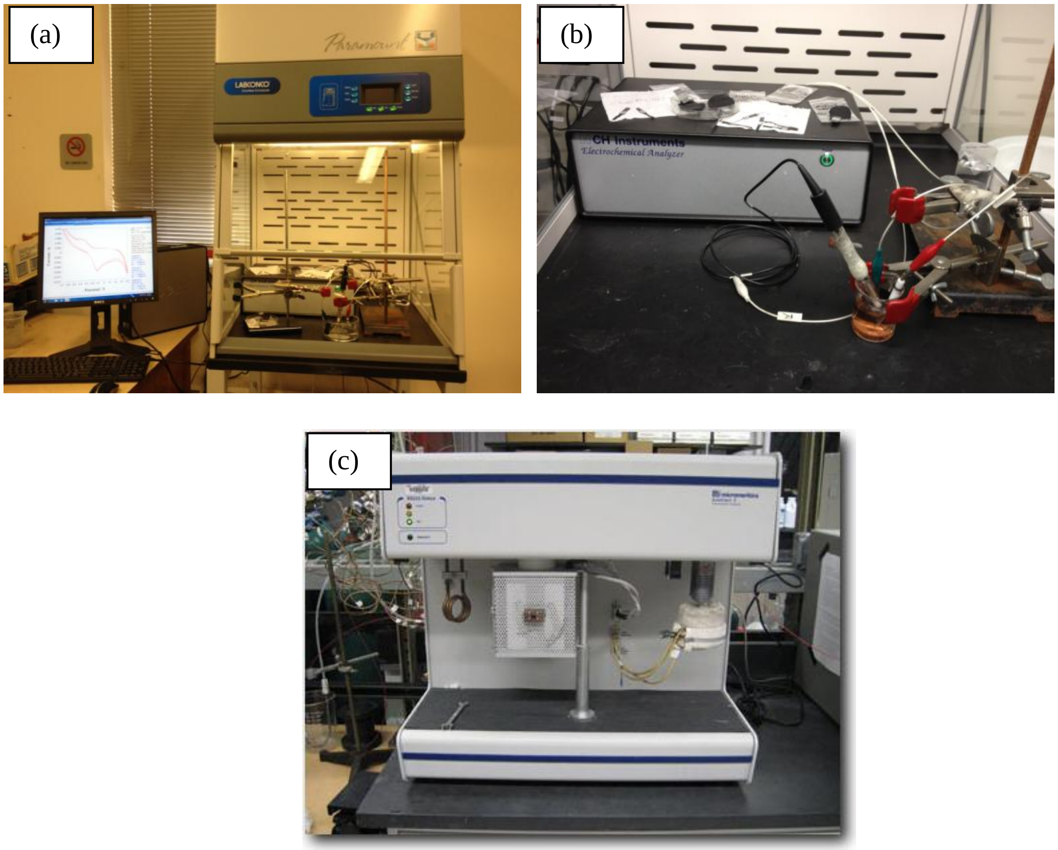


Figure 4.1 Panels (a) and (b) show set up for electrochemical charging of CNT sheet working electrodes with hydrogen - (a) Depicts overview of the experiment carried out in a portable hood showing the computer monitor, analyzer-workstation and electrochemical cell, and (b) Depicts close-up view of the analyzer- CHI 832C workstation and electrochemical cell. Panel (c) shows the AutoChem 2920 II used for the TPD measurements.

4.3 Results

CV data were recorded in 6 N KOH aqueous solution without any pretreatment (e.g., purging gas) at room temperature. The data for three sets of carboxyl functionalized MWNT sheets: As-prepared MWNT without platinum catalyst (MWNT-COOH), deposited Pt on MWNT using cyclic voltammetry (Pt/MWNT-COOH CV), deposited Pt on functionalized MWNT using by electrodeposition (Pt/MWNT-COOH ED), are shown in Figure 4.2. The platinum particle sizes are smaller under ED (ca. 20-50 nm shown in Fig 2.4) than those deposited using CV (ca. 100nm in clusters shown in Fig 3.4b). SEM images from Pt deposited on MWNT-COOH by both ED and CV methods showed that the particles were much larger than optimum sizes of 6 nm for typical catalytic particles. Hence in Fig. 4.2, the CNT sheet with Pt catalyst deposited by CV did not demonstrate sharp CV peaks due to the following redox reactions in KOH solution which generate hydrogen:

