Selected Publications in Nanomaterials Science and Engineering

A thesis submitted to the University of Dublin for
the Degree of Doctor of Science

by

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David Carey

1. Introduction

This submission of a selection of publications for the award of a ScD degree from the University of Dublin spans 25 years of original research. Following the award of a 5-year career EPSRC Advanced Research Fellowship and a series of academic posts, I am currently Professor of Electrical and Electronic Engineering at the University of Surrey and served as Head of Department between September 2015 and October 2022. I have published over 100 peer review publications in internationally leading journals.

This submission for a ScD degree is based on a selection of 69 publications grouped into the themes of Electrical Transport in Nanomaterials (23 papers, group A), Structural and Electronic Properties of Nanomaterials (26 papers, group B) and Functional Nanomaterials: Growth, Processing and Characterisation (20 papers, group C). These three thematic areas have been selected as they broadly reflect the “Structure-Property” relationships of the materials studied. Within each group, the publications are listed chronologically starting with the oldest; reference A1 refers to paper 1 in group A etc. As per submission guidelines a small number of papers have been selected, section 2, with a commentary of about 1,000 words, to showcase the contribution and impact to the field.

By the nature of nanomaterials research, these selected publications cross the traditional subject disciplines of electronic engineering, condensed matter physics, materials science and chemistry. Much of the research also has been done in collaboration with academic colleagues within Surrey, nationally and internationally, as well as with talented graduate students. In section 3 I have indicated those papers where I am the corresponding author and/or have made a major personal contribution to the research (*), those publications where I initiated the project and supervised the doctoral student (♦), or those papers where I am a co-author as part of a collaboration (↑).

2. Commentary on Selected Publications

2.1 Nanocarbon-based Cathode Science and Engineering

- Highlighted Paper A3: *Origin of electric field enhancement in field emission from amorphous carbon thin films*, **J. D. Carey***, R. D. Forrest and S. R. P. Silva, Appl. Phys. Lett. **78**, 2339 (2001).

- Highlighted Paper A14: *Carbon Nanotube – Polymer Nanocomposites for Field Emission Cathodes*, Thomas Connolly, Richard C. Smith, Yenny Hernandez, Yurii Gun’ko, Jonathan N. Coleman and **J. David Carey***, Small 5, 826 (2009).

Between 2000 and 2004 my research focussed on the study of the high field electrical transport characterisation of hydrogenated amorphous carbon (a-C:H) and diamond-like carbon (DLC) thin films. In a series of seminal publications [A1-A7], I developed a description of how the electrical transport and electron emission from a-C:H and DLC films can be related to the concentration and delocalisation of the conductive sp^2 carbon phase embedded in an electrically insulating sp^3 carbon matrix. This description of nanoscale conductive inhomogeneity explained the observation of electron emission at low applied electric fields. It has been adopted by many groups as the extent of the conductive phase can be controlled via CVD growth conditions, doping, or post-growth processing, via thermal annealing or ion implantation [C11] promoting a sp^3 C to sp^2 C bonding transformation. For example, in collaboration with IIT Delhi and NPL India we demonstrated a two-order of magnitude increase in photoconductivity response via nitrogen doping [C14], and low field electron emission in noble-metal nanocrystalline DLC films [B13, C15]. A major review of modern field emission materials was published in 2021 due to continued interest in this area. [B23]. These early papers led to the award of a five-year EPSRC career Fellowship.

In the area of carbon nanotube (CNT) cathodes, I began projects which explored electrical transport in CNTs [A8-A10] and CNT-polymer composites [A11-A14]. In these composite cathodes [A11, A14] the current-limiting step for electron emission was found to be percolation-controlled transport through the composite with capacitive coupling between nanotubes separated by the polymer acting as a tunnel barrier. We showed that by careful CNT dispersion the threshold field for electron emission could be optimised for CNT contents as low as 0.7 wt% [A14]. The importance of capacitive coupling between CNTs was also demonstrated in explaining the low electrical insertion losses in the high frequency (40-220 GHz) electrical characteristics of screen-printed CNT-PMMA coplanar waveguide composites [A17].

2.2 High Frequency Electrical Transport in Nanomaterials

- Highlighted Paper A18: *Enhanced Electrical Conductivity of Silver Nanoparticles for High Frequency Electronic Applications*, Ali H. Alshehri, Malgorzata Jakubowska, Anna Młożniak, Michal Horaczek, Diana Rudka, Charles Free and **J. David Carey***, ACS Appl. Mater. Interfaces **4**, 7007 (2012).

- Highlighted paper A20: *Engineering Graphene Conductivity for Flexible and High Frequency Applications*, Alexander J. Samuels and **J. David Carey*,** ACS Appl. Mater. Interfaces **7**, 22246 (2015).

