Institution: Imperial College London

Unit of Assessment: 8 Chemistry

Title of case study: C6 - Nanoco: a successful quantum dot nanotechnology company

1. Summary of the impact (indicative maximum 100 words)

The research on the use of single source precursors in quantum dot synthesis undertaken by Professor Paul O'Brien in the Department of Chemistry at Imperial College between 1994 and 1999 resulted in papers and a patent which led to the formation of Nanoco Group PLC, currently a world-leader in the supply of quantum dots (QDs). Quantum dots have applications in backlighting for LCD displays, LED general lighting and thin film solar cells. Nanoco was listed on AIM on the London Stock Exchange in 2009 and by January 2013 Nanoco employed 78 people, had annual revenue of £3 million, and had signed agreements with several major companies in the US and Japan including Dow Chemical, Osram and Tokyo Electron.

2. Underpinning research (indicative maximum 500 words)

The underpinning research on single source precursors, the key technology on which the company Nanoco Group PLC was based, was developed at Imperial College London by Professor Paul O'Brien during the period 1994 -1999. Specifically, Tito Trindade carried out the key seminal work on the use of group 2 and group 4 metal diselenocarbamates and dithiocarbamates as precursors for the organometallic synthesis of quantum dots [1,2]. Prior to this work, the only published and available precursor system for the preparation of high quality semiconductor nanoparticles were metal alkyls, silylated chalcogens and phosphorus-chalcogen compounds. This limited the synthesis of quantum dots to expert organometallic chemistry laboratories, and the yield of the reactions using these precursors was often extremely low.

The use of simple cadmium dithiocarbamates (which could be prepared in air under ambient conditions using commercially available starting materials) lead to the routine synthesis of CdS nanoparticles, bypassing the need for $(CH_3)_2Cd$ and $S(SiCH_3)_2$, both highly volatile and noxious compounds. Subsequently, the use of single source precursors allowed for the scale-up of quantum dot synthesis, with several grams of CdS being prepared in early 1996 by Mark Green (PhD student, funded by an EPSRC CASE award, with British Telecom). This was at the time, the largest yield of quantum dots prepared in the world via a single organometallic reaction, opening the way for potential commercialisation. Likewise, the preparation of gram scale amounts of CdSe, the standard quantum dot material, was also achieved by the O'Brien group using a range of cadmium diselenocarbamates during this period.

The initial work was protected by a key patent [3], '*Process for preparing a nanocrystalline material*', which became the basis for Nanoco. The patent, filed at Imperial College in 1995, was assigned to Nanoco in 2005 and became the first in a series of patents which were later filed through Nanoco.

The use of simple quantum dots in various applications is however limited by their air sensitivity, and for use in for real-life applications, a further inorganic shell is often required. The O'Brien group also reported the first preparation of core/shell particles using single source precursors (published in 1999) [4].

The other key family of semiconducting materials are the III-Vs, such as InP, and this was also prepared by single source precursors (published 1998) [5]. These materials are notable for not possessing cadmium, and in the case of InP, have been highlighted as the next generation of biological labels after the initial work on CdSe-based quantum dots raised questions regarding toxicity. Likewise, the O'Brien group was the first group to work on $CuInS_2$ and $CuInSe_2$ quantum dots (published 1999), again prepared by single source precursors [6]. Nanoco now works

extensively on cadmium-free quantum dots (CFQDs).

Key personnel:

- Paul O'Brien, Sumitomo/STS Professor of Inorganic Chemistry and PI, Imperial College (1994 - 1999), Sumitomo/STS Visiting Professor of Materials Chemistry, Imperial College (1999-2002)
- Tito Trindade, PhD student (1993-1996, Junta Nacional de Investigação Cientifíca e Tecnológica Praxis XXI program)
- Mark Green, PhD student (1995 -1998, EPSRC CASE award with British Telecom), RA (1998-1999)
- Neerish Revaprasadu, PhD student (1996 -1999, Royal Society, Africa Outreach Programme).

3. References to the research (* References that best indicate quality of underpinning research)

[1] * T.Trindade and P.O'Brien, '*A single source approach to the synthesis of CdSe nanocrystallites'*, Adv. Mater., 8, 161-163 (1996). DOI, **121 citations (as of 26/2/13)**

[2] * T. Trindade, P. O'Brien and Xiao-mei Zhang, '*Synthesis of CdS and CdSe nanocrystallites using a novel single-molecule precursors approach'*, Chem. Mater., 9, 523-530 (1997). DOI, **205 citations (as of 26/2/13)**

[3] * Patent: PCT Int. Appl., P.O'Brien, and T.Trindade, '*Process for preparing a nanocrystalline material*', EP 0 850 194 B1, 1997, 28 pp.

