Institution: Queen Mary University of London (QMUL)

Unit of Assessment: B8 (Chemistry)

Title of case study: CS1 – Innovative chemistry reduces the environmental impact of mining and pharmaceutical manufacture

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

The technology in this impact study is based on organofunctionalised silica materials that can address market needs for high purity in compounds that underpin many areas of the pharma, electronic and medical sectors as well as the recovery of limited resources such as precious metals that are used in diverse industries. Since the launch of the product portfolio in 2006, the materials have become embedded in purification or recovery steps in commercial production processes of leading mining (South Africa), pharmaceutical (UK) and petrochemical (Germany) companies and make a significant impact on the business of these companies as well as limiting waste of limited resources.

2. Underpinning research (indicative maximum 500 words)

Organic-inorganic hybrid materials have applications in health care, sustainable chemistry and energy transport and generation.

Many organic-inorganic hybrid materials are formed through organic modifications to common metal oxide surfaces. This process imparts novel properties that are useful in a host of applications such as in the fabrication of new biomaterials, chemical sensors, solid phase catalysts and media that are used for purification or capture of high value chemical entities including pharma intermediates/products or precious metals.

Professor Alice Sullivan has worked and published in this field for more than twenty years. While working on organically modified silicas and silica type materials (during the period 1995-2003) it became apparent to Sullivan (Professor of Inorganic Chemistry at QM) and research associate Dr John Wilson (PDRA and Academic Visitor at QM 2001-2005) that the development of these materials for a range of potential applications was severely hampered both in terms of cost and performance by the limited methods then used for surface modifier synthesis. Modifiers were largely derived from a single chloroalkylsilane source. This meant that the resulting compounds had a very limited range of functionality.

Prof. Sullivan and Dr Wilson realised that a novel approach, based on radical addition chemistry, would lead to products with better performance, lower costs at scale, and which could be applied to a wider range of problems. The process that they developed is amenable to large scale manufacture. A series of papers demonstrating some of the catalytic applications of the materials including different types of oxidation, carbon-carbon coupling and hydrogenation chemistries were published by the team between 1998 and 2011 [1-6]. These novel organic modifiers and the derived materials formed the inventive steps of a series of patent applications submitted between 2001 and 2006 [7, 8].

An initial patent application on phosphonate modified silicas was submitted by Sullivan and Wilson from Queen Mary in 2001 proceeding to grant in the US and Europe in 2006. Patents covering the other families of modified materials followed, including those with sulfur rich or nitrogen rich surface modifiers. The portfolio provided materials with excellent metal binding affinities covering the hard or soft metals in common use in the pharmaceutical, petrochemical, mining and fine chemicals sectors and supporting applications in areas of solid phase catalysis and purification and embracing ideas of sustainable chemical processing.

3. References to the research (indicative maximum of six references)

Publications

1. M. Jurado-Gonzalez, Duan Li Ou, Alice C. Sullivan, J.R.H. Wilson. 'Synthesis, characterisation and catalytic activity of porous vanadylphosphonate modified silicas'. *J. Mater. Chem.*, 2002, 12, 3605-3609

2. M. Jurado-Gonzalez, Alice C. Sullivan, J.R.H. Wilson. 'Oxidation of allylic olefins using cobalt (II) alkyl phosphonate modified silica', *Tetrahedron Letters*, 2003, 44, 4283-4286

3. M. Jurado-Gonzalez, Alice C. Sullivan, J.R.H. Wilson. 'Selective oxidations of allylic alcohols using vanadyl and cobalt(II) alkyl phosphonate modified silicas', *Tetrahedron Letters*, 2004, 45, 4465-4468

4. E. Fisset, M. Al-Hashimi, J. Wilson, AC Sullivan. 'Selective oxidations of sulfides to sulfoxides using immobilised metal alkyl phosphonate', *Tetrahedron Letters*, 2006, 46, 8017-8019

5. Al-Hashimi M., Sullivan A.C. and Wilson J.R.H. 'Palladium ethylthioglycolate modified silica – a new heterogeneous catalyst for Suzuki and Heck cross-coupling reactions', *J. Mol. Catal. A Chemical*, 2007, 273, 298-30

6. Qazi and A.C. Sullivan, 'Mesoporous silica-bis(ethylsulfanyl)propane palladium catalysts for hydrogenation and one-pot two-step Suzuki cross-coupling followed by hydrogenation', *Dalton Trans.* 2011, 40 (40),10637-10642

Patents

7. Patent Title: Organopolysiloxanes containing phosphonic groups, methods for the production and use thereof.
   SULLIVAN, A. C., & Wilson, J. R. H. (2002, July 18). WO02055587 (A1), Granted US as US 7,728,159 B2, , Date of Patent: 20th June 2006
   Granted Europe as EP 1360222B, Date of Patent: 10th August 2006

8. Patent Title: Substituted organopolysiloxanes, and use thereof.
   Wilson, J. R. H., SULLIVAN, A. C., & Man, S. P. (2006, February 9). WO/2006/013060, Granted: In Europe as EP 1786850B on 26th November 2008; also granted in China.

