Nanoparticle Based Sensors and Organic Nanospintronic transistors

Hadi Rasam AlQahtani

Supervisors
Dr Martin Grell       Dr Dan Allwood

A thesis submitted in partial fulfillment for the degree of Doctor of Philosophy with Integrated Studies (New Route PhD) in Nanoelectronics and Nanomechanics

Faculty of Science
Department of Physics and Astronomy
May 2013
Abstract

The work presented in this doctoral thesis is mainly divided into two main parts: nanoparticle swelling based sensors and organic nanospintronics.

In the swelling based sensors work, three novel experimental methods for enhancing the sensitivity of gold core shell nanoparticle (Au-CSNP) films are presented. The first method utilises a long ligand of alkane-thiols, e.g. dodecanethiols and a significant response was obtained for alkanes with long carbon chain such as decane (C_{10}H_{22}) which is found in petrol. The sensitivity of swelling- based gold core- shell nanoparticle vapour sensors can be enhanced considerably by cooling sensors below ambient temperature. We found that the sensitivity to a particular analyte scales with temperature like that of the analyte’s saturated vapour pressure and the sensitivity is linked to the analyte’s enthalpy of vaporisation. This allows for quantitative prediction of sensitivity enhancement for vapours not yet tested. We demonstrated the detection of low level of a biogenic odour that is released by E.coli bacteria (1-decanol odour) at a partial pressure in the order 100 ppb using Au-CSNPs decorated with a long –OH terminated ligand. This is an exceptionally low limit of detection for swelling- based sensors, and relies firstly, in the careful matching of the CSNPs ligands to the targeted odour, and secondly, in the very low volatility of this odour.

In the spintronic part, the organic spin field effect transistor was demonstrated for the first time and about –1400% giant magnetoresistance at was estimated at room temperature using such transistor. This probable GMR effect is exceptionally high and could have a strong impact on the field of organic spintronics. Also, we developed a platform (in-plane spin valve structure based on Ni_{80}Fe_{20} nanostructures) for studying spin transport in organic semiconductors. Using such platform, about –0.4% magnetoresistance was obtained with the electron transporter organic semiconductor PTCDI-C_{13}. Unlike vertical spin valve structures, our in-plane structure does not suffer from the ill-defined organic/ferromagnetic interface as the organic semiconductor will always be deposited on the top of the ferromagnetic contacts. This allows for the depositing of different organic layers on the same device multiple times as long as the organic materials can be washed out by a suitable solvent.
Acknowledgments

All praise and thanks are due to Allah, the one, the Lord of everything. If I were to count His bounties upon me, I would definitely fail. Peace and blessings be upon Prophet Muhammad and all other Prophets.

My deepest gratitude goes to my father Rasam AlQahtani, my mother Hadba AlQahtani, and my wife Maryam AlQahtani. I ask Allah to reward them all for what they have done for me.

I would like to express my deepest thanks and appreciations to my supervisors Dr Martin Grell and Dr Dan Allwood. I have been greatly benefited from their guidance, help, support and fruitful discussions. I was very lucky to work with them as great scientists and friends in the same time. I am indebted to Dr Matt T. Bryan for helping me a lot in the magnetic part of this project and taking me through the wonders of nanoscale patterning and answering my endless questions. Also, I would like to acknowledge the help and support that I received from Dr Tim Richardson who sadly passed away during the writing up of this thesis.

I would like to thank my examiners Prof. Alexei Nabok and Prof. Nigel Clarke who provided encouraging and constructive feedback and I am grateful for their thoughtful and detailed comments.

Special thanks to Dr. Mohammad Al-duraibi for helping me during his summer visit in 2011, Dr Lee Hague and Dr Stuart Brittle for helping me a lot especially in my first year of PhD and Dr. D. Puzzovio for helping in the decanol sensor work.

