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SYNTHESIS, CHARACTERISATION AND APPLICATION OF MICRO/NANO STRUCTURED CONDUCTING POLYMERS

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Abstract

Conducting polymer micro/nanostructures have recently received great attention because of their long conjugation length, high surface area and promising applications in a variety of fields. At the same time, fabrication of micro/nanostructures of conducting polymers with controlled morphology and size remains a challenge for Chemists and Materials Scientists. The focus of this thesis, therefore, is to develop novel conducting polymer micro/nanostructures with a well defined morphology and to consider their potential for applications as sensor and actuating elements. In each case, the structure, conductivity and electrochemical properties of the conducting polymer nanostructures have been characterized using FTIR, Raman, UV-vis, XPS and elemental analyses, conductivity measurements and cyclic voltammetry.

Hollow nanospheres of substituted polyanilines (PANI) were fabricated chemically using ammonium persulfate as the oxidant in the presence of a polymeric acid poly(methyl vinyl ether-alt-maleic acid) (PMVEA). The effects of chemical reaction conditions, including the weight ratio of monomer to PMVEA, concentration of monomer, the molar ratio of monomer to oxidant, the reaction temperature and the type of the monomer, on the formation of hollow nanospheres were systematically studied. The weight fraction of PMVEA to monomer is particularly important for determining the size and uniform shape of the substituted PANI hollow spheres. The formation mechanism for the hollow nanospheres was studied in detail for the case of poly (*o*-methoxyaniline). The hollow nanospheres were used to construct a simple electrochemical oligonucleotide (ODN) sensor, where ODN probes were covalently grafted onto the residual carboxylic acid functionalities of the hollow nanospheres.

Poly(3,4-ethylenedioxythiophene) (PEDOT) hollow microspheres ranging from 0.5 to 10 μm in diameter were synthesized by chemical oxidative polymerisation of EDOT using ammonium persulfate in a catanionic surfactant solution, obtained by mixing cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS). The effects of chemical reaction conditions, including the molar ratio of CTAB to SDBS, the concentration of total surfactants, the type of oxidant and magnetic stirring, on the formation of the PEDOT hollow microspheres were investigated systematically. The formation of PEDOT hollow spheres is presented as following a vesicle-templating mechanism, supported by Freeze Fracture TEM results. Moreover, the PEDOT hollow spheres showed a more effective electrocatalytic activity for the oxidation of ascorbic acid, compared to conventional PEDOT granular particles, which were also effective in lowering the ascorbic acid oxidation overpotential.

By extending vesicle-template method into the electropolymerisation of polypyrrole (PPy) films with *para*-toluene sulfonate (*p*TS) as the main dopant, a novel micro ring structured surface morphology was prepared by using CTAB/SDBS vesicles as templates. Spectroscopic characterisations confirmed that the micro ring structured PPy/*p*TS films showed similar molecular structure and doping degree to conventional PPy/*p*TS films, while the incorporation of some DBS anions had a minor effect on lowering film conductivity. The actuation behaviour of micro ring structured PPy/*p*TS films was investigated under electrochemical stimulation. The micro ring structured PPy/*p*TS films showed superior actuation stability compared to conventional PPy/*p*TS films.

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ABBREVIATIONS

A^-	anion
AAO	anodic aluminium oxide
AC	alternating current
Ag	silver
AgCl	silver chloride
AOT	sodium bis(2-ethyhexyl) sulfosuccinate
APS	ammonium persulfate
aq.	aqueous
C	coulomb
CA	chronoamperometry
ca.	approximately
Ca^{2+}	calcium ion
CB	conduction band
CdS	cadmium sulfide
CdSe	cadmium selenide
$Ce(SO_4)_2$	cerium sulfate
$CHCl_3$	chloroform
CH_3OH	methanol
ClO_4^-	perchlorate
cm	centimetre
cmc	critical micelle concentration
CP	chronopotentiometry or conducting polymer

CPE	carbon paste electrode
CPE_1	space charge capacitance
CTAB	cetyltrimethyl ammonium bromide
c/s	core/shell
CSA	camphorsulfonic acid
Cu_2O	cuprous oxide
CV	cyclic voltammetry
d	thickness
D	dimension
DBS	docecyl benzene sulfonate
DBSA	dodecylbenzene sulphonic acid
DC	direct current
def.	deformation
DOCES	1,2-bis(decyloxycarbonyl) ethane-1-sulphonate
DMSO	dimethyl sulfoxide
EB	emeraldine base
EDOT	3,4-ethylenedioxylthiophene
EDAC	1-ethyl-3-(3-dimethylaminpropyl)carbodiimide
EIS	electrochemical impedance spectroscopy
ES	emeraldine salt
E_{pa}	anodic peak potential
E_{pc}	cathodic peak potential
ΔE_p	potential difference between anodic peak and cathodic peak
$FeCl_3$	ferric chloride
Fe_2O_3	iron oxide

