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Development of Proof-of-concept Portable Sensors for Detection of Heavy Metals and Organic Pesticides and Investigation of Anti-biofouling Materials

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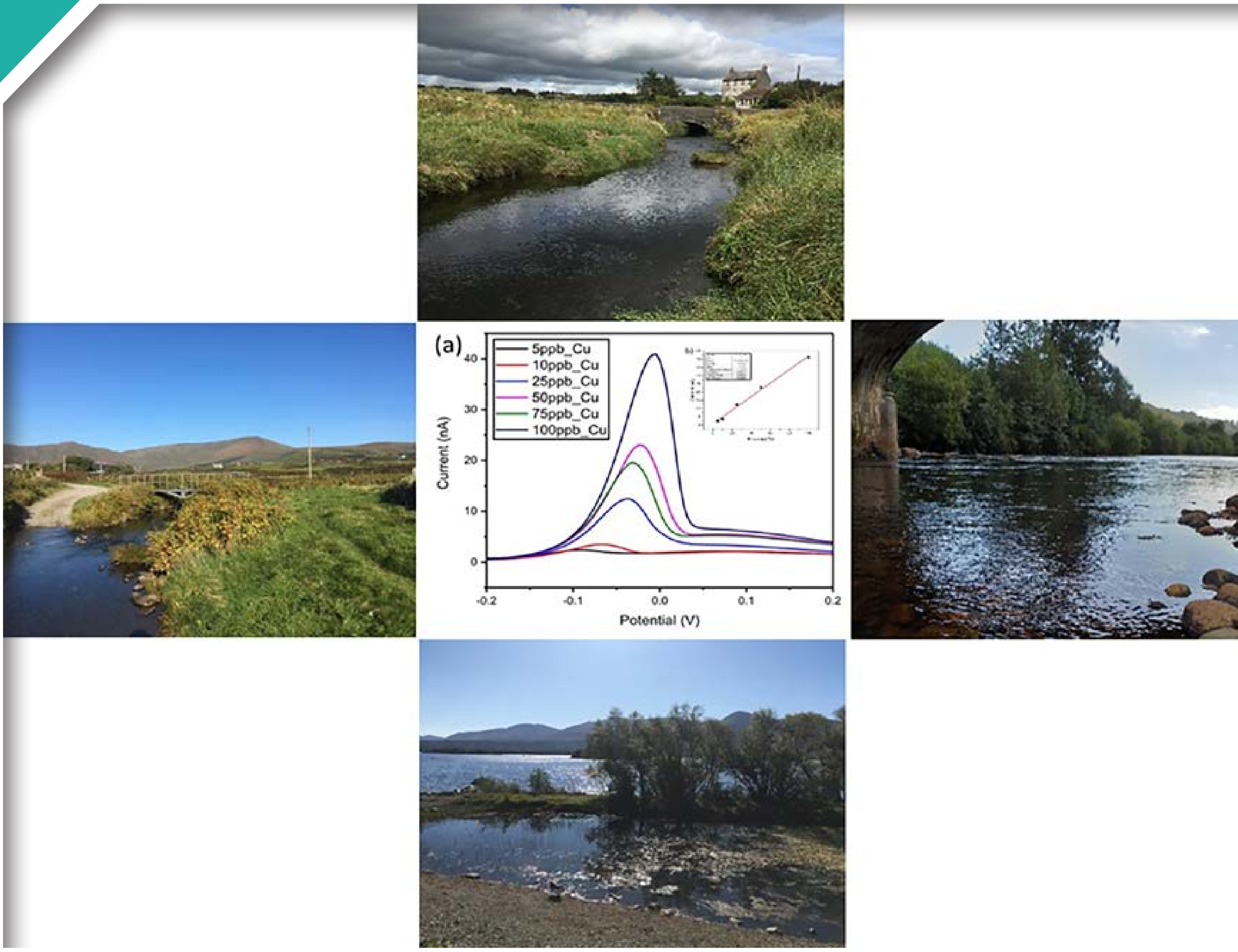

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Rialtas na hÉireann
Government of Ireland

ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: *We implement effective regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.*

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Advocacy: *We work with others to advocate for a clean, productive and well protected environment and for sustainable environmental behaviour.*

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- waste facilities *(e.g. landfills, incinerators, waste transfer stations)*;
- large scale industrial activities (*e.g. pharmaceutical, cement manufacturing, power plants)*;
- intensive agriculture *(e.g. pigs, poultry)*;
- the contained use and controlled release of Genetically Modified Organisms *(GMOs)*;
- sources of ionising radiation *(e.g. x-ray and radiotherapy equipment, industrial sources)*;
- large petrol storage facilities;
- waste water discharges;
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- Supervising the supply of drinking water by public water suppliers.
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- Generating greater environmental awareness and influencing positive behavioural change by supporting businesses, communities and householders to become more resource efficient.
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- Office of Environmental Sustainability
- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet regularly to discuss issues of concern and provide advice to the Board.

EPA RESEARCH PROGRAMME 2014–2020

Development of Proof-of-concept Portable Sensors for Detection of Heavy Metals and Organic Pesticides and Investigation of Anti-biofouling Materials

(UisceSense)

(2015-W-MS-21)

EPA Research Report

A copy of the end-of-project Technical Report is available on request from the EPA

Prepared for the Environmental Protection Agency

by

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Cover images: Left: water stream near Ballydonegan beach, Allihies, Co. Cork. Top: River Mahon, Bunmahon, Co. Waterford. Right: River Avoca, Avoca, Co. Wicklow. Bottom: Lough Leane (Ross Island), Killarney, Co. Kerry. Centre: electrochemical detection of copper solutions.

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

In 2000, the European Union adopted the Water Framework Directive (2000/60/EC) with the aim of ensuring the long-term availability of water in sufficient quantity and of good quality. One of the challenges faced by the Member States regarding the monitoring of priority substances in water is the lack of robust, reliable and cost-efficient detection methods for a number of these contaminants. In Ireland, the threat to water quality arises from a variety of fields of use, including toxicity from pesticides used in agriculture, polycyclic aromatic hydrocarbons from incomplete combustion processes, heavy metals from manufacturing and antibiotics from both human and animal consumption. The UisceSense project specifically aimed to tackle the challenge of developing innovative sensors for sensitive and real-time detection of multiple hazardous substances such as organochlorine herbicides and heavy metals. The rationale was that robust monitoring will allow a comprehensive assessment of the status of water bodies and provide the essential foundation for sound water management. The objectives of the UisceSense project were twofold:

- to develop novel sensors for *in situ*, real-time and sensitive detection of two families of target analytes, namely phenoxy herbicides (such as MCPA and 2,4-D) and heavy metals;
- to investigate novel ways to prevent biofouling – an issue encountered when sensors are left in water for prolonged periods.

Novel electrochemical sensors that include on-chip *in situ* pH control capacity were designed and fabricated during the course of this project. These proof-of-concept sensor chips do not require the addition of a reagent to detect heavy metals. We demonstrated their use for measuring copper and lead at low concentrations, namely 0.9 µg/L and 1.2 µg/L, respectively. Field measurements were carried out at sites expected to have high copper concentrations. Comparison of the results obtained with those from inductively coupled plasma mass spectrometry, or ICP-MS, revealed similar trends but discrepancies in the measured values, possibly due to the nature of the ionic species of copper detected.

Novel and robust surface-enhanced Raman scattering substrates were also fabricated using electrochemical deposition of silver dendrites. These substrates were employed to detect the herbicide 2,4-D in spiked river water: concentrations of 8 µg/L were detected without the need for sample pre-treatment.

In terms of the project's second major objective, regarding anti-biofouling, we made two major technical breakthroughs. First, a novel atomistic modelling method was applied to the problem of anti-biofouling, resulting in the creation of significant intellectual property. Second, titanium nitride films coated with a dedicated anti-biofouling layer showed promise for preventing the formation of biofilm composed of bigger bacteria.

It is envisaged that this project will provide the foundational technical data for further development of novel nanosensors for heavy metals and pesticides, as well as opening up a novel line of research into modelling of nanostructures for anti-biofouling activity.

1 Background and Objectives

1.1 Introduction

Water is a precious resource, being key to various economic activities, such as transport, agriculture, manufacturing and tourism/entertainment, and of course a major component of health through its consumption. Unfortunately, multiple threats to water quality are associated with a variety of fields of use: pollution from pesticides used in agriculture, polycyclic aromatic hydrocarbons (PAHs) from incomplete combustion processes, heavy metals from manufacturing and antibiotics from human consumption, to name but a few.

To tackle the wide variety of contamination, the European Union (EU) adopted the Water Framework Directive (WFD; 2000/60/EC) in 2000 (European Union, 2000), which targets ensuring the long-term availability of sufficient water of good quality. This Directive set clear objectives for all groundwater and surface waters in the EU to achieve “good status” by December 2015.

In its study of water quality in Ireland for the period 2013–2018 (Environmental Protection Agency, 2019), the Environmental Protection Agency (EPA) reported that 53% of rivers, 50% of lakes, 38% of transitional waters, 80% of coastal waters and 92% of groundwater were satisfactory, being at good or high status. While these results are positive for coastal waters and groundwater, a significant challenge remains to meet the requirements of the WFD. In Europe as a whole, the European Commission reported in 2018 that around 40% of surface water met the good-status criteria (European Commission, 2018). While Member States have made marked efforts to improve water quality, new contaminants not currently monitored are emerging. For example, the EPA noted that contaminants in water such as pharmaceuticals were currently not widely monitored, despite being an emerging environmental issue, and that national consideration of their presence and magnitude in the Irish environment would be needed in the near future (Environmental Protection Agency, 2015a).

One of the challenges faced by the Member States regarding the monitoring of priority substances is the lack of robust, reliable and cost-efficient methods of detection for a number of these contaminants. For those Member States that could not achieve good status, the European Commission has allowed them to rely on an exemption and to extend the deadline up to 2027 or beyond. However, at the same time, the Commission recommends that they “improve and expand monitoring and assessment tools to ensure a statistically robust and comprehensive picture of the status of the aquatic environment for the purpose of further planning” (European Union, 2000). This has been recognised in Ireland through the strategic role of environmental research in a number of the 14 stand-alone priority areas.

The UisceSense project specifically aimed to develop innovative sensors for sensitive and real-time detection of multiple hazardous substances, such as chlorophenoxy herbicides and heavy metals. Pesticides are routinely applied throughout the world to maximise crop yields and protect agricultural produce. However, concerns have been recently expressed about the negative effects of these pesticides on the activity of bees (Gill *et al*., 2012; Whitehorn, 2012), and there is a strong suspicion of adverse effects on human health (Morrissey, 2015). In addition, heavy metals are ubiquitous and can be found in batteries and cigarettes (cadmium), wood preservative (arsenic), food (mercury in fish) and more generally in residues from industries. All of these substances have been shown to have serious effects on human health, even if ingested in minute quantities (Järup, 2003).

Unfortunately, all of these contaminants may be introduced to the environment via run-off and releases from storage and transport. Depending on the contaminant, they may even progressively accumulate in surface waters and in the soil (and hence find their way into groundwater and potentially crops). To limit and control the spread of these pollutants, the EU has fixed environmental quality standards (European Union, 2015; see Table 1.1).