Reduction: $$2K^{+} + 2e^{-} \rightarrow 2K \qquad (4.1)$$

Oxidation: $$2OH^{-} \rightarrow 2OH\bullet + 2e^{-} \rightarrow O_2 + H_2 \qquad (4.2)$$

However a reduction or cathodic CV peak only is observed for the CNT sheet with catalyst deposited by ED indicating that a net cathodic reaction occurs when smaller size Pt particles are present on the working electrode. In Figures 4.3 and 4.4, CV measurements using unfunctionalized MWNT and SWNT sheets with and without catalyst deposited by CV and ED methods did not show either cathodic or anodic CV peaks. Figure 4.5 showed that pristine MWNT-COOH without catalyst coated only displays redox reactions, whereas both pristine MWNT and SWNT sheets do not display redox reactions. In Figure 4.6, Pt/MWNT-COOH (ED) showed clear electrochemical reaction compared with similarly Pt coated, unfunctionalized MWNT and SWNT sheets indicating as above that the –COOH group functionalized MWNT sheets are the most reactive. –COOH group functionalized SWNT sheets, however, were not tested in this work. In Figure 4.7, Pt/MWNT-COOH (CV) as well as similarly Pt coated MWNT and SWNT sheets did not show redox peaks.

In summary these results show that substantial redox reactions occur only on –COOH functionalized MWNT sheets. Therefore TPD measurements were carried out on the three types of MWNT-COOH sheets that were Pt coated by ED, Pt coated by CV and uncoated, relative to a control sample without Pt coating and electrochemical treatment in 6 N KOH solution. The TPD results shown in Figure 4.8 and 4.9, and Table 4.2 do indeed confirm hydrogen storage in the samples with weight percentages below 1% showing an increase in adsorption with Pt coating and decrease in Pt particle. Since the Pt particle sizes obtained here are an order of magnitude below optimum catalyst values, it is expected that a substantial increase in hydrogen adsorption would occur with reduction in Pt size.