Thanks also to Dr M.T. Bryan, M.P.P Hodges, and Dr. T.J. Hayward for doing the M-TXM measurement at the ALS beamline, Berkeley, USA. Also I would like to thank Dr P John Thomas and his group in Manchester University for supplying us with gold nanocrystals films that were used as amine sensors.

I would like to acknowledge the technical support that I received from Dan Jackson (in chemistry), Simon Dixon, Paul Kemp-Russell, Pete Robinson, and Chris Vickers (Physics workshop) Paul Hawksworth (in material science and engineering), and Saurabh Kumar (in Kroto nanoscience centre). Also I would like to thank my office and research mates in the Departments of Physics and Materials science & Engineering for their friendliness and offering help when it was needed.
Finally, I would like to thank the kind support that I received from Saudi Cultural Bureau in London throughout my tenure here and King Saud University for the provision of a doctoral fellowship.

Hadi AlQahtani
May 2013
List of Publications and Conferences

Published papers


Papers to be submitted:

1. Planar organic spin valves using nanostructured \(\text{Ni}_80\text{Fe}_{20}\) magnetic contacts.

Conferences

2. Poster in JSPS York-Tohoku Research Symposium on "Magnetic Materials and Spintronics" June 2013, University of York, York, UK.
5. Poster presentation in European Conference on Organized Films (ICOMF 12), July 2011, Sheffield Hallam University, Sheffield, UK.
6. Poster presentation in UK & RI Chapter of the IEEE Magnetics Society EGM and Student/RA Workshop, Nov. 2010, University of Sheffield, UK.
Contents

Chapter 1: Introduction and Thesis Organisation
1.1 Introduction and Motivations .......................................................... 1
1.2 Core-Shell Nanoparticle Sensors...................................................... 1
1.3 Organic Nanospintronics.................................................................... 3
1.4 Nanostructures: Importance and Classification................................. 6
1.5 How this thesis is organised? ............................................................ 8
1.6 References......................................................................................... 10

Chapter 2: Nanoscale Swelling Based Sensors: Background
2.1 Introduction ....................................................................................... 12
2.2 Swelling Based Sensors: an Overview ............................................. 12
2.3 Thermodynamics of Evaporation and Swelling ............................... 13
2.3.1 Vapour Pressure ........................................................................... 13
2.3.1.1 Intermolecular interactions.......................................................... 14
2.3.1.2 Effects of the molecular weight .................................................... 14
2.3.1.3 Saturation, Relative vapour pressure and Lower Explosive Limit ... 15
2.3.1.4 Evaporation Rate ........................................................................ 16
2.3.1.5 Metabolic Vapour Pressure Build-up ......................................... 18
2.3.2 Clausius-Clapeyron Equation and Enthalpy of Vaporisation .......... 19
2.3.3 Hildebrand Solubility Parameter ................................................... 20
2.4 Core-Shell Nanoparticles .................................................................. 23
2.4.1 Electron Transport in CS-AuNP films ........................................... 23
2.4.2 Literature Review of Nanoparticle Swelling Based Sensors .......... 26
2.5 Conclusion......................................................................................... 28
2.6 References......................................................................................... 28

Chapter 3: Nanoscale Magnetism and Spintronics
3.1 Introduction ....................................................................................... 32
3.2 Nanoscale Magnetism ....................................................................... 32
3.2.1 Spin and orbital magnetic moments ............................................. 32
3.2.2 Spin-Orbit Coupling .................................................................... 34
Chapter 4: Organic Spintronics

4.1 Introduction ................................................................. 62
4.2 Organic Semiconductors .................................................... 62
4.2.1 Charge Transport in OSCs .............................................. 65
4.2.1.1 Bulk-limited transport: Mobility .................................. 65
5.3.2.1 Four-Point Probe Measurement ................................................................................................. 106
5.3.2.2 Magnetoresistance setup ............................................................................................................ 107
5.3.2.3 Magnetic/Organic Transistor Characterising Setup ................................................................. 110
5.3.2.4 Magneto-Optical Kerr Effect Magnetometery ........................................................................... 111
5.3.2.5 Magnetic Transmission X-ray Microscopy ................................................................................... 113
5.4 Structural Characterisation .............................................................................................................. 115
5.4.1 Atomic Force Microscopy ............................................................................................................ 115
5.4.2 Scanning Electron Microscopy .................................................................................................... 116
5.5 References ........................................................................................................................................ 117

