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Carbon nanotubes and conducting polymer composites

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CERTIFICATION

I, May Tahhan, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institute.

May Tahhan

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List of Schemes

List of Abbreviations

1D	One Dimension
2D	Two Dimensions
1,2-DCB	1,2-Dichlorobenzene
AA12BE	Allyl alcohol 1,2-butoxylate ethoxylate
Abs.	Absorbance
AC	Alternating Current
AFM	Atomic Force Microscopy
Ag/AgCl	Silver/Silver-chloride
AHFP	Ammonium hexaflurophosphate
AIBN	2,2`-azobisisobutyronitrile
Au	Gold
BC	Benzalkonium chloride
C	Carbon
CNT	Carbon Nanotubes
CO	Carbon monoxide
CO_2	Carbon dioxide
CV	Cyclic Voltammetry
CV	Cyclic Voltammogrames
DDAB	Didodecyldimethyl ammonium bromide
Dex	Dextran sulfate
DNA	Deoxyribose Nucleic Acid

DOS	Density Of State
E	Chemical Potential
Fe	Iron
FMWCNT	Functionalized Mutli-Walled Carbon Nanotubes
G.C.	Glassy Carbon
HCl	Hydrochloric acid
HCNT	HiPco Nanotubes
H_2SO_4	Sulfuric acid
ITO	Indium Tin Oxide
KCl	Potassium chloride
$K_4Fe(CN)_6$	Potassium ferrocyanide
LVDT	Linear Variable Distance Transducer
MMA	Methyl methaacrylate
M.W	Molecular Weight
MWCNT	Multi-Walled Carbon Nanotubes
N_2	Nitrogen
N0.15	Noxamium 0.15®
NaCl	Sodium chloride
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
NH_4OH	Ammonium hydroxide
NIPPAm-AMPS	N-isopropylacrylamide 2-acrylamido-2-methyl-1-propanesulfonic acid

NMP	N-methyl pyrrolidone
P3HT	Poly(3-hexylthiophene)
PA	Polyacetylene
PAn	Polyaniline
PCS	Particle Coagulation Spinning
PET	Poly(ethylene terephtalate)
PMAS	Poly(methoxyaniline-5-sulfonic acid)
PMMA	Poly(methyl methacrylatye)
PmPV	Poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)
PPA	Poly(phenylacetylene)
PPEI-EI	Poly(propionylethylenimine-co-ethylenimine)
PPV	Poly(p-phenylene vinylene)
PPy	Polypyrrole
PSS	Poly(styrene sulfonate)
Pt	Platinum
PTh	Polythiophene
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride
PVP	Polyvinyl pyrrolidone
Py	Pyrrole
RBM	Radial Breathing Mode
RCNT	Rice Carbon Nanotube

SCE	Saturated Calomel Electrode
SDS	Sodium dodecyl sulfate
SEM	Scanning Electron Microscopy
SO_3H	Sulfonic acid
SWCNT	Single-Walled Carbon Nanotubes
TCNQ	Tetracyanoquinodimethane
TDM	Tangential Displacement Mode
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TTF	Tetrathiofulvalene
TX100	Triton X 100®
UV-Vis	Ultraviolet and Visible Absorption spectroscopy
VHS	Van Hove Singularities

List of Measurement Units

Å	Angstroms
λ	Wavelength
°C	Celsius degree
C	Coulomb
mC	Millicoulomb
Ω	Ohm
mΩ	Milliohm
KΩ	Kiloohm
A	Amp
mA	Milliamp
μA	Microamp
cm	Centimeter
Da	Dalton
F	Faraday
mF	Millifaraday
g	Gram
mg	milligram
L	Liter
mL	Milliliter

m	Meter
mm	Milliliter
μm	Micrometer
nm	Nanometer
min	Minute
M	Molar
mol	Mole
mmol	Millimole
N	Newton
Pa	Pascal
KPa	Kilopascal
GPa	Gigapascal
MPa	Megapascal
TPa	Terapascal
s	Second
S	Siemen
sccm	Standard cubic centimeter
V	Volt
mV	Millivolt
μV	Microvolt

Abstract

A nanocomposite is defined as a material of more than one solid phase, where at least one dimension falls in the nanometer range. The combination of carbon nanotubes (CNT) and conducting polymers offers an attractive route for the production of novel compounds that can be used in a variety of application such as sensors, actuators, and molecular scale electronic devices. The ultimate goal of this work is to develop and investigate CNT composites that provide a structural functionality together with one or more other key functions.