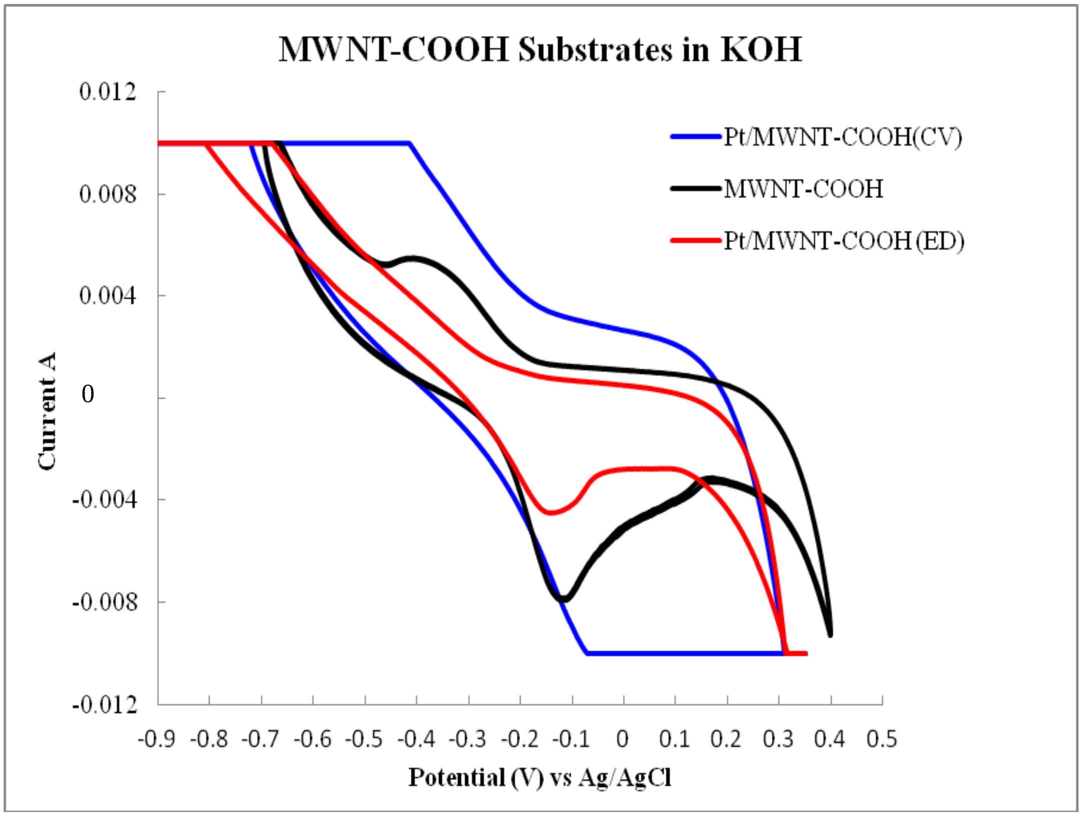


Figure 4.2 CV scans in 6 N KOH using MWNT-COOH sheets as working electrodes: Pristine MWNT-COOH (black), Pt/MWNT-COOH CV (blue), and Pt/MWNT-COOH ED (red).

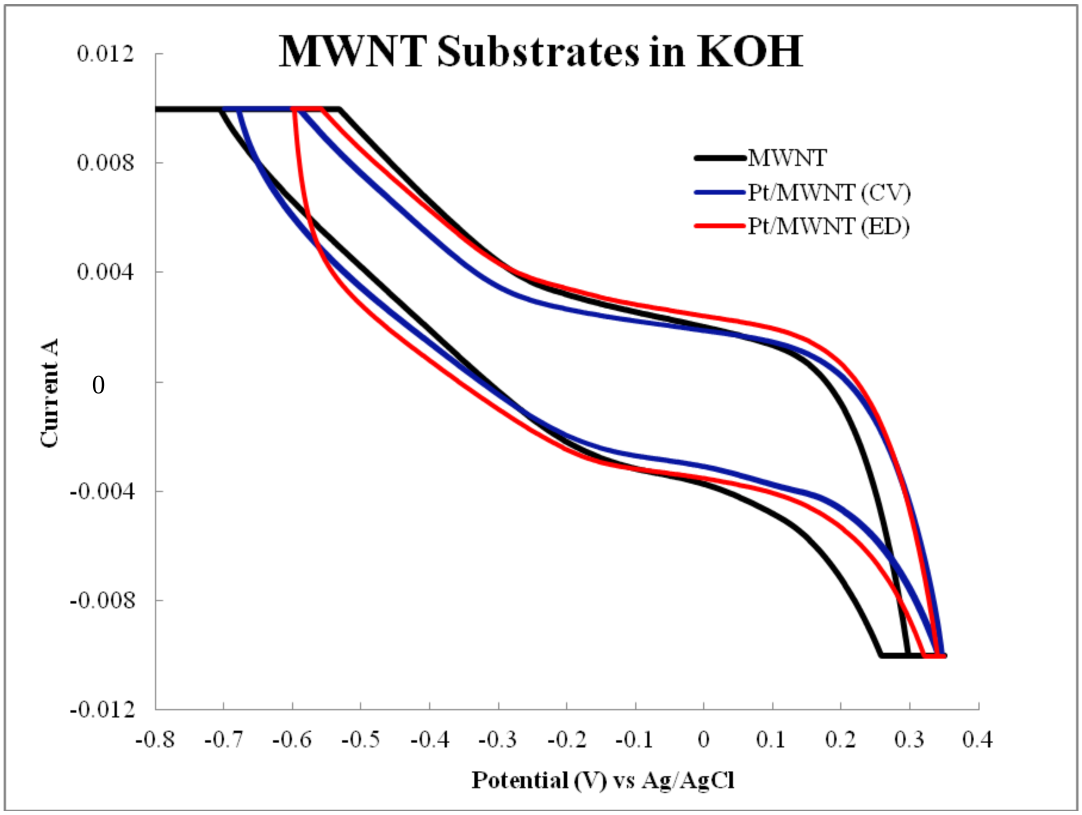


Figure 4.3 CV scans in 6 N KOH using MWNT sheets as working electrodes: Pristine MWNT (black), Pt/MWNT-COOH CV (blue), and Pt/MWNT ED (red).