Chapter 6: Highly Sensitive Nanoscale Swelling Based Sensors
6.1 Introduction ....................................................................................................................................... 119
6.2 Chemical Sensors .............................................................................................................................. 119
6.2.1 Amine Sensor ............................................................................................................................... 119
6.3 Physical Swelling Based Sensors: Novel Approaches ................................................................. 121
6.3.1 Sensors Preparation and Characterisation .................................................................................. 121
6.3.1.1 Isotherm and Structural Characterisations ........................................................................ 121
6.3.1.2 Temperature-dependent Electrical Characterisation ......................................................... 125
6.3.2 Highly Sensitive Alkane Sensor ................................................................................................. 127
6.3.2.3 Results and Discussion ........................................................................................................ 130
6.3.3 Cooled CSNP Sensors ................................................................................................................ 134
6.3.3.1 Sensing Film and Controlling Temperature ..................................................................... 134
6.3.3.2 Cooling Sensor Model: Our Hypothesis ............................................................................ 134
6.3.3.3 Results and Discussion ........................................................................................................ 136
6.3.4 Biogenic Odour Sensor ............................................................................................................... 139
6.3.4.1 Low Volatility Approach: Hypothesis ............................................................................. 139
6.3.4.2 Sensing Procedure .............................................................................................................. 140
6.3.4.3 Results and Discussion ....................................................................................................... 141
6.4 Conclusion ....................................................................................................................................... 145
6.5 References ........................................................................................................................................ 145

Chapter 7: Organic Spin Valves and Spin Transistors
7.1 Introduction ....................................................................................................................................... 148
List of Figures

Figure 1.1: A Core-Shell Gold Nanoparticle................................................................. 1
Figure 1.1: Photograph of the Buncefield fire once happened. ........................................ 3
Figure 1.3: Density of states for (a) bulk and nanosystems of (b) a quantum well, (c) a quantum wire and (d) a quantum dot................................................................. 7

Figure 2.1: Carbon black filled polymer swelling upon exposure to organic vapour........ 12
Figure 2.2: vapour pressure vs. molecular weight (increases with the number carbon atoms) of n-alkanes ........................................................................................................ 15
Figure 2.3: Evaporation in a container with a constant flow rate....................................... 17
Figure 2.4: quantum tunnelling through (a) thin barrier, (b) thick barrier. .................... 23
Figure 2.5: Tunnelling conduction process between two nanoparticles cores................. 24
Figure 2.6: Conductivity vs. interparticle separation distance of Au-CSNP films with three different ligands: C_8H_{18}SH, C_{12}H_{26}SH and C_{16}H_{34}SH ............................................. 25