A variety of novel CNT dispersions were prepared using commercially available CNT systems such as Rice single-walled carbon nanotubes (RCNT), HiPco single-walled carbon nanotubes (HCNT), and Multi-walled carbon nanotube (MWCNT). This study explored the application of novel functional dispersing agents. Deoxyribose Nucleic Acid (DNA) a biological molecule, N-isopropylacrylamide 2-acrylamido-2-methyl-1-propanesulfonic acid (NIPPAm-AMPS) a polyelectrolyte, Didodecyldimethyl ammonium bromide (DDAB) a polymerizable compound, Poly(methoxyaniline-5-sulfonic acid) (PMAS) an inherently conducting polymer, and PVA an insulating polymer were some of the agents used to disperse the CNT. These dispersions were then evaluated in term of their stability and ability to effectively disperse the CNT. Solid-state CNT composites (mats) were then prepared by means of pressure filtration of the CNT/dispersant solutions. These mats were characterized using a variety of different techniques to determine their viability to be used as mechanical actuators or electrochemical devices. The characterization methods included cyclic voltammetry, conductivity, capacitance, atomic force microscopy, scanning electron microscopy, Young's modulus, and actuation measurements.

Abstract

RCNT/conducting polymer composites were prepared by the electropolymerization of Pyrrole with a range of different dopant anions in the presence of different RCNT dispersions. In these composites, the RCNT were completely covered by the polymer, consequently the electrochemical responses of these composites were dominated by the electrochemistry of the polymers with the CNT functioning as a conductor element.

Polypyrrole was also electropolymerized using functionalized multi-walled carbon nanotubes (FMWCNT) as dopant. Electropolymerization was carried out using galvanostatic and potentiostatic techniques on gold-coated Mylar and ITO-glass. It was determined that PPy/FMWCNT composites deposited on either electrode using potentiostatic deposition exhibited redox peaks. This redox behavior was not observed when the galvanostatic deposition was employed.

HCNT/Polyaniline (PAn) composites were prepared by either casting a film from a solution of HCNT and PAn in 1,2-Dichlorobenzene, or by casting a film of PAn onto an existing HCNT mat. The latter exhibited the highest conductivity. The actuation behavior of these CNT composites was investigated and it was determined that the PAn component contributes to the actuation strain while the HCNT component contributes to Young's modulus. The combination of the HCNT (with their mechanical properties) and PAn (with its actuator behavior) offers and attractive route not only to reinforce the polymer film but also to introduce new electronic properties based on morphological modifications or electronic interactions between the two components giving a robust blend of optimum properties. These results open the door for these composites to be used in a variety of applications that require a combination of the above characteristics such as mechanically reinforced actuator devices, robotics, optical fiber switches, prosthetic devices, and anti-vibration systems.

In addition, PPy with a range of dopant anions was electrodeposited galvanostatically, potentiostatically, and potentiodynamically on the surface of four different carbon electrodes, RCNT mat (unannealed), RCNT mat (annealed), glassy carbon, and carbon foil. It was found that the method of electrodeposition was crucial to the electroactivity of the deposited polymers, particularly when deposited onto a RCNT mat due to the different interaction between the deposited polymer and the RCNT mat

Finally, HCNT/SDS, HCNT/PMAS, and HCNT/DNA fibers were prepared using the Particle Coagulating Spinning method (PCS). The annealing process resulted in a dramatic increase in conductivity of up to 2600 times higher compared to the unannealed fibers. However, the annealing process did not play any role in keeping the fibers together or modifying the alignment of the carbon nanotubes ropes within the fibers. The HCNT/DNA fibers, with their biocompatibility, high conductivity, and good mechanical properties can be used as artificial muscles, bioelectronic sensors, or even as platforms to support the growth of nerve cells.

This thesis delineates the methods of successful production of solid sate CNT mats and fibers, utilizing traditional polymeric and more novel multi-functional dispersant materials. Thereby, providing a series of new framework for which future device structures can be fabricated.

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Nadia

My Mother