Table 1.1. List of contaminants and their associated emission limit values

Parameter		Emission limit value (µg/L)
Pesticides	Total	0.5
	Individual	0.1
Heavy metals	Lead	10
	Mercury	1
	Copper	2000

The European Commission (2018) report on the implementation of the WFD recommended robust monitoring to provide data for a comprehensive assessment of the status of water bodies. This assessment would then form the basis of sound water management. The rationale underpinning the UisceSense project is that developing novel sensors that can provide sensing data *in situ* and in real time would greatly aid stakeholders to assess, manage and monitor the state of water systems and therefore help the Irish Government to achieve its policy objectives and to ensure that EU and national environmental policies are implemented in the most cost-effective manner.

The objectives of the UisceSense project were twofold: the first aim was to develop novel sensors for *in situ*, real-time and sensitive detection of two families of target analytes, namely the phenoxy herbicides 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) and heavy metals. The enabling technologies at the heart of the UisceSense sensors are electrochemistry at the microelectrode level and surface-enhanced Raman spectroscopy (SERS).

In this project, electrochemical methods were used to detect heavy metals (Pujol, 2014). Electrochemistry at the microelectrode level is a robust and highly sensitive detection method. To achieve the required level of sensitivity, the development of an electrochemical sensor requires that a large set of parameters are assessed, including:

- the composition of bare electrodes [gold (Au), platinum (Pt), etc.];
- the chemical composition and deposition of electrode modifications;
- physical parameters of microelectrode geometry, such as width and spacing between the electrodes.

Given the complexity of microelectrode electrochemistry, the first step was to model the mass transport properties of electrodes. The results of the modelling work fed the experimental, laboratory bench analysis, the results of which refined the modelling and the process was repeated.

The second enabling technology used in this project, SERS, is a spectroscopic technique that can provide a “molecular” fingerprint of the chemicals in the sample. It is well suited to the detection and identification of organic contaminants.

Field testing of these enabling technologies has shown that both have potential for widespread use, and they are currently being developed at Tyndall National Institute, other institutions and companies worldwide. This means that environmental samples could be measured in quasi-real time in the field, guiding or narrowing down sampling locations, for example during an investigation of a contamination source. Once optimised, these techniques have the potential to complement conventional monitoring based on solid-phase extraction/high-performance liquid chromatography (HPLC), gas chromatography (GC) or inductively coupled plasma mass spectrometry (ICP-MS). Such techniques require trained operators and high-end equipment, making them costly processes (Navalón *et al.*, 1997; Ferrer *et al.*, 2005; Liu *et al.*, 2010). Although not within the scope of the current project, the sensors developed are compatible with low-cost fabrication techniques. In addition, communication modules can be incorporated in the reader for remote sensing modalities.

In parallel to the detection of the pollutants mentioned above, the second objective of UisceSense was to investigate novel ways of preventing biofouling. This is an issue encountered when sensors are left in water for prolonged periods and can occur in as little as a week. As with the development of the sensors themselves, the first step was atomic/mathematical simulations to provide insight into the mechanisms of biofouling and propose strategies to avoid fouling. The strategies were then tested and the results reported.

1.2 Phenoxy Herbicides MCPA and 2,4-D

1.2.1 Overview of MCPA and 2,4-D

MCPA and 2,4-D (see chemical structures in Figure 1.1) are chlorophenoxy herbicides widely used for the control of broadleaved weeds, including thistle and dock, in cereal crops and pasture. They are two of the active ingredients of products available to amateur gardeners and professional farmers such as Agritox and Weedol. MCPA and 2,4-D are selective systemic hormone-type herbicides and work by concentrating in the meristematic tissue (the growing region of the plant) and interfering with protein synthesis and cell division. The toxicity and biodegradation of both MCPA and 2,4-D are topics of current research (World Health Organization, 2016). MCPA persists for 2–3 months in soil, whereas 2,4-D persists for about 1 month (Zimdahl, 2015). Furthermore, MCPA and 2,4-D can be expected to leach readily in most soils, with mobility increasing as organic matter content decreases (World Health Organization, 2016). Both pesticides are widely used in a range of settings such as agriculture, amenity use (golf courses, parks, sports grounds) and amateur use (home gardens). Because of their widespread use and exceedances (see below), the EPA and Teagasc have provided strong guidelines on how to administer these herbicides in a video (Department of Agriculture Food and the Marine *et al.*, 2018). However, despite these precautions, these pesticides have been found in surface waters. To tackle this issue, the National Pesticides and Drinking Water Action Group was established to support the achievement of compliance with the Drinking Water Directive pesticide standards. This group includes a wide range of key stakeholders across various sectors (government departments and agencies, local authorities, industry representative bodies, farming organisations, water and amenity sectors) and its role is to support the achievement of compliance with the Drinking Water Directive (98/83/EC) pesticide standards. This can be done through enhanced collaboration and linkages between relevant stakeholders but also by raising awareness and sharing information on the current policies and identifying gaps in implementation (Environmental Protection Agency, 2018).

In Ireland, more than 1833 tonnes of herbicides were placed on the market in 2018 (Department of Agriculture Food and the Marine, 2018). Unfortunately, as with all pesticides, point-source pollution can occur during mixing and filling the solution in the sprayer and diffuse pollution can occur through spray drift, drainage and run-off. Despite stringent guidelines for the use of pesticides, such as compulsory registration with the Department of Agriculture, Food and the Marine and establishing buffer zones (European Union, 2009), the EPA detected MCPA in 55% of rivers monitored from 2013 to 2018 (1292 samples) and 2,4-D in 29% of rivers monitored (1158 samples). In 2018, the drinking water standard for individual pesticides (0.1 µg/L) was exceeded in 42 public drinking water supplies, and MCPA was the chemical responsible for 75% of all failures detected (Environmental Protection Agency, 2019). There is a seasonal pattern in the detection of MCPA exceedances in that they are most frequent in May, June and July and again in September and October. These are typically the months during which MCPA is applied to grassland for ragwort, rush and thistle control (Environmental Protection Agency, 2015b). As a result of the numerous exceedances observed and because surface waters (rivers and lakes) account for 80% of drinking water supplies in Ireland, it may be necessary to consider regulating this substance in the future.

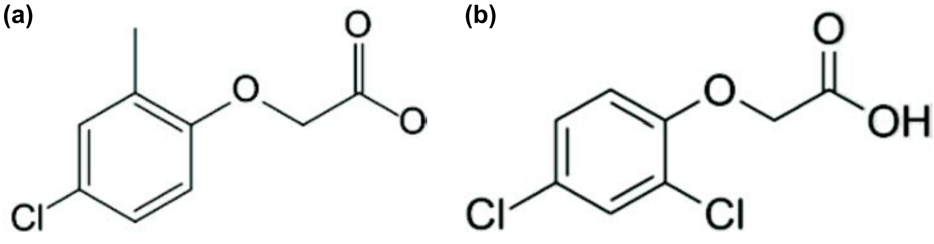

Figure 1.1. Chemical structures of (a) MCPA and (b) 2,4-D.

1.3 Current Method for Detecting MCPA and 2,4-D

1.3.1 Accredited methods

In Ireland, the accepted method for detecting MCPA and 2,4-D used in accredited laboratories is based on United States Environmental Protection Agency methods 538-1-2009 and 535-2005. These methods use liquid chromatography with tandem mass spectroscopy (LC-MS), and provide a range of measurement of 0.005–0.5 µg/L. Clearly, these technologies require extensive sample preparation and bulky equipment, and therefore cannot be used for *in situ* or online monitoring.

1.3.2 Other laboratory-based methods

Other laboratory-based methods used for the detection and quantification of chlorophenoxy herbicides are based on HPLC coupled with ultraviolet detection (HPLC-UV), and gas chromatography–mass spectrometry (GC-MS; see Table 1.2). Similarly to the accepted accredited method, these measurements tend to be time consuming and costly, often requiring complex sample preparation (Rahemi *et al.*, 2012).

1.3.3 Emerging methods

In the last decade, emerging methods of detection have been reported in the literature. For example, using electrochemical techniques, detection of MCPA down to 220 µg/L was achieved with a carbon nanotube-modified glassy carbon macroelectrode (see Table 1.3).

Another emerging method of detection is based on SERS. Raman spectroscopy is a powerful analytical technique similar to infrared absorption spectroscopy and capable of providing the molecular fingerprint of the sample under investigation (see Figure 1.2a, showing the energy band diagram involved in the Raman effect). Unfortunately, Raman spectroscopy is not an efficient process with only 1 out of ~10^8 photons being Raman scattered. However, these limitations can be overcome in SERS, in which Raman signals are typically amplified by a factor of 10^6 owing to plasmonic effects taking place in electromagnetic hot spots found in nanostructured metallic surfaces (see Figure 1.2b). To date, a wide variety of SERS substrates have been reported, such as nanoparticles (spherical, star-shaped, etc.), templated nanostructures (nanoimprint, anode aluminium oxide template) or samples defined by electron beam

Table 1.2. Laboratory-based methods for detecting 2,4-D and MCPA

Analyte	Detection method	Linear range (µg/L)	Limit of detection (µg/L)	Reference
MCPA	LC-MS	0.2–100	0.040	Pozo *et al.* (2001)
Chlorophenoxy acid herbicides	HPLC-UV	2000–10,000	10	Jankowska *et al.* (2004)
Chlorophenols	HPLC-UV	5–36	2.5	Favaro *et al.* (2008)
2-Chlorophenol	GC-MS	0.04–790	0.04	Faludi *et al.* (2015)
4-Chlorophenol				

Table 1.3. Emerging technologies for detecting MCPA and 2,4-D

Analyte	Detection method	Linear range (µg/L)	Limit of detection (µg/L)	Reference
MCPA	Cyclic voltammetry on carbon nanotube sensor	220–11,000	220	Rahemi *et al.* (2014)
MCPA	Cyclic voltammetry on carbon nanotube sensor	220–22,000	220	Rahemi *et al.* (2012)
4-Chloro-3-methylphenol	Square wave voltammetry on boron-doped diamond electrode	NA	14	Brycht *et al.* (2016)
2,4-D	SERS	22–20,0000	22	Costa *et al.* (2010)

NA, not available.