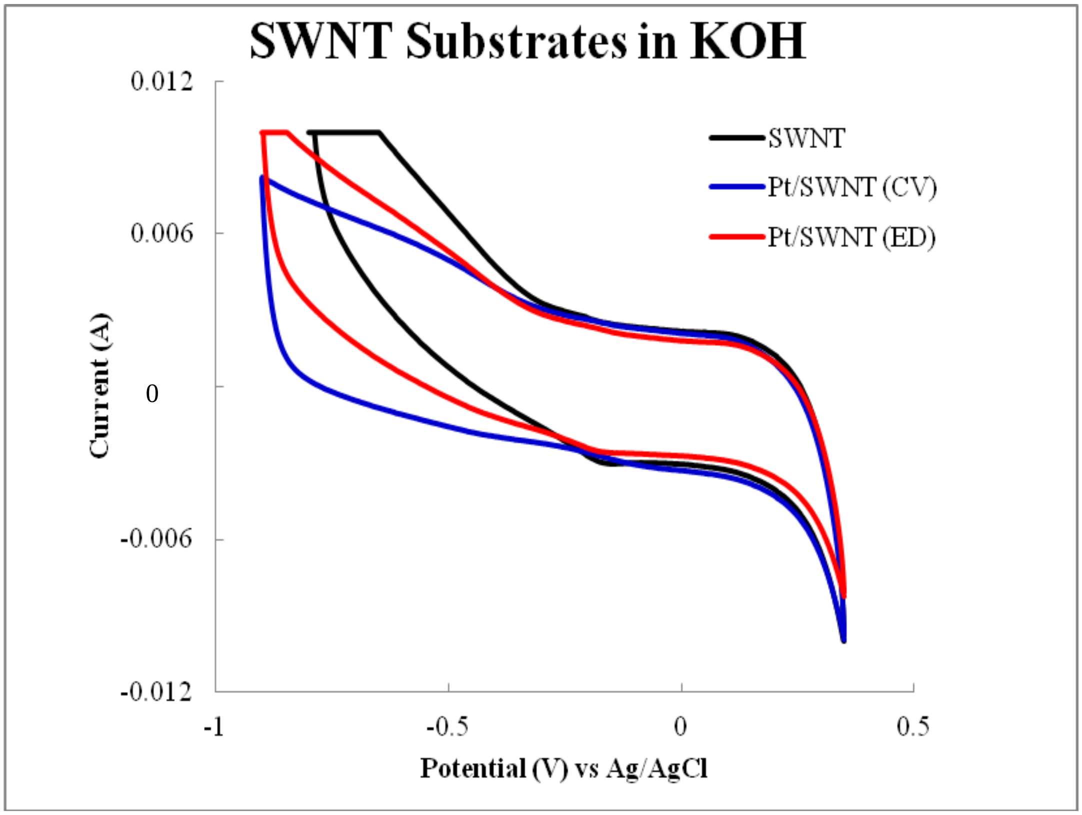


Figure 4.4 CV scans in 6 N KOH using SWNT sheets as working electrodes: Pristine SWNT (black), Pt/SWNT CV (blue), and Pt/SWNT ED (red).