Figure 3.1: Spin-orbit interaction, from electron’s perspective........................................ 34
Figure 3.2: Two types of exchange coupling: (a) Ferromagnetic and (b) antiferromagnetic ......................................................................................................................... 36
Figure 3.3: The demagnetising field in a magnetised specimen....................................... 37
Figure 3.4: Different domain configurations and the associated magnetostatic interaction................................................................................................................................. 39
Figure 3.5: A Bloch wall vs Neél wall.............................................................................. 41
Figure 3.6: Damped precession motion of a magnetic moment (m) around the effective magnetic field according to the LLG equation......................................................... 42
Figure 3.7: The initial magnetisation and demagnetising curves for ferromagnetic with cubic structure............................................................................................................. 43
Figure 3.8: The effect of reduced dimensionality on the domain structure of an FM sample such as iron............................................................................................................. 44
Figure 3.9: Coercivity vs. particle size.............................................................................. 45
Figure 3.10: Two types of head to head domain walls in magnetic nanowires.............. 45
Figure 3.11: Electron diffusion motion in solids............................................................. 47
Figure 3.12: Hall magnetoresistance.............................................................................. 47
Figure 3.13: AMR effect due to spin orbit interaction........................................48
Figure 3.14: Two different geometries of a GMR device.................................50
Figure 3.15: Parallel and anti-parallel configurations of a GMR sensor.............51
Figure 3.16: Exchange coupling strength vs. spacer layer thickness for a GMR device ...52
Figure 3.17: Magnetostatic interaction between two FM layers..........................53
Figure 3.18: Switching behaviour of an array of 20 nm thick Ni_{80}Fe_{20} wires with two pointed ends..........................................................54
Figure 3.19: The orange peel coupling caused by the edge roughness...............54
Figure 3.20: schematic showing the density of states for for up-spin and down-spin electrons in: a) ferromagnetic, and b) non-magnetic materials..............................55
Figure 3.21: The effect of having two different spin density of states in a GMR device...57
Figure 3.22: two spin channels model................................................................59

Figure 4.1: The benzene ring and its resonance structure................................63
Figure 4.2: Organic electronic structure vs. inorganic electronic structure........64
Figure 4.2: Energy schematics for metal/organic interface when considering: (a) hole injection into p-type organic semiconductor, (b) electron injection into n-type organic semiconductor .................................................................67
Figure 4.4: Three transport mechanisms in OSCs: (a) thermoionic emission........69
Figure 4.5: Two different structures of OFETs: (a) Bottom gated OFET, (b) Top gated OFET..........................................................71
Figure 4.6: schematics showing: (a) Typical output characteristics of a field effect transistor: $I_{SD}$ vs $V_{SD}$ at different applied gate voltage, (b) transfer characteristics ......73
Figure 4.7: (a) electrolyte-gated OFET, (b) electric double layer (EDL) .................74
Figure 4.8: Planar geometry of an organic spin valve........................................78
Figure 4.9: vertical geometry of an organic spin valve......................................79
Figure 4.10: An intrinsic organic magnetoresistance displayed at room temperature by ITO/PEDOT/Alq_{3}/Ca structure at different electric bias voltages.........................82
Figure 4.11: Gated organic spin valve: (a) device schematic, (b) unsaturated output characteristics due to the short channel effect.........................................................84
Figure 4.12: Conductivity mismatch ..................................................................85

Figure 5.1: Langmuir-Schaefer printing technique...........................................90
Figure 5.2: A photograph of resulting device ................................................................. 92
Figure 5.3: (a) oil-water interfacial deposition of Au-NPs. (b) the Au-NPs films .......... 93
Figure 5.4: Monolayers resulted from (a) thiols bind to gold and (b) silane bind to OH group in an oxide layer on a silicon or glass substrate ................................................................. 94
Figure 5.5: A schematic showing the main components of a thermal evaporator .......... 95
Figure 5.6: A sketch showing the spincoating procedure .............................................. 96
Figure 5.7: A sketch showing the sputtering process ..................................................... 97
Figure 5.8: A photograph for the Raith 150 electron beam lithography machine ......... 98
Figure 5.9: Defining a metallic nanostructure on a substrate by means of electron beam lithography and thermal evaporation ................................................................. 99
Figure 5.10: Photolithography patterning for micron and submicron structures .......... 100
Figure 5.11: Driving circuit of CS-AuNP films .............................................................. 101
Figure 5.12: Oscilloscope screenshots, showing V_{in} (1 V/div, top and orange coloured), and V_{out} (50 mV/div, bottom and blue coloured) of dodecanethiol Au CSNP films. Time scale is 1 sec/div. .................................................................................................................. 101
Figure 5.13: Basic square wave generator circuit ....................................................... 102
Figure 5.14: Schematic showing the temperature controlled sensing and gas delivery set-up ......................................................................................................................... 104
Figure 5.15: Thermoelectric elements of n- and p-type based on the Peltier effect, the inset shows a commercial Peltier element ................................................................. 105
Figure 5.16: A schematic of four-point probe configuration ......................................... 106
Figure 5.17: Magnetoresistance setup connected ....................................................... 108
Figure 5.18: The graphical user interface (a) and the Block diagram (b) of the MR developed labview code ........................................................................................................ 109
Figure 5.19: A schematic showing the contacting method of water gated organic field effect transistors ........................................................................................................ 110
Figure 5.20: Magnetoresistance measurement setup of the of gated spin valve transistors ..................................................................................................................... 111
Figure 5.21: Schematic showing the basic MOKE magnetometer and its working modes: transverse (T-mode), longitudinal (L-Mode) and polar mode (P-mode) ........ 112
Figure 5.22: An advanced MOKE setup for ferromagnetic nanostructures .......... 113
Figure 5.23: M-TXM beamline at ALS, Berkley, USA ................................................. 114
Figure 5.24: A schematic showing the AFM basic structure ......................................... 116
Figure 5.25: the basic structure of an SEM.................................................................117