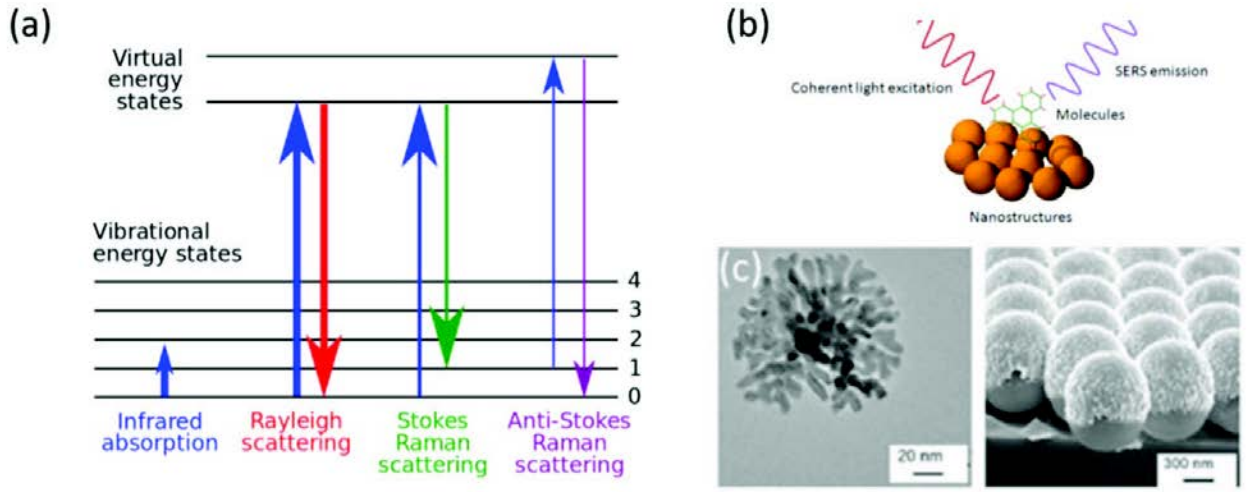

Figure 1.2. (a) Energy band diagram showing the Raman effect. (b) Schematic diagram showing the SERS enhancement on nanostructure metallic surfaces. (c) Examples of some SERS substrates.

lithography (see Figure 1.2c for examples). SERS has thus far found a wealth of applications in chemical, environmental and biological sensing (Kahraman *et al*., 2017). Limits of detection down to 22 µg/L of 2,4-D have been achieved using SERS substrates functionalised with molecularly imprinted polymer (see Table 1.3).

1.4 Heavy Metals

1.4.1 Overview of heavy metals

Heavy metals are necessary components in a variety of manufacturing industries worldwide. Cadmium (Cd), found naturally at concentrations of up to 0.1 mg/L in the Earth's crust, and lead (Pb), found at 10 mg/L in the Earth's crust, are two common heavy metals used primarily in the production of batteries. Eighty-three per cent of the global production of Cd is used for rechargeable Ni-Cd batteries, and 88% of Pb in lead–acid batteries (Figure 1.3) (Wedepohl, 1995; Wilburn, 2007, 2014). In addition, Cd is a component in a variety of corrosion prevention finishes and is used as a pigment in paints (Bernhoft, 2013). Copper (Cu) can be released into the environment through excessive use or improper disposal of Cu-based agrochemicals. The release of heavy metals into the environment can also be the result of accidental industrial release or improper disposal of heavy metal-containing products. Another possible source of pollution in the environment is long-range cross-boundary processes. Ireland is is a signatory to the Convention on Long-range Transboundary Air Pollution which recognises these issues (Environmental Protection Agency, 2008).

The WFD strictly regulates the limits for heavy metals in water, with maximum allowed concentration values of 14 µg/L for Pb and 0.45 µg/L for Cd (European Union, 2000). Similarly, the safe limit for Cu concentration in drinking water is 2 mg/L (Environmental Protection Agency, 2014). Moreover, the Irish standard for Pb in drinking water was reduced to 10 µg/L at the end of 2013 (Environmental Protection Agency, 2015b). In 2018, Pb was detected in 14 public water supplies in Ireland. In addition to this, Pb pipework is still widely used private homes in Ireland. To tackle the issue of Pb contamination, a National Lead Strategy was published by the government in June 2015 (Department of Housing, Planning and Local Government, 2015). While a lack of Cu in the human body can lead to anaemia, leucopenia or osteoporosis, at high concentrations Cu can pose a threat. Excessive concentrations of Cu can cause gastrointestinal disturbance, respiratory difficulties, liver and kidney failure, and chronic exposure to Cu can cause Wilson's disease (Xiong *et al*., 2017). Pb and Cd in drinking water pose a serious threat to health, as they are readily absorbed by the body once ingested and can lead to cancer, kidney damage, osteoporosis, damage to the nervous system and psychosis (Järup, 2003). Even small amounts of these heavy metals can bioaccumulate over time to cause possible health issues (Rajeshkumar *et al*., 2018).

Figure 1.3. A typical lead–acid battery (left) and a selection of rechargeable Ni-Cd batteries (right).

1.4.2 Method of detecting heavy metals

Accredited methods

Detection and quantification of Pb and Cd is most commonly performed using ICP-MS, flame atomic absorption spectroscopy (FAAS) or atomic fluorescence spectroscopy (AFS; see Table 1.4). These systems are expensive to both purchase and run, as they require specialist training as well as costly gases. In addition, these methods cannot be used in the field, necessitating the collection and transport of a sample from the point of interest. There is therefore a need for small, portable and cost-effective systems for analysis of heavy metals *in situ*.

Electrochemical methods

While the current standard method for heavy metal analysis will remain in use, it is impractical to run an ICP-MS on site where the analysis is most needed. Electrochemical methods of analysis allow easier and cheaper on-site analysis using a miniaturised analysis system. Ultra-microelectrodes are electrodes with at least one critical dimension $<25\,\mu m$. Using microelectrodes overcomes a variety of issues inherent in macroelectrode design. Because of the planar diffusion of analytes to the macroelectrode surface, the diffusion layer is very small compared with the critical dimension of the surface. This results in a time-dependent and diffusion-limited response. This causes slow mass transport of the analyte during electrochemical analysis at the surface, such as cyclic voltammetry and square wave stripping voltammetry. The planar diffusion affects the shape and magnitude of the cyclic voltammogram obtained. When the critical dimension is reduced to the micro- or nano-scale, radial diffusion can be obtained (see Figure 1.4). In this case, the diffusion layer is larger than the critical dimension. This results in a time-independent and steady-state system with increased rates of mass transfer. This increased mass transfer allows low concentrations of analytes to be studied. The radial diffusion allows higher current densities and higher signal-to-noise ratios. It also allows low-volume analysis and high-speed electron transfer kinetics.

To increase sensitivity, analysis may include a pre-concentration step in which the analyte is first electrodeposited on the working electrode before being “stripped” off in a quantitative step (see Figure 1.5). The miniaturisation, low power consumption and increasing sensitivity of the electrochemical methods make them an ideal candidate for *in situ* analysis of samples.

Table 1.5 below shows the emerging electrochemical methods of detection and their sensitivities. For the detection of Pb, Au screen-printed electrodes showed detection limits down to 0.5 µg/L, significantly below the current maximum allowed concentrations of 10 µg/L.

It should be noted that all the current electrochemical sensors (Table 1.5) for heavy metals are based on sensors at the macro- and micro-levels (from 1 mm and larger to 100 µm). The sensors developed during the UisceSense project use 1-µm microbands and display enhanced mass transport. Therefore, the UisceSense nanosensors would have a much lower detection limit than the macro- and micro-sensors that are currently available. Furthermore, none of the current electrochemical sensors have on-chip *in situ* pH control capabilities (a major advantage of the UisceSense sensors platform) and therefore require the addition of acids to make the measurements. Finally, these sensors can be multiplexed, allowing for the detection of more than one target from a single sensor.

Table 1.4. Comparison of detection methods for lead and cadmium

Method	Analyte	Limit of detection (µg/L)	Range (µg/L)	Reference
FAAS	Pb, Cd, Cr, Cu, Ni	1040 (Pb) 98 (Cd) 1240 (Cr) 3440 (Cu)	Not mentioned	Zhong *et al.* (2016)
Fluorometry	Pb	35	105–51,800	Talio *et al.* (2019)
ICP-MS	Cu	0.1	Down to 0.0005	Nham (1998)
ICP-AES	Hg	240	Up to 500,000	Bidari *et al.* (2012)

ICP-AES, inductively coupled plasma atomic emission spectroscopy.

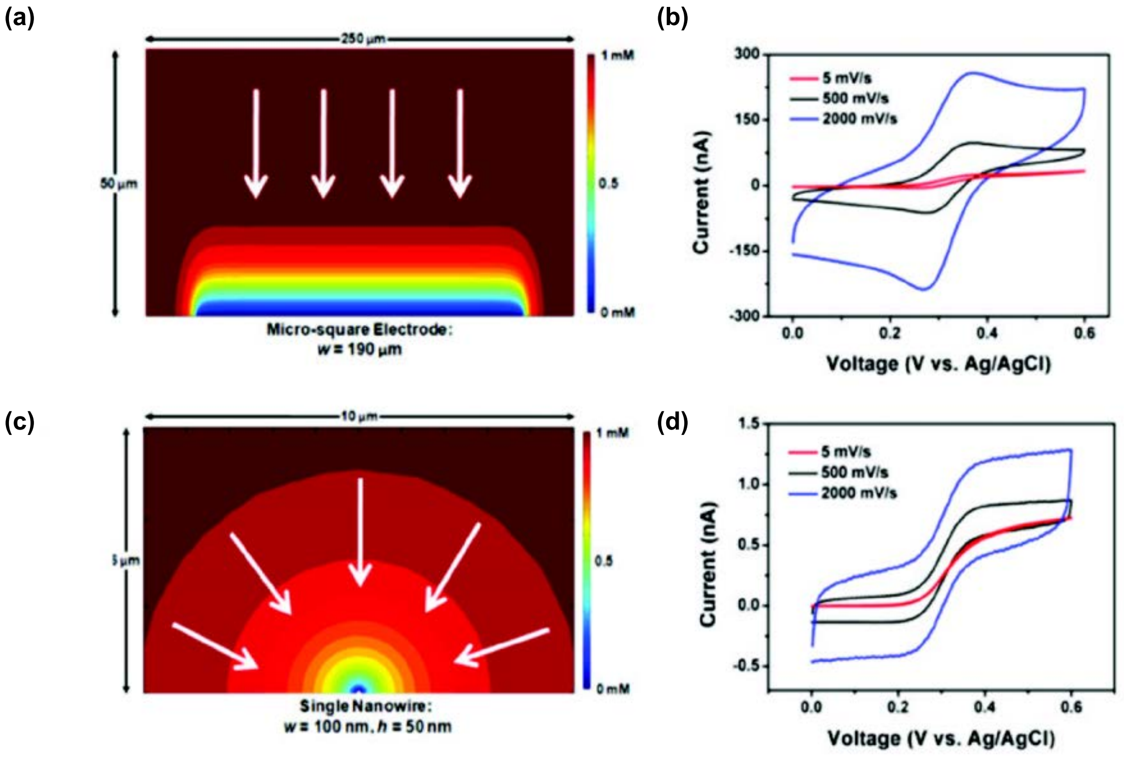

Figure 1.4. Simulated diffusion profiles for (a) planar and (c) microelectrode. The associated cyclic voltammograms are shown in (b) and (d), respectively.