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

Sullivan's research [1-6] led to a range of patented products [7, 8] that were brought to market by the spin-out company PhosphonicS [a]. The company, which was established in 2003 and has shown substantial growth throughout the REF period, manufactures and supplies these products at the metric tonne scale around the globe. Current applications of Sullivan's technology by PhosphonicS clients include precious metal recovery in the mining, pharmaceutical and petrochemical markets.

The initial phase of translation of Sullivan's research into commercially viable products began in 2003 with the formation of PhosphonicS Ltd (Founders Sullivan and Wilson) supported by Dr Malcolm Sims then Director of Queen Mary Innovation and Enterprise (now Queen Mary Innovation Ltd). The first staff and lab space were paid for using funds from a DTI Smart Award and the Combined London Colleges University Challenge Seed Fund.

PhosphonicS' development progressed through a series of stages focused on product development in the chemistry laboratories at Queen Mary during 2003-2006 and continued, following Series A funding totalling £1.5 million, with a move to premises at Milton Park, Abingdon, Oxford. Sullivan maintained her academic position at Queen Mary while acting in an advisory capacity to the company.

The company continued to grow with the benefit of long-term investor support from the original investor-shareholders who provided additional amounts of £1.3M in 2008 and £450k in 2009.

PhosphonicS is a cleantech company that provides novel technology to recover precious metals from process, waste and effluent streams and providing both financial and environmental benefits to industrial end users and metal refiners. The innovative chemistry underpinning PhosphonicS materials [1-6] gives them leading performance for the recovery of precious metals such as platinum and rhodium from large volume low concentration (parts per million) waste streams, making recovery both cleaner and more economic than alternative options. PhosphonicS' materials are also applied in the metric-tonne volumes as next-generation metal and organic scavengers in the pharmaceutical, and fine and speciality chemical industries for product purification purposes.

'Case study' examples of the application of PhosphonicS materials are available from the company website [b, c] and include the recovery of rhodium from a waste stream that was previously being transported and burned with no precious metal recovery. PhosphonicS provided the plant with innovative materials that remove 95% of the rhodium from the waste stream, of which 97% can then be reclaimed from the scavenger. Another PhosphonicS client utilises the materials in the manufacture of active pharmaceutical ingredients. The client uses platinum as a catalyst, which must be removed from the product before use, with final concentrations no greater than 10 ppm. The PhosphonicS scavenger removes 98% of the platinum, 98% of which can be recovered.

In 2010 the company secured second round financing of £3.5m (US$5.75m), led by French venture capital company Seventure Partners (Press Release April 2010). The new capital allowed the company to expand its core team into larger premises, increase the number of international agents and secure further manufacturing options for its products.

In 2011 PhosphonicS also forged a strategic liaison with multinational company W.C. Heraeus [d], who offer batch refinery. W.C. Heraeus is offering PhosphonicS' scavenger processes to its customers with low-grade waste streams to enable them to capture and recycle more of their precious metal waste.

Building on the success of Sullivan's novel technology, the number of PhosphonicS employees had grown from six in 2005 to 25 in March 2012; the majority at PhD level. The company has also been able to support PhD CASE students at Queen Mary University of London. According to publically available accounts, the average net worth (net asset value) of PhosphonicS over the last three years (averaging end of year returns for 2010 - 2012) was £1.3m [g].

In February 2013 Seventure Partners invested a further £2.1 million into PhosphonicS. To date, the company has raised approximately £9 million of private equity investment over 10 years of trading. The investment is facilitating ongoing acceleration of the launch of the precious metal scavenger product range in numerous international markets, especially mining and petrochemical, and to invest in co-developing some major catalyst applications with industry clients.

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

a) Spin-out company website: www.phosphonics.com

b) Details of Precious Metal Recovery Case Studies from PhosphonicS clients: www.phosphonics.com/pmr-case-studies.html

c) Details of purification of small molecules case studies from PhosphonicS clients, which include Astra Zenica, Global Pharmaceutical Company, Exelixis and Clauson Kaas: www.phosphonics.com/purification-case-studies.html

d) Strategic agreement with Hiraeus: www.phosphonics.com/1/post/2011/08/first-post.html

e) PhosphonicS company profile: www.rsc.org/chemistryworld/2012/05/support-specialists

f) PhosphonicS product overview: www.sigmaaldrich.com/technical-documents/articles/chemfiles/phosphonics-heterogeneous.html

g) PhosphonicS publically available account information for the company showing net worth: www.duedil.com/company/04829817/phosphonics-limited