Quantum dot and carbon dot polymer nanocomposites for latent fingermark detection

A thesis submitted to the School of Chemical & Physical Sciences, Faculty of Science & Engineering, at The Flinders University of South Australia in fulfilment of the degree of Doctor of Philosophy

March 2014

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Declaration

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

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Acknowledgements

The research presented in this thesis has been conducted at Flinders University, Adelaide, South Australia. Furthermore the project was funded by The Department of Justice of South Australia.

I am extremely grateful to my supervisor, Amanda Ellis, and co-supervisors Hilton Kobus and Joe Shapter for their supervision and guidance. In particular I would like to give a special thanks to my primary supervisor, Amanda Ellis for her encouragement, patience, and for believing in me over the last few years during this research. Your positive attitude and strong work ethic towards research in science has moulded me into the confident researcher I am today. I am certain that your wealth of knowledge, constructive criticism, and constant strive for excellence has made the last few years possible, it has been a great pleasure to be your student.

I must thank members of the ever changing Ellis research group, staff and academia at Flinders University, and members of the Flinders Centre for NanoScale Science and Technology, for their help, support, and amity over the past years.

Thanks to Kez, as a colleague, travel buddy and good friend. Jade, my bestie thanks for your mental-moral support and advice. Additional shout outs to Christine (my lunch buddy), Praveen, Luke, Bloky, Ra, Jess, Claire, Tony, Marky, Taryn, and Lee-Ann.

Finally I would like to thank my family in Adelaide and Darwin for their love, support (financially and mentally) and patience, which has always helped me towards achieving my goals. Love you all xo.

Abstract

Over the last decade interest in fluorescent nanoparticles for forensic applications has greatly increased. This thesis describes the synthesis of fluorescent nanoparticles with polymer grafted from their surface for latent fingermark detection. This allows for essential colour contrast for fingermark visualisation and subsequent person identification.

In the first part of the thesis cadmium sulfide (CdS) quantum dots (QDs) were synthesised. These QDs have size tuneable fluorescence, which was investigated using theoretical calculations of band gap energies measured by UV-visible spectrophotometry. Once synthesised a chain transfer agent (CTA) was immobilised onto the QD surface using a Steglich esterification method. Subsequently reversible addition fragmentation chain transfer (RAFT) polymerisation (a controlled polymerisation technique), was used to graft dimethylacrylamide (DMA) from the surface of the QDs *via* the CTA on its surface. This gave a CdS/p(DMA) nanocomposite, which was water soluble. Aqueous solutions of CdS/p(DMA) were then applied as a solution reagent to successfully detect latent fingermarks deposited on non-porous substrates. The fluorescently developed fingermarks were visualised and photographed using a Polilight® (UV = 350 nm).

The RAFT process was versatile in that different monomers could be used, and hence different polymers with suitable physical attributes were synthesised. Random copolymers of DMA with methyl methacrylate (MMA) and styrene (Sty) were then grafted from the CdS QDs to give CdS/p(DMA-*co*-MMA) and CdS/p(DMA-*co*-Sty). This ultimately led to the synthesis of fluorescent powders that could be dusted onto the latent fingermarks for detection. The powders were found to give better ridge definition than the solution form.

Despite protection of the CdS QDs in the core of the polymers synthesised, there was always a residual concern for the use of the heavy metal, Cd, in the synthesis of these and other conventional QDs. Over the past decade years, research into nanocarbons has grown

exponentially, with our interest particularly focused on using fluorescent carbon nanoparticles (C-dots) for this thesis. C-dots, in literature, have been reported as non-toxic, biocompatible, alternatives to conventional QDs. C-dots were synthesised *via* thermal oxidation of activated charcoal (AC) in nitric acid. They were inexpensive to synthesise. Their optical properties were visually comparable to the CdS QDs, and emission intensities were found to be defined by working pH (acidity/basicity). We applied the same polymerisation techniques (RAFT) to synthesise C-dot/polymer nanocomposites to successfully detect latent fingermarks that were deposited on non-porous materials. Visually, these were comparable to the QD/polymer nanocomposites previously synthesised and applied successfully to the detection latent fingermark on non-porous surfaces.

Lastly, the RAFT process was further exploited - by which the active end group (given by the RAFT agent) of the polymer was modified in a straightforward manner. Divinyl sulfone (DVS) modified magnetic beads were attached to CdS and C-dot polymer nanocomposites *via* a one-pot aminolysis/thiol-ene click reaction. This resulted in a magnetic fluorescent CdS QD or C-dot polymer powder that could potentially be used as a type of “Magna Powder” in latent fingermark detection.

Publications

Journal articles

Dilag, J., Kobus. H, Ellis, A.V, CdS/polymer nanocomposites synthesised *via* surface initiated RAFT polymerization for the fluorescent detection of latent fingermarks. *Forensic Science International,* **228**, 105 (2013).

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Dilag, J., Kobus, H., Ellis, A.V., Nanotechnology as a new tool for fingerprint detection, *Australian Research Network for Advanced Materials and the Australian Research Council Network for Nanotechnology (ARNAM/ARCNN) Joint Workshop*, Adelaide, SA, Australia, June 2010.