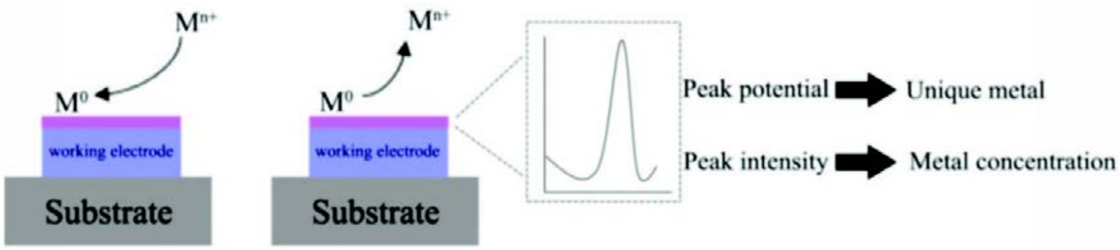

Figure 1.5. Schematic diagram showing pre-concentration with anode stripping voltammetry. Source: March *et al.* (2015). Reproduced under the terms and conditions of the Creative Commons attribution licence CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Table 1.5. Current electrochemical detection methods and their sensitivities

Analyte	Electrode	Linear range (µg/L)	Limit of detection (µg/L)	Limit of quantification (µg/L)	Reference
Cu	Multi-wall carbon nanotubes – carbon paste electrode	6–6,300,000	630		Ganjali *et al.* (2011)
Cu	Sol gel Au nanoparticle – carbon paste electrode	30–630,000	25		Mashhadizadeh *et al.* (2011)
Cu	Ion-selective electrode	60 to saturation	60		Metrohm (no date)
Pb	Au screen-printed electrode	1.5–50	0.5	–	Laschi *et al.* (2006)
Pb	Hanging mercury drop electrode	517–207,000	103	207	Krystofova *et al.* (2010)
Pb	Carbon paste electrode	1242–20,700	103	227	Krystofova *et al.* (2010)
Pb	Carbon-tipped electrode	1035–103,500	103	227	Krystofova *et al.* (2010)

Other portable methods commercially available

A review of commercially available instruments has identified a number of existing products. These include a portable field kit from FREDsense that allows detection down to 1 µg/L of arsenic, iron and manganese. The measurement takes about 1 hour and this instrument relies on electrochemical signals from tuneable bacteria that are sensitive to the targeted compounds. In addition, ANDalyze have developed a handheld fluorimeter with detection limits of 2 µg/L for Pb, 40 µg/L for Cu and pass/fail at 2 µg/L for mercury (Hg). The underlying technology relies on the use of a DNAzyme reaction that fluoresces in the presence of the target contaminant. Finally, OndaVia is developing a portable instrument based on Raman spectroscopy for the high-range (µg/L) detection of Pb using consumable cartridges. These technologies have limitations in terms of costs (cartridges cost in the order of US$200 for the OndaVia product and probes in excess of €3000 for the ion-selective electrodes), speed (1-hour measurement for the FREDsense sensors) or accuracy (±15% accuracy for the ANDalyze sensor).

1.5 Biofouling and Anti-biofouling

1.5.1 *Biofouling*

Biofouling relates to the growth of biological organisms (such as bacteria, algae and barnacles) on surfaces immersed in an aqueous environment (see Figure 1.6). Biofouling is a major issue for activities taking place

Figure 1.6. Example of biofouling on a current measurement instrument. Credit: NOAA, Great Lakes Environmental Research Laboratory.

in the sea or fresh waters and is estimated to cost industry at least US$1.5–3 billion annually in the USA alone (Ware *et al.*, 2018). For example, it has been shown that the roughness induced by the growth of organic entities on the surface of vessels incurs a powering penalty of up to 86%, resulting in a significant increase in fuel consumption (Callow *et al.*, 2011). Similarly, biofouling drastically reduces the efficiency of heat exchangers in power stations' cooling systems (Yang *et al.*, 2015). Biofouling occurs on the surface of any type of sensor left in water for a period of time thereby affecting their reliability and/or accuracy. Depending on the environment, this can happen rapidly within a few days or over a longer period (months). This is the major obstacle that has so far prevented the deployment of sensors in remote locations.

While biofouling depends on the particular species present as well as a variety of factors such as temperature, pH, location, nutrient/oxygen content and water flow (Callow *et al.*, 2011), it is generally accepted that surface colonisation occurs in three steps (see Figure 1.7). First, organic carbon residues such as glycoproteins are adsorbed at the surface immediately after submersion. Following this, typically within a few hours, bacteria start colonising the surface to create a continuous biofilm. The final stage, taking place over days or weeks, is the attachment of bigger organisms such as larvae, seaweed or barnacles.

1.5.2 Anti-biofouling approaches

From a generalised perspective, a functional sensor device is composed of two major components: (1) the bulk substrate, the conductive silicon-based layer; and (2) the sensor circuitry, the electrodes and coatings that perform the actual detection. As each of these components has specific functional requirements, they are discussed separately below with regards to biofouling and anti-biofouling strategies.

Anti-biofouling coatings

To prevent biofouling, the current approach commonly used is to protect surfaces with coatings containing biocides such as tributyltin oxide or Cu-based paint. However, both of these biocides are pollutants and their use is therefore being restricted or strictly regulated (Yebra *et al.*, 2004). To address this challenge, novel anti-biofouling approaches are being investigated by numerous laboratories around the world. Because of the variety of the organisms and their attachment mechanisms, it is widely accepted that a multidisciplinary approach – including development of new materials, novel strategies such as micro- and nanostructuring, engineering designs for enhanced hydrodynamics – will be required to effectively prevent biofouling. Strategies currently being investigated include the use of bioinspired surfaces with increased roughness, such

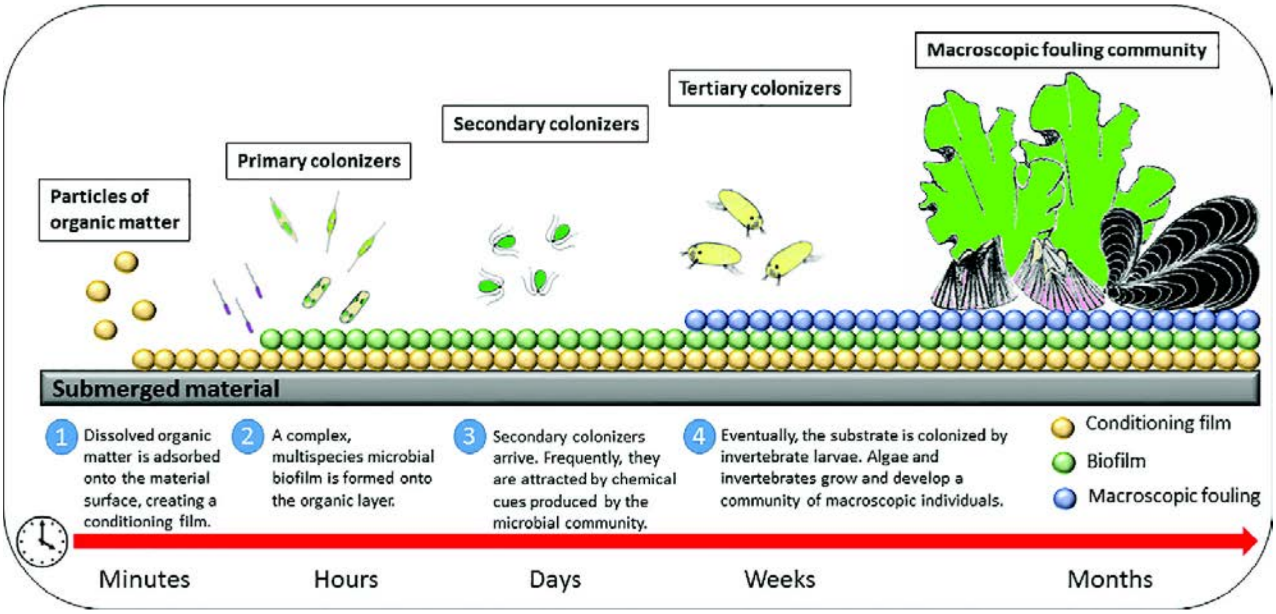

Figure 1.7. The stages of biofouling. Source: Martín-Rodríguez *et al.*, 2015. Reproduced under the terms and conditions of the Creative Commons attribution licence CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

as polydimethylsiloxane, mimicking a shark's skin (Ganguli *et al*., 2009), amphiphilic nanostructured material (i.e. with both hydrophilic and hydrophobic behaviour) (Callow *et al*., 2011), superhydrophilic zwitterionic polymers or superhydrophobic surfaces doped with carbon nanotubes. While a lot of these new surfaces/coatings have shown encouraging experimental results, the reasons for their success often remain unclear. In this regard, modelling at the atom level, as undertaken in UisceSense, provides vital insight into the biofouling process and informs the development of new materials or designs with efficient anti-biofouling capabilities.

Computational modelling of materials for anti-biofouling applications

An important activity within the project was the undertaking of density functional theory (DFT) simulations to find the best anti-biofouling materials and to ensure the robustness of the sensing platform in the harsh environment that river/sea water constitutes. In this regard, titanium nitride (TiN) has been shown to be a promising candidate due to its good electrical and thermal conductivity, ultra-hardness (comparable to that of diamond), resistance to corrosion, biocompatibility, non-release of toxic substances and compatibility with standard microelectronics fabrication methods (Toth, 1971; Johansson, 1995; Pierson, 1996; Vaz *et al*., 2003). First principles studies were undertaken using large-scale state-of-the-art DFT simulations, which are widely used for modelling and predicting the properties of a vast range of materials, surfaces, interfaces and interactions with molecules; these are all crucial for the TiN base sensor devices and their fouling within the UisceSense project.

Specifically, the simulations in the project were undertaken within the well-known and widely used generalised gradient approximation (GGA) to the exact exchange–correlation functional. The DFT-GGA simulations describe the structural parameters of TiN with excellent agreement compared with experimental values (Marlo and Millman, 2000). In addition, a previous study showed that the TiN-100 surface has the lowest surface energy while TiN-111 was shown to be energetically unfavourable (Mehmood *et al*., 2015). The TiN-100 surface is terminated with a neutral layer with stoichiometric amounts of Ti and N. However, it is known that TiN spontaneously forms a thin oxide layer when it is exposed to air (Mehmood *et al*., 2015). When oxidation occurs under normal atmospheric conditions, this will proceed along a path showing features of both a thermodynamically stable transition and adsorption with formation of metastable intermediate structures. In fact, at high temperatures, an ordered oxide structure will grow on the surface, preventing the substrate from further oxidation because of the high level of energy needed to adsorb more incoming oxygen (O_2).

However, when the temperature is very low, vacancies and defects are prone to remaining trapped inside the structure (Zimmermann *et al*., 2009). Thereafter, a DFT study on TiN showed that when O_2 is absorbed on a Ti site in the surface layer, it can either spontaneously dissociate or form a titanium dioxide (TiO_2) layer, similar to the oxidation of some metal surfaces (Hong *et al*., 2014). The results of these studies could be used as a guide to define the TiN surface for the simulations of biofouling undertaken in this project. To complement these ideas and to improve the anti-biofouling characteristics of TiN, previous experimental work has tested the addition of some doping elements. In particular, substitution of aluminium (Al) in the TiN matrix is known to increase the resistance to oxidation (Rebouta *et al*., 1995), which has also been observed with the addition of silver (Ag) or Cu nanoparticles and this can also enhance the antibacterial properties (Valodkar *et al*., 2011).