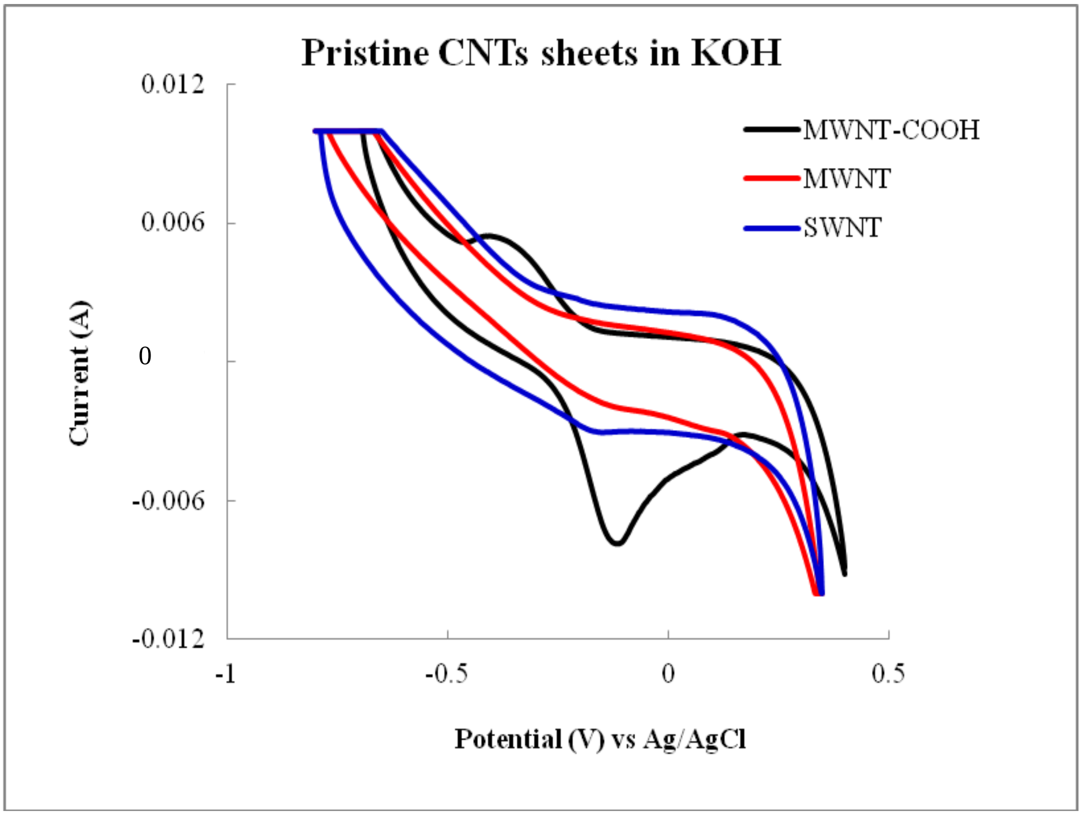


Figure 4.5 Comparison of CV scans from three types of pristine CNT-sheets, MWNT-COOH (black), MWNT (red) and SWNT (blue) in 6 N KOH.