[4] N. Revaprasadu, M. A. Malik, P. O'Brien, G. Wakefield, '*A simple route to synthesise nanodimensional CdSe-CdS core-shell structures from single molecule precursors'*, Chem. Commun., 1573-1574 (1999). DOI, **37 citations (as of 4/7/13)**

[5] M. Green and P. O'Brien, '*A novel metalorganic route for the direct and rapid synthesis of monodispersed quantum dots of indium phosphide'*, J. Chem. Soc. Chem. Commun., 2459-2460 (1998). DOI, **32 citations (as of 26/2/13)**

[6] M.A. Malik, P. O'Brien, G. Wakefield and N. Revaprasadu, '*A novel route for the preparation of CuSe and $CuInSe_2$ nanoparticles*', Mat. Res. Soc. Symp. Proc., 536, 371-377 (1999). DOI, **89 citations (as of 26/2/13)**

4. Details of the impact (indicative maximum 750 words)

The work carried out at Imperial between 1994 and 1999 was the basis of the initial patent [3], applied for in 1995. This patent, which was assigned to Nanoco from Imperial, was the first in the Nanoco IP portfolio as described in Nanoco's 2009 admission document to AIM, the London Stock Exchange's international market for smaller growing companies: *'Nanoco's earliest patent family dates back to 1995 and contains granted patents in the US, Germany, France and the UK relating to the use of metal complexes to produce nanocrystalline material known as the Single Source Precursor technology. The Single Source Precursor technology was developed by Professor Paul O'Brien while he was at Imperial College, London and all IP was subsequently assigned to Nanoco'* [A, p24].

This Imperial research provided the backbone for the spin-out of the company which occurred in 2001 after Prof. O'Brien had moved to the University of Manchester. Further patents did not follow until 2004 after Nanoco had been running for 3 years, and as such, the initial patent can be viewed as the cornerstone of Nanoco's commercialisation strategy and the emergence of Nanoco in general. A letter from the Non-Executive Chairman of the Nanoco Group confirms the role of the Imperial research in the early life of the company [B].

Highlights of post 2008 impact

In **2008** Nanoco won the UK Trade & Industry Business Innovation Award in the category of Clean Technologies [C], signed a distribution agreement with Japan-based Kisco, a major electronics materials supplier, and signed a supply and licence agreement with a major Japanese LED manufacturer [D].

In **2009**, in addition to successfully floating on AIM (AIM:NANO) [A], Nanoco signed a joint

development agreement with Japan based Fine Polymers (owned by Kisco) to service the LED markets outside Japan [D]. Revenues in the year to 31 July 2009 were £1.99 million, comprising of milestone payments from strategic partners and income from the sale of products by distribution partners. The company's cash, and cash equivalents, at the financial year's end (7/2009) were £6.59 million [D].

2010 saw a joint development agreement signed with a major Japanese electronics company for LED backlighting of televisions and a joint development agreement signed with Tokyo Electron for a photovoltaic film, marking the first agreement in the solar power sector [E]. In terms of manufacturing, significant progress was made with procurement of a new production facility in Runcorn, Cheshire as the company's first commercial production plant and the addition of a series of scale-up reactors, critical for the progression of quantum dots from very small scale laboratory manufacture to mass production, in the Manchester headquarters. Turnover for the year (to 7/2010) was £2.9 million [E].

In **2011** the Runcorn production facility was designed and built on time and on budget. 1kg of red CFQDs were produced at Runcorn and shipped to a Japanese LED customer triggering a $2 million payment [F]. Manufacturing quantum dots on this scale was a world-first technical achievement and underlined the scalability of Nanoco's technology. A follow-on product development agreement, worth $800,000, was signed with a major Japanese company whose products include LCD TVs [F, G]. This agreement, which followed an 18 month JDA, focused on the final steps in combining CFQD into an LCD TV for commercial launch [F]. A JDA was signed with one of the world's largest lighting companies in August 2011 for use of QDs in general lighting [G]. The company's cash, and cash equivalents, at the financial year's end (7/2011) were £17.1million, up from £5.68M the previous year, and its turnover £2.6 million [F].

In January **2012** Nanoco received a $1 million payment from major Japanese LED corporation for achieving the specified performance criteria for green QDs and in May 2012 it received $2 million payment for the delivery of 1kg of the green QDs, a major technical achievement. These payments follow similar payments achieved for the successful development and delivery of red quantum dots in 2011. This Japanese corporation is now working to incorporate the Company's CFQD directly onto LEDs for small size LCD displays [H]. Following significant technical progress achieved during the year a further thin film solar development agreement was signed with Tokyo Electron. In October 2012, Nanoco signed a follow-on joint development agreement with Osram, one of the world's largest lighting companies [G]. Production scale-up plans were also on track in 2012 with the production capacity design of an upgraded Runcorn lab increased to 400kg a year, reflecting a greater projected demand for quantum dots [I, J]. Turnover for the year was £2.95m and the company's cash, and cash equivalents, at the financial year's end (7/2012) were £15.5 million [H].

