2006

Synthesis, characterisation and application of inherently conducting polymer nanoparticles

Orawan Ngamna
University of Wollongong

SYNTHESIS, CHARACTERISATION AND APPLICATION OF INHERENTLY CONDUCTING POLYMER NANOPARTICLES

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from the

UNIVERSITY OF WOLLONGONG

by

ORAWAN NGAMNA, B.Sc.(Food Technology)

INTELLIGENT POLYMER RESEARCH INSTITUTE

DEPARTMENT OF CHEMISTRY

February 2006

This work is dedicated to my dad and mom, Mr. Surin and Mrs Pratin Ngamna for their unconditional love and support.

CERTIFICATION

I, Orawan Ngamna, declare that this thesis, submitted in fulfilment 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 institution.

Orawan Ngamna

February 2006

ACKNOWLEDGEMENTS

Firstly I would like to thank my family: dad, mom, P'Nong and Ekkapol for giving me life as well as unconditional love and support.

Thanks also to Unilever Thai Holdings Ltd. for financial support during my Master's degree. P'Noo (PYT) and Rene (RL) who encouraged and supported me to undertake further study and to pursue a PhD as well as P'Tee, P'Pensri, K. Adisai (AMV) and all friends in Unilever are really appreciated.

My life in IPRI would not be possible without the great help and support from both of my supervisors- Prof. Gordon G. Wallace and Dr. Simon E. Moulton. I appreciate the time that Simon has given to my work and thesis, and also his encouragements throughout my time in IPRI. Gordon is an absolutely exceptional professor who cares not only about the research outcome, but also for the well-being of every one under his reign, and is always understanding and helpful. I have never felt left behind or unappreciated whilst working in his 'Evil Empire'. Thanks to Peter (and Uncle Pete's magic toys), Dr. Chee, Violeta (for the nice TEM and AFM images) and Elvis, who always has something to do for other people in IPRI. Thanks to all those involved in collaborative works: Siree, Aoife and Jenny. Thanks to P'Yingpit, Maria, Fatemeh, Vahid, Brianna, Carol, Kerry, Aoife, Su Ryon, Changkee and Eve for all of their encouragements and for always making my work in the lab and my personal life fruitful. My gratitude to Leon, Bjørn, Chee, Peter, Toni and George for comments/proof reading my final thesis chapters. Last but not least, I would like to thank Ngae for being such an unbelievable friend throughout both good and tough times and always be there for me.

Finally, I would like to thank Prof. Gordon Wallace again for giving me the IPRI scholarship throughout my PhD studies.

PUBLICATIONS

1. S.E. Moulton*, P.C. Innis, L.A.P. Kane-Maguire, O. Ngamna, and G.G. Wallace, "Polymerisation and characterisation of conducting polyaniline nanoparticle dispersions", *Current Applied Physics*, 2004, **4** (2-4), 402-406.

2. A. Morrin, O. Ngamna, A.J. Killard, S.E. Moulton, M.R. Smyth*, and G.G. Wallace*, "An Amperometric Enzyme Biosensor Fabricated from Polyaniline Nanoparticles", *Electroanalysis*, 2005, **17** (5-6), 423-430.

3. O. Ngamna, A. Morrin, S.E. Moulton, A.J. Killard, M.R. Smyth, and G.G. Wallace*, "An HRP based biosensor using sulphonated polyaniline", *Synthetic Metals*, 2005, **153** (1-3), 185-188.

4. A. Morrin, F. Wilbeer, O. Ngamna, S.E. Moulton, A.J. Killard, G.G. Wallace, and M.R. Smyth*, "Novel biosensor fabrication methodology based on processable conducting polyaniline nanoparticles", *Electrochemistry Communications*, 2005, **7** (3), 317-322.

5. J.M. Pringle*, O. Ngamna, J. Chen, G.G. Wallace, M. Forsyth and D.R. MacFarlane, "Conducting Polymer Nanoparticles Synthesized in an Ionic Liquid by Chemical Polymerisation", *Synthetic Metals*, in press.

6. O. Ngamna, S.E. Moulton and G.G. Wallace, “Incorporation of Dye into Conducting Polyaniline Nanoparticles”, *Polymer*, accepted.