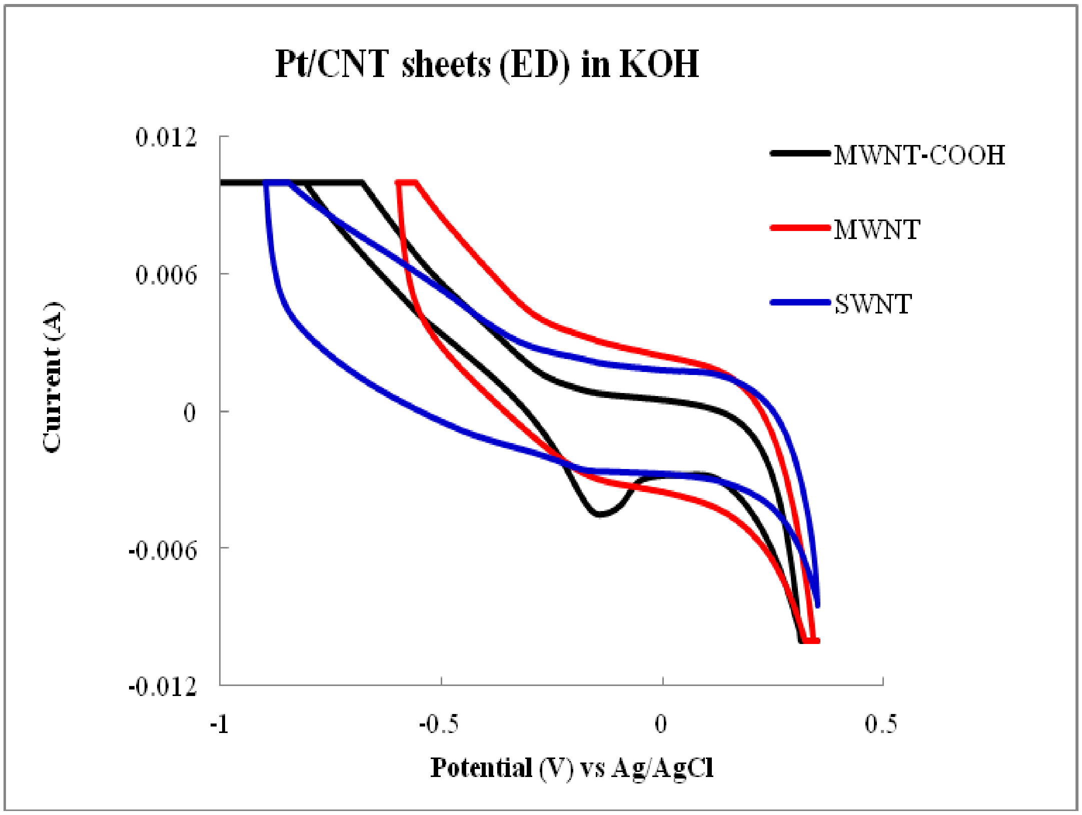


Figure 4.6 Comparison of CV scans from three types of ED deposited Pt CNT sheets in KOH, MWNT-COOH (black), MWNT (red) and SWNT (blue).

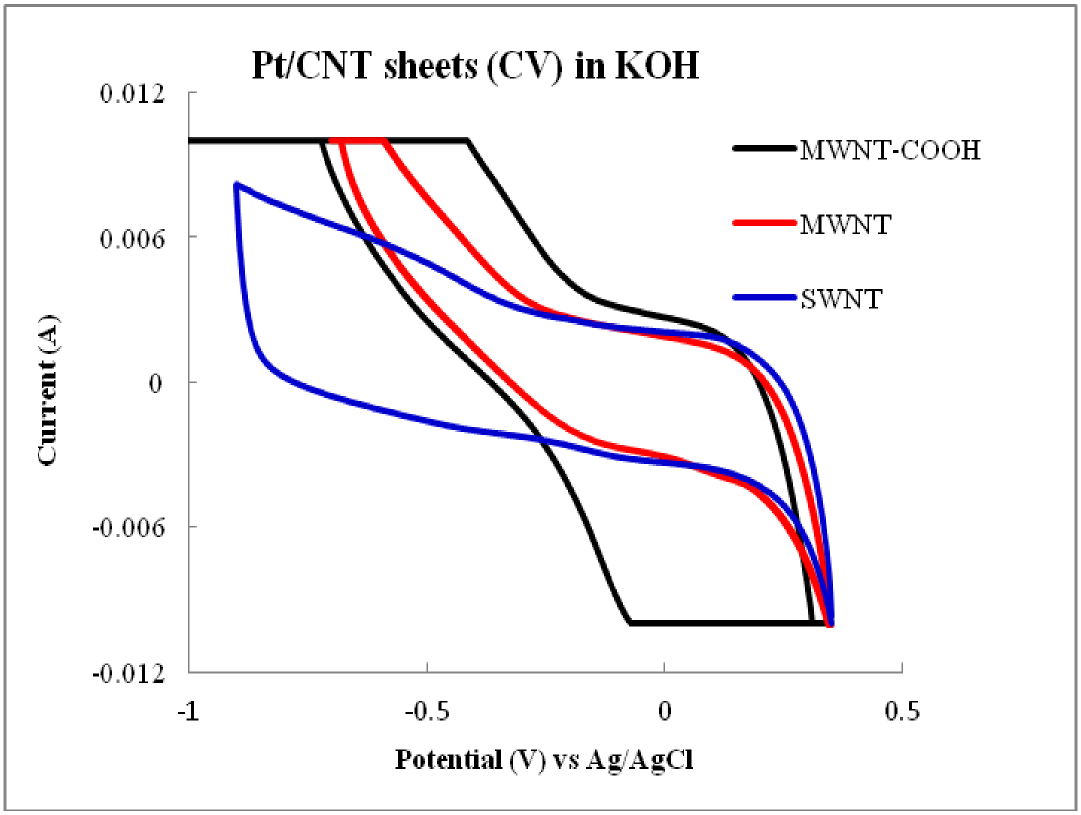


Figure 4.7 Comparison of CV scans from three types of CV deposited Pt- CNT sheets in KOH, MWNT-COOH (black), MWNT (red) and SWNT (blue).