- Highlighted Paper A22: *Graphene Microstrip Patch Ultrawide Band Antennas for THz Communications*, Mojtaba Dashti and **J. David Carey***, Adv. Funct. Mater. **28**, 1705925 (2018).

In collaboration with IEMT Warsaw, we established [A18] that coplanar waveguides with nanosilver grains annealed at low temperatures (350^{o}C) can exhibit significantly reduced electrical loss between 40-220 GHz compared to waveguides composed of micron-sized silver grains annealed to 850^{o}C. The broader impact of this study showed the advantages of using nanometals (lower melting point, increased grain packing and smoother surface) when compared to micron-sized grains. High frequency electrical properties of nanomaterials were explored in [A20-A23]. In [A20] we showed for the first time how to selectively tune the dynamical 2D electrical conductivity and dielectric properties of graphene from DC to optical frequencies. A broader impact of this study was the demonstration of efficient n- and p-type doping of graphene by industry-compatible and solution-processable molecules. We exploited our understanding of the controllable 2D dynamical electrical conductivity and proposed a new graphene-based tuneable surface impedance patch antenna operating between 1-5 THz with several hundred GHz bandwidth; this may be important for short range 6G device-to-device communications. [A22]

2.3 Electronic and Structural Properties of Two-Dimensional Materials

- Highlighted Paper B10: *Ab initio investigation of molecular hydrogen physisorption on graphene and carbon nanotubes*, Daniel Henwood and **J. David Carey***, Phys. Rev. B **75**, 245413 (2007).

- Highlighted Paper B14: *Molecular Doping and Band Gap Opening of Bilayer Graphene*, Alexander J. Samuels and **J. David Carey***, ACS Nano **7**, 2790 (2013).

- Highlighted Paper B15: *Beyond Graphene: Stable Elemental Monolayers of Silicene and Germanene*, Nathanael J Roome and **J. David Carey***, ACS Appl. Mater. Interfaces **6**, 7743 (2014).

Paper B10 explored by *ab initio* calculations the possible use of single walled CNTs and single layer graphene as candidate materials for hydrogen storage. Reflecting the challenge of modelling molecular interactions in van der Waals bonded materials, different functionals (LDA and GGA-based, van der Waals corrected) were employed to provide rigour and confidence in calculating upper and lower bound estimates of the binding energy in different sites and in different molecular orientations, and charge transfer. The overall aim of this project was to see if these materials could be compatible with the US DoE's hydrogen storage targets. Our results reveal that H_2 preferentially is physisorbed on the inside of the nanotube with low charge transfer with a binding energy larger by a factor of two compared to adsorption on the exterior. The low H_2 binding energies would mean low temperatures would be required for use as a storage material.

Studies of molecule adsorption on 2D materials were extended to the doping and band engineering of AB stacked bilayer graphene [B15] where decoration of one layer of the bilayer would break the inversion symmetry leading to a tunable energy bandgap of up to 150 meV with the band gap scaling linearly with charge density. Both n-type and p-type doping was demonstrated for the first time using π electron containing molecules. The opening of a bandgap in BLG would improve the on/off current ratio of graphene-based transistors and a tunable energy gap in the mid-infrared region enables the development of graphene-based photonic detectors.

In [B16] we have led the understanding of the structural, electronic and vibrational properties of two new 2D group IV van der Waals materials, silicene and germanene. Our calculations proposed a route to material stabilisation and calculated a 25-fold reduction in electron-phonon coupling constants (benchmarked to graphene). The correct choice of substrate coupled with reduced carrier scattering subsequently led to the world's first substrate-stabilised silicene transistor (Nature Nano. 2015) with high carrier mobilities >100 cm^2/Vs. B16 is a leading paper in non-carbon elemental 2D materials being important for the 2D materials growth, characterisation and devices communities as it links the stable layer's vibrational (Raman fingerprint) and transport properties to its electronic and structural properties.

2.4 Functional Material Growth and Processing

- Highlighted Paper C19: *Controlled Sonication as a Route to in-situ Graphene Flake Size Control*, Piers Turner, Mark Hodnett, Robert Dorey and **J. David Carey♦**, Sci. Rep. **9**, 8710 (2019).