Figure 6.1: Octylamine odour sensing using gold nanocrystals........................................120
Figure 6.2: Langmuir isotherm of core/shell nanoparticles: (a) Dodecanethiol AuNPs isotherm, (b) Hexanethiol AuNPs isotherm, (c) Undecanethiol AuNPs........................................123
Figure 6.3: (a) Tapping mode AFM height image rendered in 3d of dodecanethiol Au-CSNP film .................................................................124
Figure 6.4: SEM images of hexanethiol Au-CSNP film composed of 4 monolayers deposited by the Langmuir–Schäfer technique.................................................................124
Figure 6.5: the change in the electrical resistance of dodecanethiol CS-AuNP films upon varying the temperature between 22 and 50 °C. (c) the resistance percentage change vs. temperature of undecanol thiol CSNP films.................................................................126
Figure 6.6: (a) Oscilloscope screenshots, showing $V_{in}$ (orange, 1V/div), and $V_{out}$ (blue, 50mV/div) of Au CSNP films prior to exposure, during exposure to 1500 ppm of decane odour, and during recovery.................................................................128
Figure 6.7: Response of Au CSNP films to hydrocarbon odours of different Hildebrand parameters and hydrogen bonding strength.................................................................131
Figure 6.8: ‘ Headspace’ exposures to decane and hexane. The recovery starting point in each case is indicated by “Off”.................................................................132
Figure 6.9: (a) Resistance change under exposure/recovery cycles, beginning with 15 ppm decane odour. (b) $\Delta R/R$ plateau vs. vapour pressure.................................................................133
Figure 6.10: Resistance change ($\Delta R/R$) vs time of under odour exposure / recovery cycles to 0.1$p_{sat}$ of decane (1a), toluene (1b), and pentane (1c)..................................................................137
Figure 6.11: Arrhenius plot of temperature- dependant sensitivity for exposure to decane (blue circles), toluene (red squares), and pentane (green triangles)..................................................................138
Figure 6.12: Resistance of Au-undecanethiol CSNP film under repeated exposure/recovery cycles to 1% $p_{sat}$ (112 ppb) decanol odour. .................................................................141
Figure 6.13: Resistance of Au-undecanethiol CSNP films under exposure/recovery cycle to 1% $p_{sat}$ (112 ppb) 1-decanol (a) and 10% $p_{sat}$ (1.1 ppm) 1-decanol (b)..........................143
Figure 6.14: Arrhenius- like plot of sensor response at different temperatures for 1% $p_{sat}$ (squares) and 10% $p_{sat}$ (triangles) 1-decanol exposure.................................................................144