TABLE OF CONTENTS

PART II – Synthesis and Characterisation of Conducting Polymer Nanoparticles

Chapter 3 – Synthesis and Characterisation of Polyaniline Nanoparticles

Chapter 4 – Incorporation of Dye into Polyaniline Nanoparticles

ABBREVIATIONS

μ	micro
μ	viscosity
λ	wavelength
k_B	Boltzman's constant
γ	surface tension
Ω	Ohm
ν	frequency
ºC	degree Celsius
Θ	angle
η	refractive index
σ	conductivity
ρ	resistivity
υ	scan rate
A	ampere
Å	angstrom
A^-	anion
A_i	acivity of species i
ABTS	2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)
AFM	atomic force microscopy
Ag/AgCl	silver/silver chloride reference electrode
Ag/Ag^+	silver/silver ion reference electrode
APS	ammonium peroxydisulphate

BSA	bovine serum albumin
BFEE	boron-fluoride ethyl ether
C	Cunningham slip correction factor
ca.	approximately
CB	Carbolan Blue
CCD	charge-coupled device
cm	centrimeter
cm^{-1}	wave number
CMC	critical micelle concentration
CV	cyclic voltammetry
d	diameter
Da	dalton
D_{AB}	diffusion coefficient
DBSA	dodecylbenzene sulphonic acid
DLS	dynamic light scattering
E	potential
E^0	standard reduction potential
EB	emeraldine base
emiTFSA	1-ethyl-3-methylimidazolium-bis(trifluoromethane-sulfonyl)amide
ES	emeraldine salt
F	Faraday constant
g	gram
GC	glassy carbon

HCSA	camphorsulphonic acid
HPLC	high performance liquid chromatography
HRP	horseradish peroxidase
h	hour
ICP	inherently conducting polymer
IL	ionic liquid
ITO	indium tin oxide
k	thousand
L	litre
LB	leucoemeraldine base
m	metre
M	molar
MAS	2-methoxyaniline-5-sulphonic acid
mg	milligram
min	minute
ml	millilitre
mM	millimolar
MoAb	monoclonal antibody
mS	millisiemen
Mw	molecular weight
nm	nanometre
OCP	open circuit potential
PANI	polyaniline
PB	perniganiline base

PBS	phosphate buffer saline
PEI	poly(ethyleneimine)
PLL	poly(L-lysine)
PMAS	poly(2-methoxyaniline-5-sulphonic acid)
PPy	polypyrrole
PS	perniganiline salt
PSS	poly(sodium 4-styrene sulfonate)
Pt	platinum
PTh	polythiophene
PTTh	polyterthiophene
PVA	poly(vinyl alcohol)
PVP	poly(4-vinylpyridine)
PVS	polyvinylsulphonate
Py	pyrrole
r	radius
RM	rapid mixing
RMS	root mean square
rpm	round per minute
S	siemen
SCE	saturated calomel electrode
SDS	sodium dodecylsulfate
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SPM	scanning probe microscopy

T	temperature
TBAP	tetrabutylammonium perchlorate
TEM	transmission electron microscopy
Th	thiophene
TTh	terthiophene
V	volt
vs.	versus
w/v	weight by volume
w/w	weight by weight

ABSTRACT

Synthesis of inherently conducting polymers (ICPs) nanoparticles is an option to improve the processability and conductivity of ICPs. In this thesis, the synthesis and application of ICPs nanoparticles has been demonstrated. Various polymerisation methods, such as emulsion polymerisation, use of steric stabiliser and synthesis in ionic liquid (IL) media, have been used to synthesise polymer nanoparticles. These synthesis methods render the ICPs nanoparticles stable as dispersions which are more processable and contain peculiar and fascinating properties superior to their bulk counterparts. These nanoparticles are further applied as mediators for biosensors. They have been fabricated into sensors using electrodeposition, evaporative casting, or ink-jet printing methods. Electrodeposition method results in formation of ultra thin nanostructured polymeric films that enhance sensor performance. Evaporative casting method is an easy one-step method, but precision is hard to achieve and dense films with rough morphology are formed. Ink-jet printing can be used to produce precise and accurate patterns and also this approach is amenable to mass production.