With the purpose of quantifying biofouling and seeking a descriptor to study the anti-biofouling properties of materials, wettability could be a crucial parameter to take into account. Wettability is defined as the ability of a solid surface to maintain contact with a liquid whose surface tension is reduced so that the liquid spreads over the surface of the solid. In fact, some previous experimental and theoretical studies reported that surface wettability influences the attachment strength of fouling organisms on artificial substrata (Loeb and Fletcher, 1979; Brewer, 1984; Valodkar *et al*., 2011). Specifically, super-hydrophobic materials are characterised by their low friction and low surface energy, which prevent the attachment of large organisms (Ma *et al*., 2006). Unfortunately, most super-hydrophobic materials are polymers, which are well known to show a lack of mechanical strength and long-term stability, making them impractical for sensor applications (Tian *et al.*, 2015). However, super-hydrophilic materials (e.g. diamond-like carbon (DLC)) are considered superior to hydrophobic materials in preventing the attachment of bacteria and the formation of a biofilm (Tian *et al.*, 2015). This effect is due to their high level of hydration; therefore, a very high level of energy is necessary to remove the water, preventing proteins and microorganisms from attaching to the surface. Previous studies have shown that polycrystalline diamond and DLC provide biocompatible, ultra-hard, low-friction, wear-resistant coatings (Tang *et al.*, 1995; Hauert, 2003). Moreover, it is suggested that DLC should increase its hydrophilic character and therefore display better anti-biofouling properties when doped. In effect, DFT calculations have shown that the adhesion energy of biomolecules decreases with increasing concentration of dopants such as silicon, nitrogen or fluorine (Si, N or F) because of the increasingly polar character of the surfaces. This effect makes the surface able to attract further water molecules more strongly than the clean surface and results in stronger interactions with water (Borisenko *et al.*, 2009; Kajita *et al.*, 2016).

Nevertheless, the binding of organisms is an extremely complex phenomenon that depends on variables such as the type of protein, the surface termination or the type of surface plane (Tian *et al.*, 2015). However, although diverse experiments on several materials immersed in water have been carried out (Pelleg *et al.*, 1991; Hegde, 1993; Oh *et al.*, 1993), theoretical studies aiming to gain physicochemical insights into micro- and macro-fouling attachment, to our knowledge, are lacking. To this end, atomistic simulations by means of first principles DFT within the framework of the Vienna Ab initio Simulation Package (Hafner, 2008) were carried out to study the interactions of simple amino acids that make up peptides present in proteins (e.g. glycine) with model TiN- and TiN + O_2-oxidised surfaces, see Figure 1.8. These results were used to determine the fundamental factors that drive biofouling and will serve as a guide for the design of future novel materials for anti-biofouling applications.

1.5.3 Anti-biofouling strategies for sensors

Unfortunately, while the strategies presented in section 1.5.2 above can be used for housing the sensors, they cannot be applied to the sensors' surfaces, as they would interfere with the measurements. To address this, new approaches are being investigated and studied by researchers and manufacturers. These include illuminating the sensors with ultraviolet (UV), laser or ultrasonic irradiation, removing the biomaterials with purely mechanical devices such as wipers or scrapers, automatic dispensing of biocides, acid or chlorine, and electrochemical-based techniques (electron transfer to the organic species and localised sea water electro-chlorination) (Delauney *et al.*, 2010).

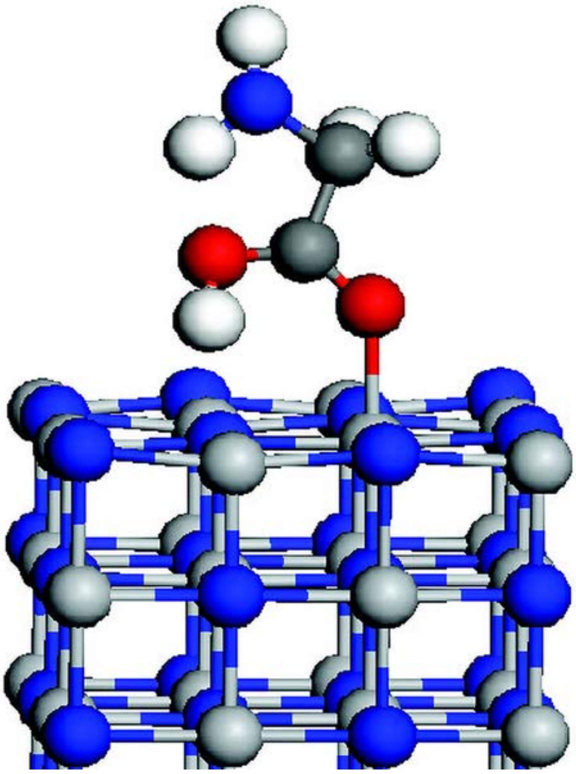

Figure 1.8. Model of glycine absorbed onto TiN-100 surface.

Illumination with a laser or ultrasonic radiation is not practical for field deployment because of high energy consumption and high costs, although prices are dropping rapidly. Releasing biocidal agents and mechanical removal do not always remove all materials and rely on mechanical parts that are prone to failure in turbid, high-flow environments. Illumination with UV light is gaining increased attention owing to the reduced financial and energy costs of light-emitting diodes, but they require a transparent antifouling coating themselves so that the light is not blocked.

Electrochemical-based anti-biofouling techniques

Alternatively, electrochemical-based techniques have been shown to be promising (Sultana *et al*., 2015). Electrochemical control prevents the formation of biofilm through the application of a constant potential that produces electrochemical reactions on the target surface. The exact method of action of this kind of antifouling method is not yet fully understood, but it is thought to occur via two pathways. The first is direct electron transfer to the microorganisms, which weakens the binding between the electrode surface and the bacteria through electrostatic forces (bacterial cells usually have a net negative surface charge) (Busalmen *et al*., 2001, 2005; Hong *et al*., 2008). The second process is the generation, via electrochemical reactions, of strong oxidants such as hydrogen peroxide (H_2O_2) or free chlorine in the volume just above the surface of the sensor (Liu *et al*., 1997; Sandvik *et al*., 2013). The H_2O_2 is formed through the partial reduction of O_2 on the metal surface according to equation 1.1:

$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2 \qquad (1.1)$$

The chlorine (Cl) is generated by so-called Cl evolution following equations 1.2 to 1.4:

- electrochemical production of Cl from Cl^- ions dissolved in water:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1.2)$$

- hydrolysis of Cl in water and with formation free Cl, i.e. hypochlorous acid (HClO) and hypochlorite anions (ClO^-)

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (1.3)$$

$$HClO \leftrightarrow ClO^- + H^+ \qquad (1.4)$$

Such reactions are currently used for disinfection of water (Matsunaga *et al*., 2000) but have not yet been widely adapted to sensors. A possible reason for this is that H_2O_2 or Cl can be harsh on the materials themselves.

Titanium nitride for electrochemical-based anti-biofouling

In this respect, TiN has proved very promising. TiN is a ceramic material that can be readily deposited by sputtering (Kawamura *et al*., 1998; Ponon *et al*., 2015). Sputtering is a process whereby microscopic particles of solid material are ejected from a target after it is bombarded by an energetic gas plasma. These particles are subsequently deposited on the substrate of choice. TiN is widely used in the mechanical industry for its extreme hardness (coating on drill bits), for decorative purposes owing to its golden appearance, in the medical industry because of its inertness (coating of medical implants) and in the microelectronic industry as a blocking layer. These properties make it an attractive candidate for electrochemical-based anti-fouling, whereby the application of potential pulses of about 1 V prevents the growth of organisms (Nakayama *et al*., 1998a,b; Bunn, 2014). This approach has been shown to be effective in the prevention of fouling of TiN electrodes submerged in sea water (see Figure 1.9).

Interestingly, TiN can also be used in electrochemical sensing applications (Kirchner *et al*., 2007), and it has

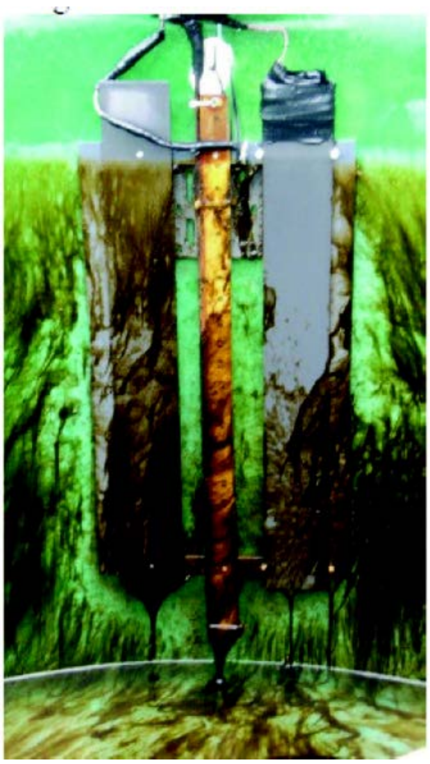

Figure 1.9. An electrode with an engineered sheet resistance and with a potential applied (right) compared with an electrode with no potential applied (left). Biofouling on the electrode with power applied stops at a local potential of 1.05 V against Ag/AgCl. Source: Reprinted, with permission, from Bunn *et al*., 2014. © 2014 IEEE.

recently been investigated as a possible plasmonic material with SERS capabilities (Lorite *et al*., 2013; Zgrabik *et al*., 2015; Zhong *et al*., 2015). Both electrochemical and SERS methods have recently been used to demonstrate sensitive detections of pollutants such as pesticides or heavy metals (see section 1.3). Altogether, this makes TiN a potential material of choice, capable of both preventing biofouling and sensing of the targeted emerging pollutants.

2 Results

2.1 Simulation and Design

2.1.1 *Non-technical summary of results*

In this section, we describe how simulations were carried out to investigate the possibility of locally changing the pH at the surface of the sensors using electrochemical processes. In addition, atomistic simulation models were developed to study the interaction of pesticide molecules with the sensor surface and to give insight into biofouling processes and provide strategies to mitigate them.

2.1.2 *Electrochemical sensors*

One of the most critical parameters for nanosensor development is the distance between the electrodes: given the minute distances, diffusion can play a major role in whether a nanosensor displays the desired functionality or not. Simulations have been undertaken using COMSOL Multiphysics packages to inform the optimum design of the microelectrodes for enhanced mass transport, leading to greater sensitivities. Simulations revealed that an electrode-to-electrode distance (G) in the order of 5 µm is necessary to prevent overlap of diffusion profiles around each electrode (see Figure 2.1).

Simulations were also undertaken to study the possibility of changing the pH *in situ* at the surface of the electrode. These simulations showed that it should be possible to control the pH locally at the surface of the electrode. This is important, as electrochemical detection of heavy metals is more sensitive at low pH. Fabricating sensors in which the pH can be altered without the use of additional reagents would be greatly beneficial for *in situ* measurements of not just metals but also other key analytes of environmental interest such as nitrates. To optimise the electrochemical-based *in situ* pH control capabilities, an interdigitated comb electrode configuration was modelled and selected, in which one comb of electrodes (the protonator) was used for changing the local pH while the other comb was used for sensing (see Figure 2.2).

2.1.3 *Interaction of target molecule with sensor surfaces*

Electrochemical detection of the pesticides was initially tried on unmodified Au electrodes, but no tangible results were obtained. To elucidate the reasons for this, it was decided to carry out atomistic simulations to study the interaction of the molecules with the metals. The results of this analysis show that the interaction between the surface and the analyte had adsorption energies of around 5.2 eV, i.e. the interaction is endothermic and thus unfavourable (see Figure 2.3).