Figure 7.1: (a) planar structure of Ni$_{80}$Fe$_{20}$ nanowires forming a platform for organic spintronics ................................................................................................................150
Figure 7.2: (a) An SEM image of nano-channel (~120 nm wide), scale bar is 100 nm, (b) The probability distributions of the edge roughness amplitude of the channel..........................151

Figure 7.3: Wide and narrow Ni$_{80}$Fe$_{20}$ nanowires (~120 μm in length) were contacted for electrical measurement.................................................................152

Figure 7.4: I-V characteristics of narrow and wide Ni$_{80}$Fe$_{20}$ nanowires..........................152

Figure 7.5: MOKE Magnetisation hysteresis loops for: The single Ni$_{80}$Fe$_{20}$ wires.........154

Figure 7.6: M-TXM images of (a) positive and (b) negative magnetic field sweeps for the in-plane spin valve structure..........................................................157

Figure 7.7: (a) An SEM image of the multi-nanowires planar spin valve structure (scale bar is 10 μm)...................................................................................................................158

Figure 7.8: I-V characteristics of the Ni$_{80}$Fe$_{20}$/PTCDI-C13 device.............................159

Figure 7.9: (a) Magnetoresistance loop of Ni$_{80}$Fe$_{20}$/PTCDI-C13 planar nanostructure. (b) Corresponding MOKE loop of similar device.........................................................160

Figure 7.10: A hysteresis loop obtained by sweeping the field below ±15 mT (the switching field of the narrow wire)..............................................................161

Figure 7.11: a Schematic of our water-gated in-plane organic planar spin transistor...164

Figure 7.12: Chemical structure of two h-polaron transporter organic semiconductors: (a) P3HT and (b) pBTTT..............................................................165

Figure 7.13: I-V curves of the planar organic spin valve with P3HT as organic active material: (a) 130 nm for channel length and 20 μm for channel wide (b) 120 nm channel width 60 μm channel length and..............................................................165

Figure 7.14: Ni$_{80}$F$_{20}$/P3HT interface with the important energy levels that determine the injection efficiency..........................................................166

Figure 7.15: The output characteristics of water-gated in-plane spin transistor with two different organic semiconductor channels: (a) P3HT and (b) pBTTT..............................167

Figure 7.16: Saturated transfer characteristics at source-drain voltage of -1V for two water gated spin transistors: (a) P3HT with a channel of about 130 nm in length and 20 μm in width. (b) pBTTT with a channel width of 40 μm........................................168

Figure 7.17: The effect of magnetic field (100 mT) on the output characteristics of water gated Ni$_{80}$Fe$_{20}$/P3HT/Ni$_{80}$Fe$_{20}$ spin transistor at different gate voltages.........................170
**List of Tables**

Table 2.1: Intermolecular interactions that associated with hydrocarbon solvents ........ 14
Table 2.2: Some physical and thermodynamics properties of several hydrocarbon solvents. ...................................................................................................................... 20
Table 2.3: Hildebrand parameter (δ) for a variety of solvents ........................................ 22

Table 3.1: Easy axes and anisotropy constants in some ferromagnetic materials .......... 37
Table 3.2: Domain wall parameters for some bulk FM materials .................................. 41

Table 4.1: Some dielectric constants of inorganic insulators used for OFET gating ......... 74
Table 4.2: Examples of commonly used organic semiconductors in the field of organic spintronics and other fields accompanied with their motilities ........................................... 75
Table 4.3: The main achievements in the field of organic spin valves ............................ 83

Table 6.1: Au-CSNP ligands, chemical formula, dispersion solvents and ...................... 121
Table 6.2: Properties of solvents ................................................................................ 130
Table 6.3: Comparison between literature values of enthalpy of vaporisation ............ 138
Table 6.4: Decanol properties: saturation pressure, solubility parameter and enthalpy of vaporisation ........................................................................................................ 142

Table 7.1: Switching fields of a planar spin valve device comprising ............................ 161
Table 7.2: Comparing the MR, spin diffusion length and spin relaxation time of our device show in red with the devices reported in literature ......................................... 162