The papers in group C focus on how the choice of growth and/or material processing parameters influences properties of nanomaterials. In collaboration the UK National Physical Laboratory we have studied ultrasonication, one of the most widely used methods for nanomaterial dispersion. The intrinsic mechanism for sonication is poorly understood with procedures typically specifying extrinsic parameters such as electrical input power and time. In [C16] the debundling of CNTs by sonication was explored and this paper was awarded the 2014 Rutherford Prize for the Best Paper in Acoustics and Ionising Radiation and a Best Poster Prize at NanoteC'12. For graphene we showed [C19] for the first time that it is inertial cavitation, as opposed to stable cavitation, that determines the exfoliation of graphene from graphite allowing control over flake dimensions, size distribution, exfoliation rate and yield. We reported few-layer graphene yields of up to 18% in three hours by optimising inertial cavitation dose during sonication. This paper, published in June 2019, was the 50th highest downloaded paper in 2019 in Materials Science from Nature Scientific Reports. The broader impact of [C19] is that inertial cavitation is the driving mechanism for exfoliation, size-selected flakes of 2D van der Waals nanomaterials.

3. List of Publications

Due to copyright restrictions, copies of the publications have removed from the electronic version of the thesis. The page numbers listed below refer to the unredacted version of the thesis.

Group A: Electrical Transport in Nanomaterials

Ref	Details of publication	Page
A1	Influence of sp^2 clusters on the field emission properties of amorphous carbon thin films, **J. D. Carey*,** R. D. Forrest, R.U.A. Khan, and S.R.P. Silva, Appl. Phys. Lett. **77**, 2006 (2000). https://doi.org/10.1063/1.1312202	1
A2	Conditioning of hydrogenated amorphous carbon thin films for field emission via current stressing, **J. D. Carey*** and S.R.P. Silva, Appl. Phys. Lett. **78**, 347 (2001). https://doi.org/10.1063/1.1339999	4
A3	Origin of electric field enhancement in field emission from amorphous carbon thin films, **J. D. Carey***, R. D. Forrest and S. R. P. Silva, Appl. Phys. Lett. **78**, 2339 (2001). https://doi.org/10.1063/1.1366369	7
A4	Electron field emission from amorphous semiconductors, **J.D. Carey*** and S.R.P. Silva, Solid State Elect. **45**, 1017 (2001). https://doi.org/10.1016/S0038-1101(00)00215-X	10
A5	**(invited)** Engineering the next generation of large-area displays: prospects and pitfalls, **J.D. Carey***, Phil. Trans. Roy. Soc. A **361**, 2891 (2003). https://doi.org/10.1098/rsta.2003.1283	18
A6	**(invited)** Enhancing the electrical conduction in amorphous carbon and prospects for device applications, S.R.P. Silva and **J.D. Carey***, Diam. Relat. Mater. **12**, 151 (2003). https://doi.org/10.1016/S0925-9635(03)00016-5	35
A7	Role of nanostructure on the electron field emission from amorphous carbon thin films, **J.D. Carey***, R.D. Forrest, C.H. Poa and S.R.P. Silva, J. Vac. Sci. Technol. B **21**, 1633 (2003). https://doi.org/10.1116/1.1593642	43
A8	Electron field emission from room temperature grown carbon nanofibers, R. C. Smith, **J. D. Carey♦**, C. H. P. Poa, D. C. Cox and S. R. P. Silva, J. Appl. Phys. **95**, 3153 (2004). https://doi.org/10.1063/1.1647261	50
A9	Interpretation of enhancement factor in non-planar field emitters, R. C. Smith, R. D. Forrest, **J. D. Carey♦**, W. K. Hsu and S. R. P. Silva, Appl. Phys. Lett. **87**, 013111 (2005). https://doi.org/10.1063/1.1989443	55
A10	The effects of aspect ratio and anode location on the field emission properties of nanotubes, R.C. Smith, **J. D. Carey♦**, R.D. Forrest and S.R.P. Silva, J. Vac. Sci. Technol. B **23**, 632 (2005). https://doi.org/10.1116/1.1880072	58
A11	Charge transport effects in field emission from carbon-nanotube polymer composites, R.C. Smith, **J.D. Carey***, R.J. Murphy, W.J. Blau, J.N. Coleman and S.R.P. Silva, Appl. Phys. Lett. **87**, 263105 (2005). https://doi.org/10.1063/1.2158023	62
A12	**(invited)** Carbon based electronic materials: applications in electron field emission, **J.D. Carey***, R.C. Smith, and S.R.P. Silva, J. Mater Sci: Mater Electron **17**, 405 (2006). https://doi.org/10.1007/s10854-006-8087-6	65
A13	Temperature dependent thermal conductivity of carbon nanotube/epoxy composites, Michael B. Jakubinek, Mary Anne White, Paul C. P. Watts, **David Carey**†, Mater. Res. Soc. Symp. **1022**, II03-06 (2007). No doi for this article; a copy is available from the author.	73

Group B: Structural and Electronic Properties of Nanomaterials

Group C Functional Nanomaterials: Growth, Processing and Characterisation