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Lists of abbreviations, symbols and units

Symbol/acronym/unit	Translation/explanation
Ω	Ohms
ℏ	The Dirac constant
δ	Chemical shift
%	Per cent
^{13}C NMR	Carbon 13 nuclear magnetic resonance spectroscopy
^{1}H NMR	Proton nuclear magnetic resonance spectroscopy
a.u	Arbitrary units
AC	Activated charcoal/carbon
AF	Autofocus
AIBN	Azobisisobutyronitrile
Al	Aluminium
Ar	Aromatic ring
C	Carbon
C=O	Carbonyl
C_{12}CTA	C_{12} chain transfer agent
Ca	Calcium
$CDCl_3$	Deuterated chloroform (chloroform-d)
$CdCl_2$	Cadmium chloride
C-dot	Carbon dot
CdS	Cadmium sulfide
CdSe	Cadmium selenium
cm^{-1}	Wavenumber
COOH	Carboxylic acid
co	Co-polymer
cps	Counts per second
CTA	Chain transfer agent
Cu	Copper
D_2O	Deuterated water
D-band	Disorder band
DCC	Dicyclocarbodimmide
°C	Degrees Celsius
DHU	Dicyclohexylurea
DMA	*N*-n-dimethylacrylamide
DMAP	4-dimethylaminopyridine
DMF	*N*-*N*-Dimethylformamide
DMSO-d_6	Deuterated dimethylsulfoxide
DTP	2,2'- dithiodipyridine
DVS	Divinyl sulfone
Eg	Band gap energy
eV	Electron volts
FTIR	Fourier transform infra-red

G	Generation
g mol^{-1}	Grams per mole
G-band	Graphite band
h	Hour
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
HPLC	High performance/pressure liquid chromatography
I	Intensity
Ind-Zn	1-2-indandione/zinc
J	Joule
K	Potassium
Kg	Kilogram
L	Litre
λ	Lambda (wavelength)
M , mol L^{-1}	Moles per litre
MHz	Mega Hertz
min	Minute
mL	Millilitre
MMA	Methyl methacrylate
M_N	Molecular weight number average
M_w	Molecular weight
mW	Mega Watts
MWCNT	Multiwalled carbon nanotubes
N or N_2	Nitrogen
Na	Sodium
Na_2S	Sodium sulfide
$NaBH_4$	Sodium borohydride
NaCl	Sodium chloride
nano	Nanometer
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
Nd	neodymium
nm	Nanometer
O	Oxygen
OH	Hydroxyl
p	Poly- (e.g., p(DMA) = poly(dimethylacrylamide))
PAGE	Polyacrylamide gel electrophoresis
PAMAM	Polyamidoamine
PDI	Polydispersity index
PEG	Polyethylene glycol
Ph	Phenyl
pH	Power of Hydrogen (per Hydrogen)
π	Pi
PPE	Personal protective equipment
ppm	Parts per million
QD	Quantum dot

QY	Quantum yield
r	Radius
R6G	Rhodamine 6G
RAFT	Reversible addition fragmentation chain transfer
RT	Room temperature
S	Sulfur
s	Second
Si	Silicon
σ	Sigma
SIP	Surface initiated polymerisation
sp	Sharp principle orbital
Sty	Styrene
T_d	Degradation temperature
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
UV	Ultra violet
UV-vis	Ultra violet-visible
V	Volts
wt/wt %	Weight per weight per cent
Xe	Xenon
YAG	yttrium aluminium garnet
ZnS	Zinc sulfide

Thesis Guide

Chapter #	Short description
1	Introduction: Background information about the significance of latent fingermark detection, and conventional methods of detection, quantum dots (QDs) including a literature review of QDs in latent fingermark detection, carbon dots, reversible addition fragmentation chain transfer (RAFT) polymerisation and RAFT end-group removal/modification.
2	Experimental methods: Details pertaining to the synthesis and characterisation of Cd QD and C-dot polymer nanocomposites and magnetic CdS and C-dot polymer nanocomposites.
3	CdS/polymer nanocomposites: Describes the synthesis and characterisation of the CdS QDs used for the synthesis of CdS/polymers: CdS/p(DMA), CdS/p(DMA-*co*-MMA) and CdS/p(DMA-*co*-Sty) *via* surface initiated RAFT polymerisation.
4	C-dot/polymer nanocomposites: Describes the synthesis and characterisation of the C-dots used for the synthesis of C-dot/polymer: C-dot/p(DMA) *via* surface initiated RAFT polymerisation.
5	RAFT end group modification: The synthesis of magnetic CdS/p(DMA-*co*-MMA) and C-dot/p(DMA-*co*-MMA) – describes the synthesis of these magnetic nanocomposites *via* a one-pot aminolysis/thio-lene click chemistry reaction.
6	Application of CdS QD and C-dot polymer nanocomposites to latent fingermark detection: Describes the preparation and application of the synthesised nanocomposites from Chapters 3, 4, and 5 to latent fingermark detection. This chapter will contain its own introduction and experimental sections describing the preparation of latent fingermarks, the CdS and C-dot polymer nanocomposites as reagents for fingermark detection.
7	Conclusions and future directions: Concluding remarks on the research presented in the thesis, and potential research projects related to the research presented.