In January **2013** Nanoco announced a worldwide licensing agreement with the Dow Electronic Materials division of the Dow Chemical Company [G]. Under the terms of the agreement, Dow will have exclusive worldwide rights for the sale, marketing and manufacture of Nanoco's CFQDs for use in electronic displays such as TVs, computer screens, tablets and smartphones. Nanoco will receive royalty payments from Dow related to its sales of CFQDs. Dow's experience of manufacturing scale-up was a key component of the licensing agreement and it is expected that full commercial production will begin in 2014 [G]. Following the announcement of the "*transformational global licensing agreement*" with Dow, Nanoco shares rose more than 21 per cent [K].

As of January 2013 Nanoco employed 78 staff at its Manchester headquarters and Runcorn plant [G]. By November 2013, the market capitalization of Nanoco was approximately £340 million [B].

Selected highlights of technological impact

Nanoco is "*the only company in the world that has managed to manufacture quantum dots without the use of cadmium, a toxic chemical effectively banned from most consumer products*" [L]. Nanoco's main US rivals, Nanosys and QD Vision, use the heavy metal – "*the presence of which in*

the environment, even in small quantities, can potentially be harmful to human health" [J] This gives the company a "dominant position in a potentially huge global market for quantum dot technology" [J]. In many regions of the world there is now, or soon to be, legislation to restrict and in some cases ban heavy metals in many household appliances such as IT & telecommunication equipment, lighting equipment, and electrical and electronic tools. In Europe, the restricted metals include cadmium. There are similar regulations in place or soon to be implemented worldwide including China, Korea, Japan and the US. Nanoco has developed and is currently extending the range of restricted metal free quantum dots [M].

Quantum dots prepared by Nanoco have numerous optical and structural advantages over traditional dyes, phosphors and fluorophores, and the scale up of high quality materials afforded by the single source route pioneered at Imperial allows the materials to realistically be used in application. The use of Nanoco's green and red emitting quantum dots, when applied to a blue emitting LED are the basis of extremely efficient sold-state lighting; whereas traditional light bulbs are up to 5% efficient with a life time of 500 hours, quantum dot/LED lighting is suggested to be over 60% efficient with a life time of 50,000 hours [N]. Similarly, Nanoco's QDs are to be incorporated into organic LEDs, which have benefits including improved energy efficiency, lower cost and improved display quality whilst removing the need for filters or backlights.

Future impact

The Quantum Dot and Quantum Dot Display markets, worth $150.1 million in 2012, are anticipated to reach $6.4 billion by 2019 as technology matures and is designed into products [O].

5. Sources to corroborate the impact (indicative maximum of 10 references)

[A] Nanoco Group PLC, Admission to AIM document, 2009 (available here).
[B] Letter from Non-Executive Chairman, Nanoco Group plc, 4/11/13 (letter available from Imperial on request)
[C] Clean Technology award, 2008 http://www.nanotech-now.com/news.cgi?story_id=31228 (archived here on 10/7/13)
[D] Nanoco Group PLC, Annual Report and Accounts, 2009 (available here)
[E] Nanoco Group PLC, Annual Report and Accounts, 2010 (available here)
[F] Nanoco Group PLC, Annual Report and Accounts, 2011 (available here)
[G] Nanoco Group PLC, Interim Report For the six months ended 31 January 2013 (available here)
[H] Nanoco Group PLC, Annual Report and Accounts, 2012 (available here)
[I] "Nanoco performance triggers 1m dollar payment ", Manchester Evening News article, 31/1/12, http://www.manchestereveningnews.co.uk/business/innovation/nanoco-group-continues-to-build-momentum-873420 (archived here on 10/7/13)
[J] "Nanoco strives to join up the 'quantum dots'", FT article, 15/10/12, http://www.ft.com/cms/s/0/47cae7c6-1492-11e2-8cf2-00144feabdc0.html#axzz2Ydiga9dT (archived here on 10/7/13)
[K] "Yesterday's trading: Footsie climbs as company earnings buoy investor mood; Nanoco rockets after Dow deal", Daily Mail article, 23/1/13, http://www.thisismoney.co.uk/money/article-2267143/MARKET-REPORT-Nanoco-rockets-Dow-deal.html#ixzz2YeQhl6YJ (archived here)
[L] FE Trustnet.com article, 26/6/13, http://www.trustnet.com/News/435479/fidelitys-stock-picks-for-a-high-growth-investor/2/1/ (archived here)
[M] Nanoco Cadmium-free quantum dots "CFQD™" webpage, http://www.nanocotechnologies.com/content/AdvancedMaterials/CadmiumFreeQuantumDotsQFQDHeavyMetalFree.aspx (archived here on 10/7/13)
[N] Nanoco Solid State lighting webpage, http://www.nanocotechnologies.com/content/CommercialApplications/Lighting.aspx (archived here on 10/7/13)
[O] PR Newswire article, 25/6/13, http://www.prnewswire.com/news-releases/quantum-dot-and-quantum-dot-display-qled-market-shares-strategies-and-forecasts-worldwide-nanotechnology-2013-to-2019-212987981.html (archived here)