FFTEM	freeze fracture transmission electron microscopy
FTIR	fourier transform infrared spectroscopy
h	hour
H^+	hydrogen cation
H_2A	ascorbic acid
HCl	hydrochloric acid
H_2O_2	hydrogen peroxide
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
HSO_4^-	bisulfate
ITO	indium-tin oxide
I	current
i_{pa}	anodic current peak
i_{pc}	cathodic current peak
K^+	potassium ion
KCN	potassium cyanide
KE	kinetic energy
$K_4[Fe(CN)_6]$	potassium ferrocyanide
$K_2Cr_2O_7$	potassium dichromate
KIO_3	potassium iodate
$LiClO_4$	lithium perchlorate
l_c	chain length of hydrophobic group in surfactants
$\Delta l/l_0$	strain (displacement length/original length)
Li	lithium
µL	microlitre

M	moles per litre
mA	milliampere
M_n	number average molar mass
M_w	weight average molar mass
mL	millilitre
mg	milligram
mm	millimeter
mV	millivolt
mM	milli moles per litre
µm	micrometer
µM	micro molar per litre
m-MA	*meta*-methylaniline
o-MA	*othor*-methylaniline
m-MOA	*meta*-methoxyaniline
o-MOA	*ortho*-methoxyaniline
MPa	mega pascal
NapTS	para-toluene sulphonate sodium salt
$Na_2S_2O_8$	sodium persulfate
Na_2HPO_4	dibasic sodium phosphate
N_2	nitrogen
NH_3	ammonium
N_2H_4	hydrazine
$(NH_4)_2Ce(NO_3)_6$	ceric ammonium nitrate
$(NH_4)_2S_2O_8$	ammonium persulfate
nm	nano meter

μm	micrometer
NO_3^-	nitrate
β-NSA	β-naphthalenesulfonic acid
ODN	oligonucleotide
P	packing parameters for surfactants aggregates
PA	polyacetylene
PANI	polyaniline
PADPA	p-amino-diphenylamine
PBS	phosphate buffer solution
PC	propylene carbonate
PD	polydispersity
PdS	palladium sulfide
PEDOT	poly(3,4-ethylenedioxythiophene)
PMVEA	poly(methyl vinyl ether-alt-maleic acid)
P*m*MA	poly(*m*-methylaniline)
P*o*MA	poly(*o*-methylaniline)
P*m*MOA	poly(*m*-methoxyaniline)
P*o*MOA	poly(*o*-methoxyaniline)
PPy	polypyrrole
PT	polythiophene
PP	polyphenylene
PPP	polyparaphenylene
PPV	polyparaphenylene vinylene
PS	pernigraniline salt
PS	polystyrene

Pt	platinum
PTSA	pyrene-1,3,6,8-tetrasulphonate
PSA	pyrenesulphonate
PSS	poly(styrene sulphonic acid)
p-TSA	*para*-toluenesulphonic acid
*p*TS	*para*-toluenesulphonate
Q	charge
QCM	quartz crystal microbalance
R_2	charge transfer resistance
s	second
S	siemen
S^{2-}	sulfide
SA	salicylic acid
SCE	saturated calomel electrode
SDBS	sodium docecyl benzene sulfonate
SDS	sodium dodecylsulfate
SHE	standard hydrogen electrode
SEM	scanning electron microscopy
SiO_2	silicon dioxide
SO_4^-	sulfate
str.	stretching
T	temperature
t	time
TiO_2	titanium oxide
TS	toluene sulphonate

TEM	transmission electron microscopy
TPB	tetraphenylborate
TX-100	polyoxyethylene isooctylcyclohexyl ether
Uv-vis	ultraviolet-visible
V	volt
V	volume of hydrophobic head in surfactants
VB	valence band
W_1	Warburg impedance
wag.	waging
wt	weight
X^+	cation
XPS	X-ray photoelectron spectroscopy
ρ	resistivity
σ	conductivity
Ω	ohm
α_0	cross section area of hydrophilic head group in surfactants