Consequently, the sensor would need to be modified to enable adsorption of 2,4-D. Based on this result, the development of an electrochemical sensor for pesticides was not studied further, as modification

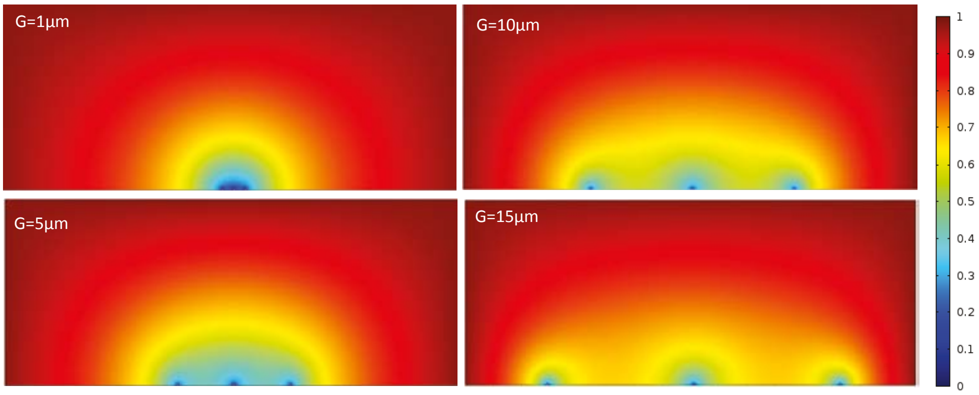

Figure 2.1. Diffusion profile for different inter-electrode distances. The overlap in diffusion profile starts to disappear at $G < 5$ µm.

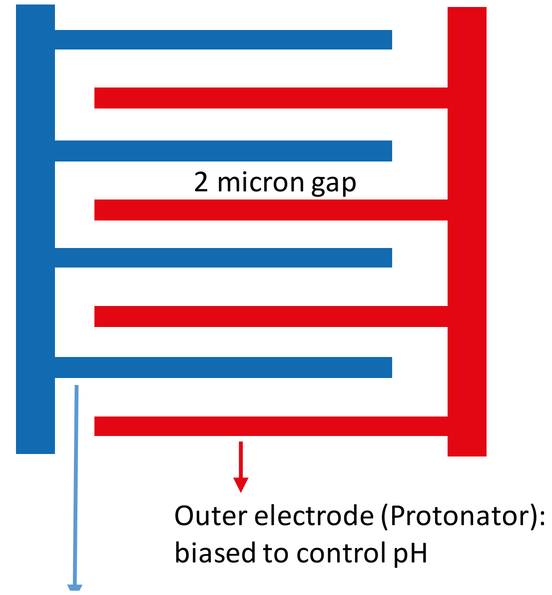

Figure 2.2. Schematic diagram of an interdigitated microelectrode used for sensing of heavy metals.

layers would affect the electrochemistry. Thus, a purely SERS-based approach was adopted for sensing herbicides. Simulations were carried out for the vibrational modes of MCPA, thus allowing signature vibrations to be examined experimentally.

2.1.4 *Anti-biofouling*

Simulations using DFT were used to model the varying surfaces of TiN for anti-biofouling applications – starting with the simplest material, a perfect TiN surface, and increasing the complexity to include (1) O_2 deposition on TiN, (2) models of the TiN-TiO_2 interface, (3) interaction of amino acids with TiN-TiO_2, (4) chemically modifying the TiO_2 layer with a range of chemical species and assessing their stability and (5) interactions of the amino acids with the chemically modified TiN-TiO_2 material (see Figure 2.4).

With respect to the models of TiN-TiO_2 interfaces, three papers on this topic have been published (see section 5.1).

2.2 Sensor Fabrication and Characterisation

2.2.1 *Non-technical summary of results*

In this section, we describe how sensors based on TiN material were fabricated but were found to be unsuitable for electrochemical-based sensing.

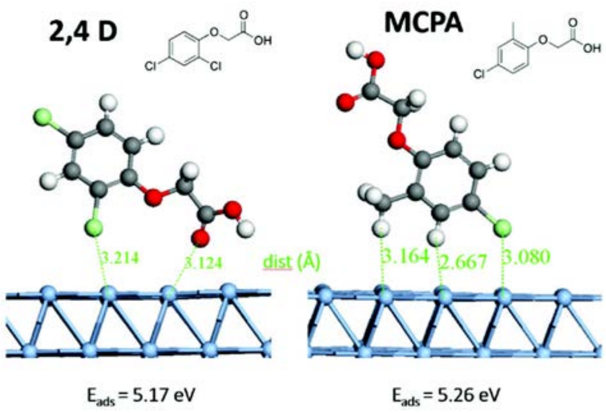

Figure 2.3. Atomistic simulations showing the affinity of (left) 2,4-D and (right) MCPA with a Ag surface. Similar results were obtained for an Au surface.

Sensor chips with Au and Pt microelectrodes were then fabricated and used for sensing applications in section 2.3. In addition, SERS sensors based on Ag nanodendrites were fabricated and used for detection of the herbicide 2,4-D.

2.2.2 *Fabrication and characterisation of TiN electrochemical sensors*

Based on the modelling simulations from the section above, initial work on a working electrode focused on TiN.

TiN films were fabricated and subsequently characterised using atomic force microscopy and scanning electron microscopy (see Figure 2.5). The optical properties of the material were assessed using ellipsometry and Raman spectroscopy. From this, it was found that the fabricated TiN did not have good plasmonic properties and could not therefore support SERS effects. Given that the TiN could not be used for SERS, an electrochemical TiN sensor was produced. Electrochemical sensor chips bearing the micro-SD design explained in section 2.1 were fabricated using processes commonly used in semiconductor foundries.

A detailed electrochemical analysis of these TiN sensors found that they degraded, probably due to oxidation, during electrochemical sensing experiments, so that they could not be used for sensing applications (see Figure 2.6). Although TiN could not be used for sensors, it was nevertheless still studied for its anti-biofouling properties.

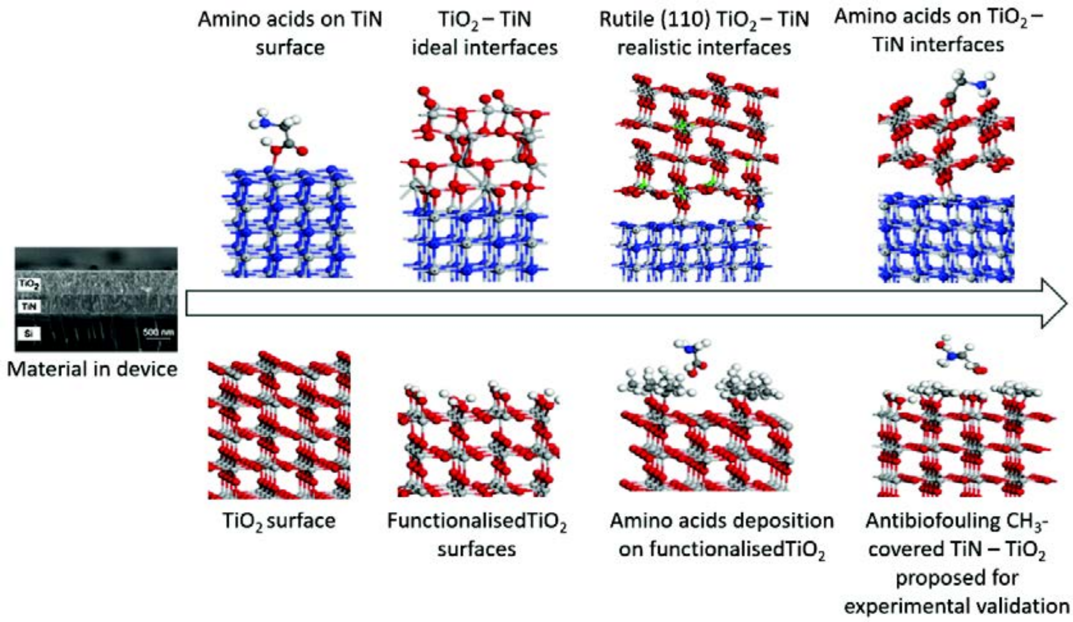

Figure 2.4. Schematic diagrams representing the progress of our DFT simulations. The timeline represents the work carried out from the beginning of the project. Bare and oxidised TiN surface models are depicted above the timeline. Bare and functionalised TiO_2 surfaces are shown underneath. Ti^{4+} atoms are light grey, Ti^{3+} atoms are green, O atoms are red, N atoms are dark blue, H atoms are white and C atoms are dark grey.

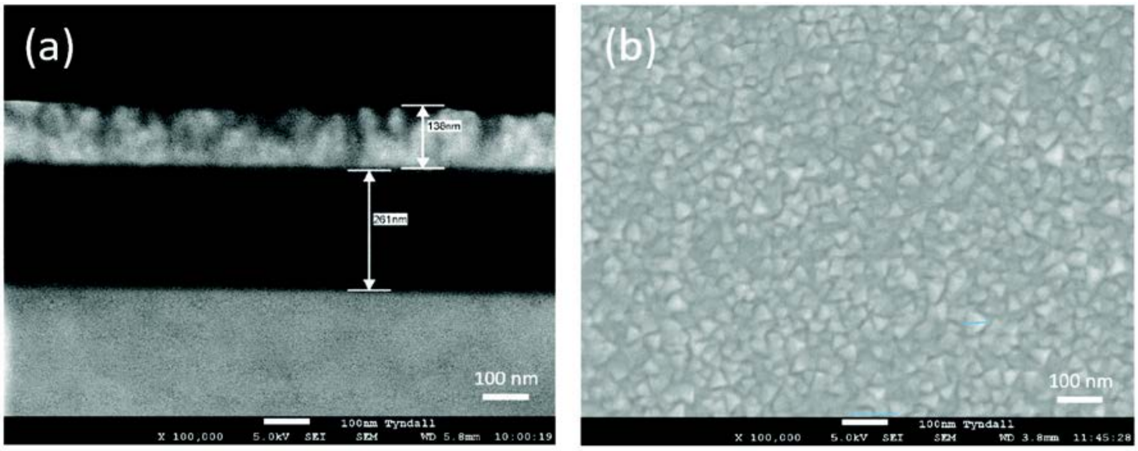

Figure 2.5. Scanning electron microscope imaging of the TiN thin film: (a) cross-section and (b) top view.