Polyaniline (PANI) nanoparticles; *nano*PANI-dodecylbenzene sulphonic acid (DBSA) have been synthesised using emulsion polymerisation (Chapter 3). The *nano*PANI-DBSA obtained has a conductivity of 34±7 S/cm with particle size in the range of 10±2 nm. The *nano*PANI-DBSA has been used as a mediator layer in biosensor applications as demonstrated in Chapter 7. These nanoparticles were fabricated onto the conductive electrode using an electrodeposition method with subsequent immobilisation of the enzyme horseradish peroxidase (HRP). Sensor performance was examined using

amperometric method and HRP/hydrogen peroxide (H_2O_2) configuration as a model system. The nanodomain of the *nano*PANI-DBSA particles contributed to highly ordered nanostructure patterning on the electrode surface. This uniform surface showed improved enzyme deposition characteristics, a lower background signal and better sensor performance at a lower HRP loading when compared to the sensors fabricated from electropolymerisation of the bulk monomer.

*Nano*PANI-DBSA particles aggregate at high concentrations; hence they are not amenable to ink-jet printing. *s*PANI-DBSA was prepared from centrifugation of the *nano*PANI-DBSA dispersions and used as a material for ink-jet printing. HRP was pre-mixed with the *s*PANI-DBSA nanodispersions before fabrication onto ITO-coated mylar using ink-jet printing. The print quality from the *s*PANI-DBSA nanodispersions was inconsistent and the catalytic signal of this biosensor was very low. These resulted in no further ink-jet printing work for this material.

The PANI-DBSA-rapid mixing (RM) nanodispersions were synthesised using a RM method. These dispersions contained nanometre size PANI particles dispersed in aqueous media. These nanoparticles have been successfully printed using ink-jet printing as outline in Chapter 9. This work has demonstrated the ink-jet printability of conducting polymer nanoparticles and their use as working electrodes for biosensors. The sensor response from these ink-jet printed PANI-DBSA-RM was higher than the sensor response from evaporative casting of poly(2-methoxyaniline-5-sulphonic acid) (PMAS) in Chapter 8.

The addition of functional group into PANI nanoparticles was also investigated. Carbolan Blue (CB) dye was incorporated into the PANI backbone using emulsion polymerisation method as demonstrated in Chapter 4. The dye was proved to have strong interaction with PANI backbone using Raman spectroscopy and centrifugation test. The distinct solution colour after a reduction process could lead the PANI-DBSA-CB to be a potential candidate of the material for electrochromic devices.

Synthesis of polypyrrole (PPy) nanoparticles is demonstrated in Chapter 5. Poly(vinyl alcohol) (PVA) was used as the steric stabiliser to produce PPy-DS-PVA nanoparticles. These nanoparticles were well dispersed in water with particle size in the order of 52±5 nm. Aggregation was obvious in concentrated solutions and leaded to poor ink-jet printed quality of the PPy-DS-PVA nanoparticles.

The water soluble polymer, PMAS, was also used to fabricate biosensors using evaporative casting method in Chapter 8 and ink-jet printing in Chapter 9. In chapter 8, its solubility enabled PMAS to pre-mix with the HRP enzyme prior to complexing with the polycations poly(L-lysine) hydrochloride (PLL) and subsequently casting onto ITO coated mylar substrate. This biosensor format has proven ability to easily fabricate the conducting polymer nanoparticles by one-step evaporative casting. The optimised sensors exhibited good sensor response, high selectivity and very good long-term stability. The ink-jet printed films from PMAS and PLL solutions (Chapter 9) showed better electroactivity compared to the evaporative cast films which could lead to better sensor performance. However, the problem of PLL blocking the print head resulted in the discontinuation of its use.

The polyterthiophene (PTTh) aqueous dispersed nanoparticles were also successfully synthesised in the presence of surfactant (DBSA) and in ionic liquid; 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)amide (emiTFSA) as demonstrated in Chapter 6. The dispersion of PTTh-DBSA nanoparticles has shown poor colloidal stability and poor electroactivity. Although the PTTh nanoparticles synthesised in emiTFSA needed

2-3 minutes sonication to be dispersed in water, they have shown good electrochemistry and being test in another study in our laboratories for its use in photovoltaic devices.

These processable ICPs nanoparticles are promising materials for biosensor applications, electrochromic devices and solar cells. Assembly of these nanoparticles on to conductive substrates leads to highly ordered nanostructured ICPs on the surface and improves the biosensor performances. Also these nanoparticles prove their ability to be processable in mass production scale.