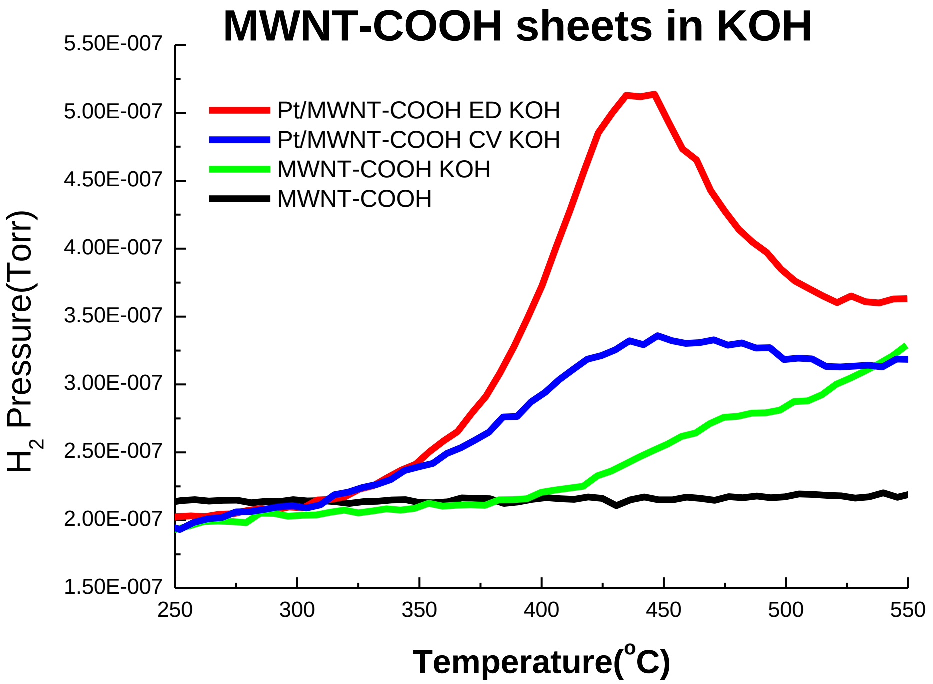


Figure 4.8 Comparison of TPD scans from ED (red) and CV (blue) Pt-coated and uncoated (green) MWNT-COOH sheets relative to MWNT-COOH sheet that had not been electrochemically treated or coated (black).

Table 4.2 Weight % of hydrogen on different MWNT-COOH substrates calculated from the TPD data.

Sample	H_2 Storage Amount (mol H_2/g CNT)	wt% H_2
MWNT-COOH	0	0.00
MWNT-COOH in KOH	0.92×10^{-3}	0.18
Pt/MWNT-COOH (CV) in KOH	1.50×10^{-3}	0.30
Pt/MWNT-COOH (ED) in KOH	2.33×10^{-3}	0.47