2.2.3 Fabrication and characterisation of gold or platinum sensor chips

Sensor chips were successfully fabricated using advanced microelectronic fabrication techniques. Au and Pt were used as active materials for the working electrode. Those chips could readily be used for sensing applications and were used for the rest of the project. Figure 2.7 shows a schematic outline of the fabrication approach. A four-level lithography mask approach was adopted. Chips were fabricated such that each chip contained a pin-out [either micro-SD or

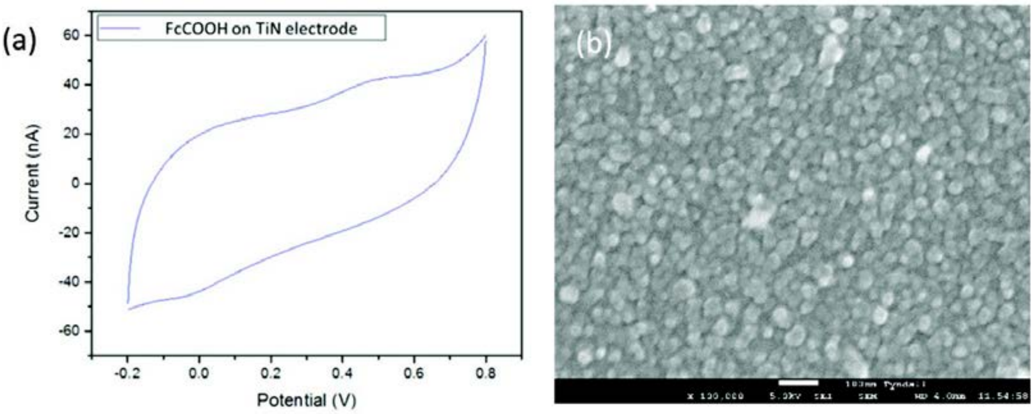

Figure 2.6. (a) Cyclic voltammogram of a TiN electrode and (b) scanning electron microscope imaging of TiN after electrochemical characterisation.

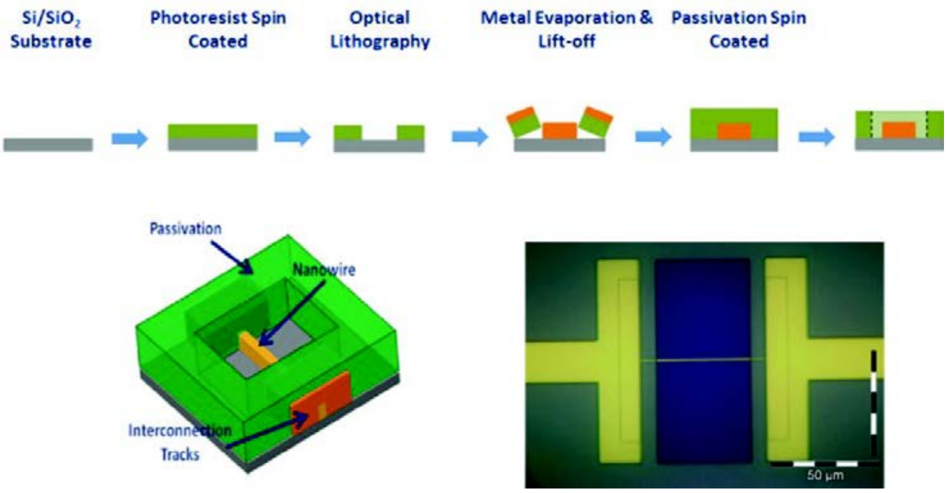

Figure 2.7. Process flow for fabricating the Au/Pt sensors.

HDMI (high-definition multimedia interface)] for easy electrical connection. Each chip had multiple sensors, as well as the counter and reference electrodes required for electrochemistry.

A dedicated fluidic cell was manufactured to carry out field measurements, which highlighted some issues with the micro-SD design, such as the trapping of air bubbles above the surface of the sensors. To improve on this, sensor chips were fabricated using a second design based on HDMI connectors.

2.2.4 Fabrication and characterisation of SERS sensors

In addition to electrochemical sensors, a SERS chip was developed and optimised. Silver nanoparticles were chemically synthesised for SERS-based detection of herbicides. However, these nanoparticles could not stay on the surface during sensing experiments. To overcome this, Ag nanodendrite SERS active surfaces were fabricated using electrochemical deposition (see Figure 2.8). Those substrates were found to be SERS active and were functionalised with thiolated cyclodextrin to allow detection of 2,4-D down to 8 µg/L (see below).

2.3 Sensing Platform Demonstration and Testing

2.3.1 Non-technical summary of results

In this section, we describe how the electrochemical sensors fabricated in section 2.2 were used to detect heavy metals, using samples prepared in the laboratory and samples collected in locations

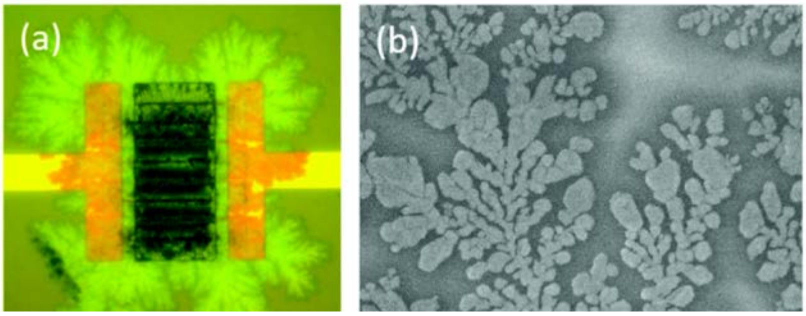

Figure 2.8. (a) Optical and (b) scanning electron microscope images of Ag nanodendrites SERS sensors fabricated using electrodepositing of Ag salts.

expected to have high levels of Cu. The SERS sensors were also used for detection of herbicides, and 2,4-D was detected in spiked river solutions. Finally, anti-biofouling strategies, both on individual metallic sensors and on bulk substrate levels, were tested experimentally.

2.3.2 Detection of heavy metals

Electrochemical in situ pH control

On-chip*, in situ* pH control, as modelled in section 2.1, was experimentally demonstrated using a pH indicator dye, methyl red (see Figure 2.9). It was observed that electrodes made of Au degraded during such experiments, but electrodes made of Pt were found to be more robust.

The electrochemical sensors fabricated in section 2.2 were used for sensing of heavy metals in laboratory settings. Concentrations as low as 1.2 µg/L, 0.9 µg/L and 1.3 µg/L were measured in the laboratory for Pb, Cu and Hg, respectively.

In-field detection of heavy metals

These sensors were also used for in-field testing of Cu, a compound most likely to be found and detected at the concentrations the sensors were able to detect. Cu levels of 17 µg/L, 20 µg/L and 4 µg/L were measured with the electrochemical sensors at the Avoca, Ross mines and Allihies sites (see Figure 2.10). ICP-MS analysis of these samples gave values of 22 µg/L, 27 µg/L and 7 µg/L, respectively. Although the trends are similar, the discrepancies indicate that further development of the electrochemical sensors is required. The underestimation of the results for Cu obtained from the electrochemical sensors compared with those from the commercial ICP-MS analyses could be attributed to the fundamental differences in the techniques. Electrochemistry will detect only soluble ions free in solution, while ICP-MS will detect both these and ions that have been chelated to organic molecules.

Samples from Bunmahon and Hollyford mines and from Gunpowder Mills and Inniscarra (River Lee) were analysed using the electrochemical sensors (see Figure 2.11). Water from these sites was also expected to contain some Cu. However, currents of 1.3 nA and 1 nA were obtained for Bunhamon and Hollyford, respectively, while the other two sites did not show any peaks. These values translate into Cu concentrations of 1 µg/L for the Bunmahon site and below 1 ppb (parts per billion) for the other locations. Grab samples analysed using accredited ICP-MS showed concentrations of less than 3 µg/L for all four sites (see Table 2.1).

2.3.3 Detection of 2,4-D herbicide

The SERS sensors developed in section 2.2 were used for the detection of 2,4-D. These sensors were able to detect 8 µg/L of the herbicide in spiked river water (see Figure 2.12). Further work is required to be able to measure concentrations below the limit of 0.1 µg/L.

2.3.4 Anti-biofouling study

The anti-biofouling study was done both at the sensor level and at the bulk surface level. This later step was informed by the outputs of the atomistic modelling carried out in section 2.1.

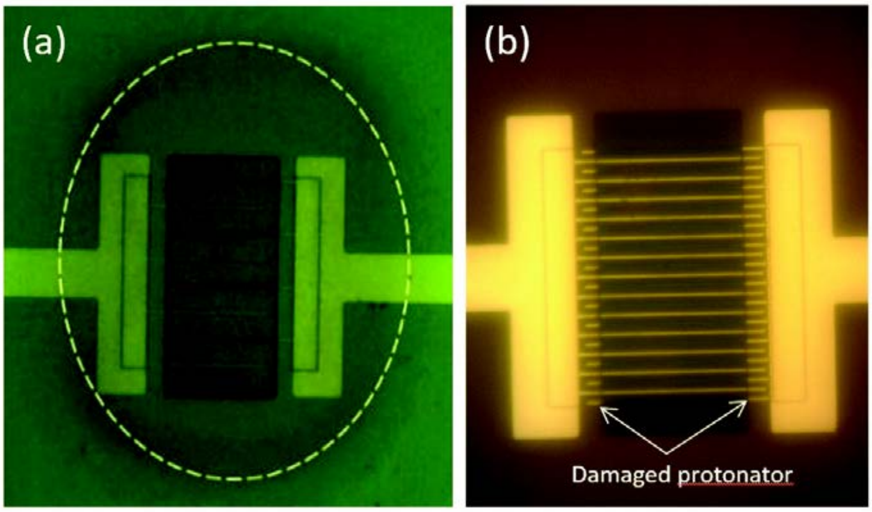

Figure 2.9. (a) Screenshot of the pH control experiment. The dashed line shows the change in colour of the pH dye, indicating the diffusion of H⁺. (b) Degraded protonator after a pH control experiment.

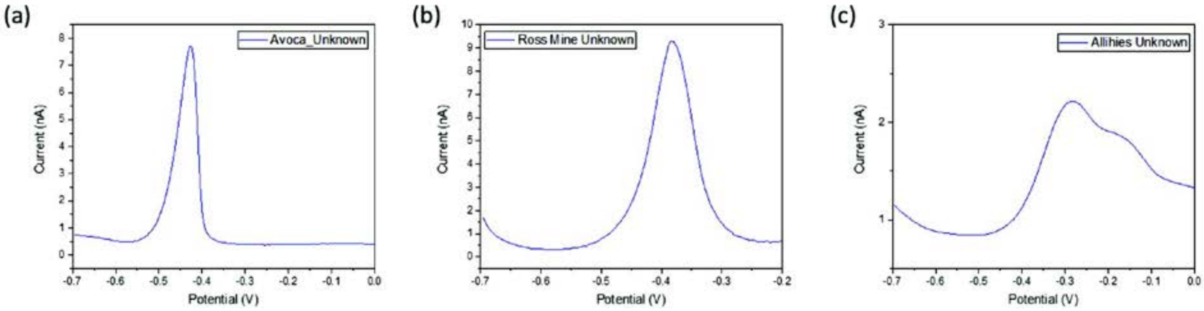

Figure 2.10. Square wave voltammogram from (a) Avoca, (b) Ross mines and (c) Allihies.