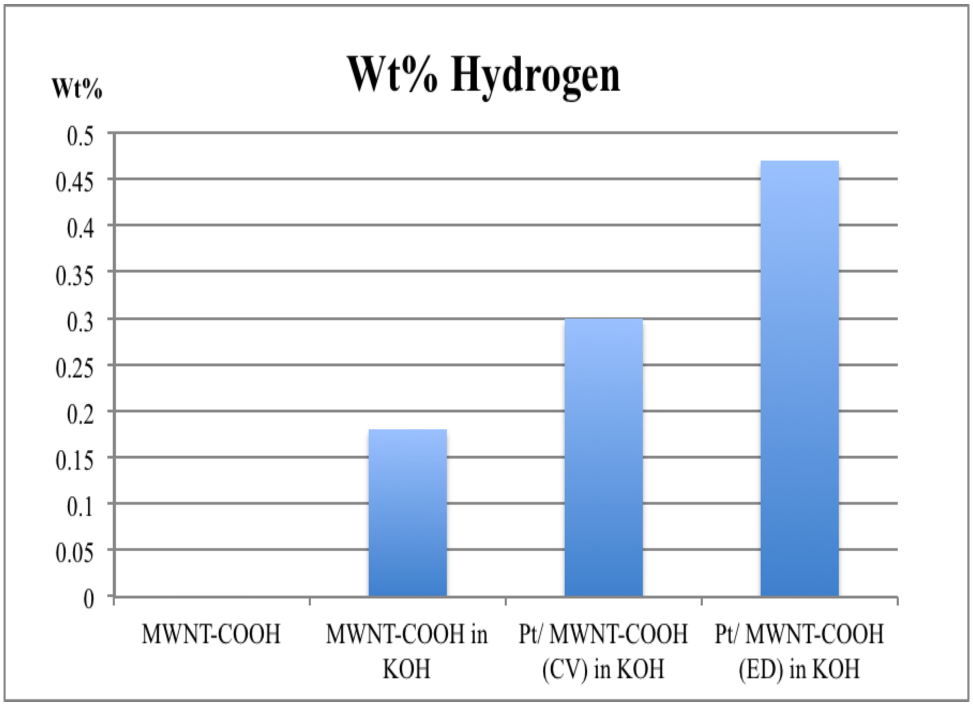


Figure 4.9 Comparison of weight % hydrogen adsorption on MWNT-COOH substrates by CV and ED methods, without Pt deposition, and without either Pt deposition or electrochemical treatment (as reference background).

CHAPTER 5

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In summary, three different types of carbon nanotubes, single-walled, multi-walled, carboxyl functionalized multi-walled carbon nanotubes, were made into sheets. These different types of CNT sheets were coated with transition metal platinum catalysts. Two electrochemical methods, cyclic voltammetry (CV) and electrodeposition (ED), were used to deposit Pt particles on the SWNT, MWNT, and MWNT-COOH sheets. SEM images were examined for the existence and homogeneity of the platinum particles attached to the carbon nanotube (CNT) substrates. EDX spectra were used to analyze the elemental composition on the substrates. After deposited Pt, CNTs sheets went for hydrogen storage experiment by placing the Pt/CNTs nanocomposite substrates in 6 N KOH aqueous solutions and carrying out cyclic voltammetry. Temperature-programmed desorption (TPD) measurements were then used to determine the weight % of hydrogen adsorbed.

SEM images in Ch. 2 of Pt/MWNT-COOH by ED showed smaller size of platinum particles (ca. 20-50 nm) while SEM images in Ch. 3 showed that the platinum particles in Pt/MWNT-COOH by CV had a larger average size (ca. 50-100 nm) with a lot of agglomerated clusters. From the TPD measurements, Pt coated CNT substrates using both methods showed better hydrogen storage capacity than the pristine CNT, which showed not only that using transition metal as catalyst improved hydrogen storage capability, but the data also indicated that this project was on the right path. The hydrogen capacity of Pt/MWNT-COOH by ED was better than that of Pt/MWNT-COOH by CV based on the TPD data. This suggests that the smaller the nanoparticle size the better the hydrogen storage capability. However, the overall hydrogen uptake remains below 1 weight % indicating that further improvements are necessary.

The US Department of Energy (DOE) announced a 6.0 wt% target for on-board hydrogen storage for automobiles in 2010 and a 9.0 wt% target by 2015. None of the more conventional storage methods (compression, liquefaction, or storage as metal hydrides) can meet these targets [64]. However, emerging materials such as MOFs, boron nanotubes, and carbon nanotubes or graphene modified as nanocomposites by metal deposition or infiltration into porous networks, could potentially provide this level of storage capability. To improve the performance of electrochemical hydrogen storage, future studies on CNTs to improve performance are proposed as follows:

(1) Decrease catalyst particle size to near 5 nm using pulsed electrochemical deposition or sputtering, and optimize CNT sheet thickness.
(2) Using different types of functional groups, for example, amine functional group, NH_2 on the sidewall of the CNTs.
(3) Evaluate transition metals other than Pt, such as Ti, and also a non-transition metal such as Ca, deposited on the CNTs.
(4) Use both TPD and electrochemical discharge methods to obtain a more accurate percentage of hydrogen stored.

Once a material with high electrochemical hydrogen uptake is found, measurements on the material as a function of temperature and pressure using direct hydrogen adsorption techniques can be carried out.

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