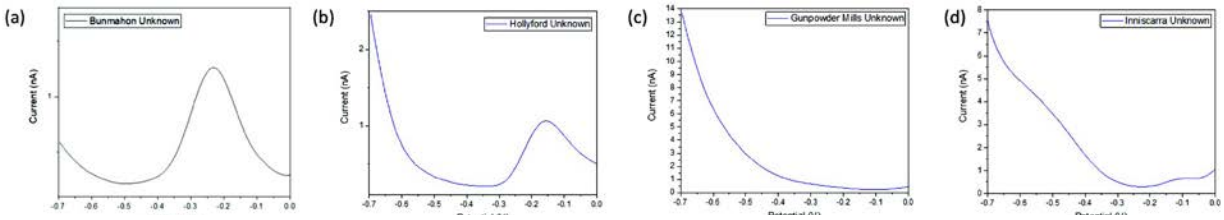

Figure 2.11. Square wave voltammograms for (a) Bunmahon, (b) Hollyford, (c) Gunpowder Mills and (d) Inniscarra.

Individual metallic sensor anti-biofouling strategies

At the sensor lever, sacrificial polymer layers were initially deposited over the fabricated sensor electrodes to protect them from biofouling. However, the stripping of this layer using electrochemistry was found to be incomplete, which would prevent reliable measurement. Consequently, sacrificial layers composed of Ag were successfully deposited and were found to strip more readily upon application of a negative potential (see Figure 2.13). These results show that first encapsulating a sensor with a protective metal overlayer followed by its removal would be an effective approach to ensure that sufficiently clean sensors are available for sensing. Furthermore, building in redundant sensors, in such a fashion, would also increase the deployable lifetime of a sensor device.

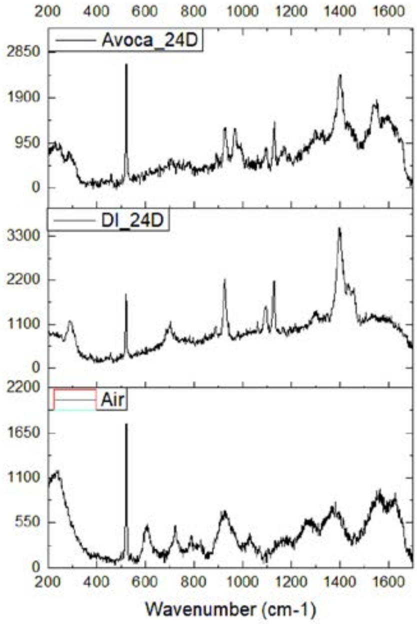

Figure 2.12. Raman spectra of sensors in (bottom) air, (middle) 0.1 µg/L of 2,4-D in deionised water and (top) Avoca river sample spiked with 8 µg/L of 2,4-D.

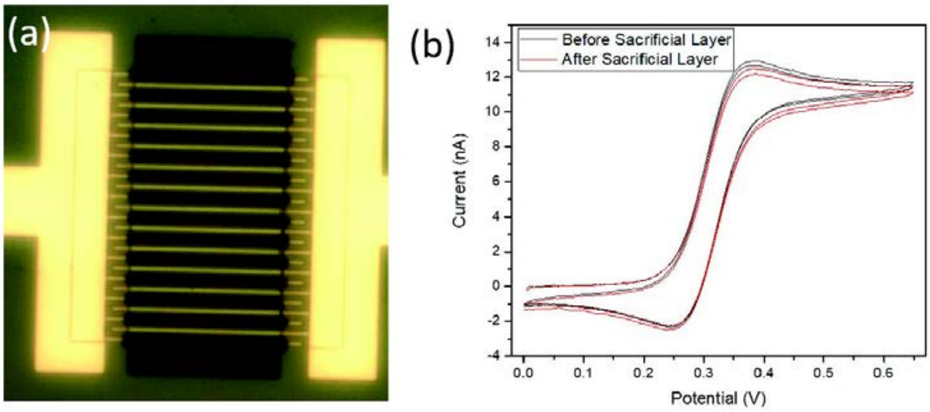

Figure 2.13. (a) Electrode coated with Ag sacrificial layer. (b) Cyclic voltammogram of ferrocene carboxylic acid before and after deposition of Ag sacrificial layer.

Bulk substrate anti-biofouling strategies

At a bulk substrate level, the TiN samples whose preparation is described in section 2.2 were tested by a partner at the Agricultural University of Athens who specialises in biofouling studies (see Figure 2.14). The results suggest that the samples prevented the attachment of larger microorganisms (tens of microns in diameter) but was less effective for smaller ones. Further work is ongoing to confirm these observations.

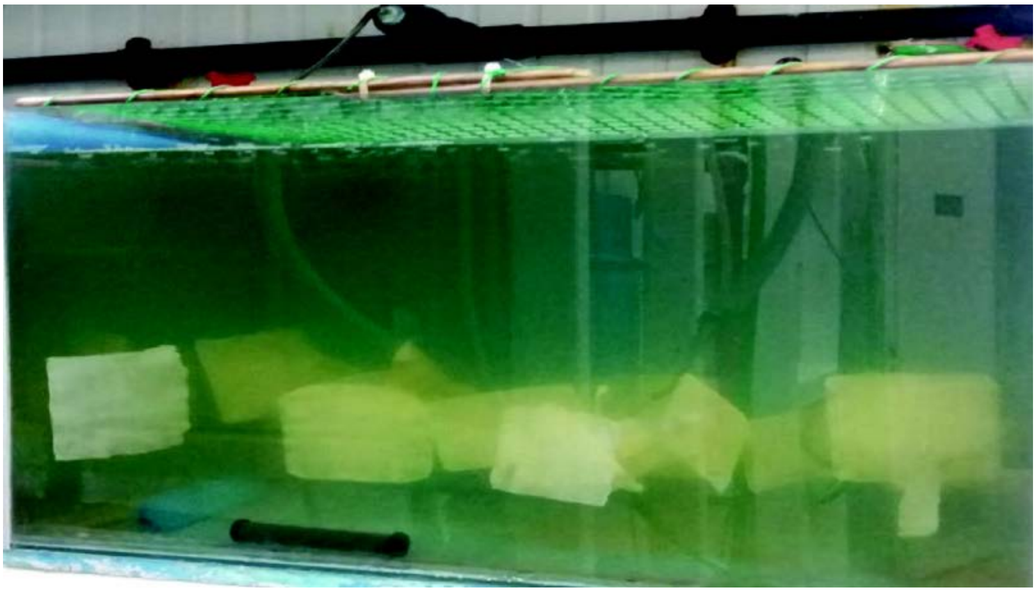

Figure 2.14. Treated samples immersed in the tank.

3 Conclusions from Research Findings and Future Research Needs

3.1 Conclusions from the Research Findings

3.1.1 Modelling

- Mathematical modelling of atomistic interactions was shown to be an invaluable tool for sensor design, particularly for determining electrode spacing and configuration. In this project, electrode spacing was shown to be optimal at 5 µm to minimise the overlapping diffusion profile.
- Modelling of the atomistic interactions between the analyte and the surface material of the electrode is absolutely crucial to the development of sensors. In this project, atomistic simulations demonstrated that the interactions of the pesticide MCPA with an Ag-enhanced electrode were unfavourable and that such an electrode could not be used to detect this pesticide.
- Atomistic modelling can be used to simulate the vibrational nodes of analytes, allowing identification of high-intensity peaks in the Raman spectrum, thereby facilitating development of SERS sensors.
- Atomistic modelling is a viable tool for identifying potential candidate molecules with anti-biofouling properties. In the UisceSense project, this modelling identified a novel class of molecules with potential resistance to biofouling. Currently, an invention disclosure form regarding this work has been submitted to the University College Cork Technology Transfer Office.

3.1.2 Sensor fabrication and characterisation

- Two prototype sensors – one based on electrochemistry for detection of heavy metals and one based on SERS for detection of organic pesticides – were developed during the UisceSense project. These sensors require further optimisation for use in monitoring under the WFD.
- Using electrochemical nanosensors, the pH can be adjusted *in situ* (with no reagents) to optimise conditions for detecting analytes, particularly for heavy metals. In UisceSense, this novel technique can be used for detection of Cu and Hg. Adjusting the local pH without the need to transform and use reagents in the field would facilitate environmental monitoring.
- TiN sensors are not suitable for electrochemical detection of water samples because of their high resistivity and degradation under mild potentials.
- Although Au is a suitable material for electrochemical sensing, it is not suitable for *in situ* electrochemical pH control because of the high potentials needed to generate H^+ ions. Pt is a much more suitable material, as it is more robust and inert than Au. In this project, the majority of results were obtained using Pt as a protonator.
- A prototype fluidic cell has been developed. Additional work is required to optimise the design in terms of sample capture in different water currents.
- Nanostructured surfaces that are suitable for detection using the SERS technique can be constructed using electrodeposition of Ag nanoparticles.
- Cyclodextrin deposited on Ag nanoparticles can assist in the detection of certain pesticides by facilitating van der Waals-based attraction of the analyte to the plasmonic hotspots on the surface of the sensor. In this project an enhancement factor of 2×10^6 was achieved for 2,4-D using cyclodextrin.

3.1.3 Biofouling

- TiN is a suitable candidate material for the development of anti-biofouling passivation layers, although it is not a suitable material for use in the electrochemical electrode (due to degradation).
- UV curing of an anti-biofouling layer under vacuum results in a more homogeneous deposition of the molecules on the TiN surface than previously described methods.

3.1.4 Sensing platform demonstration and sensing

- Proof of concept was demonstrated for the use of electrochemical sensors, developed in the UisceSense project, to monitor heavy metals in river water: Cu was detected at levels down to 3 ppb.
- *In situ* pH control is as efficient as pH control using mineral acids. This permits the use of reagent-free sensors (i.e. those developed in this project) for environmental monitoring.

3.2 Key Results and Future Research Needs

3.2.1 Key results and breakthroughs

The following breakthroughs were achieved during the UisceSense project:

- development of electrochemical sensor chips with the potential for multiplexed detection of heavy metals;
- demonstration of local pH control at interdigitated microelectrodes for reagent-less detection of heavy metals;
- development of novel SERS substrates based on two-dimensional Ag nanodendrites;
- functionalisation of SERS substrates for detection of organic pesticides and proof of concept of a detection limit 10 times lower than that of current state-of-the-art sensors based on similar technologies;
- development of novel atomistic simulation models of anti-biofouling processes, which were used to derive novel approaches to antibiofouling;
- initial experimental verification of an anti-biofouling coating – more work is required.

3.2.2 Future research needs

Further research is needed to ensure that the technology developed is field-ready and validated and that field data are collected to make the technology acceptable to regulators for compliance monitoring. Such research includes:

- Further assessment and testing of the anti-biofouling properties of the novel class of molecules identified by atomistic modelling is needed, particularly with a view to understanding the effects of the size of the fouling species on the degree and time taken to foul a surface. This will provide important information on the development of future anti-biofouling layers.
- Further field-based proof of concept for the use of electrochemical nanosensors for detection of heavy metals from river water is needed. Mass deployment of large numbers of sensors (~500) is now required to provide sufficient data to allow optimisation and validation of the sensors and the development of suitable algorithms required to perform edge analytics.
- The design of the fluidic cell system needs to be optimised to ensure sample capture over a wide range of water currents and other environmental conditions.
- The use of TiN as an anti-biofouling material needs to be optimised and further work on the novel UV curing process developed in this project is needed.
- While proof of concept for the use of SERS for monitoring pesticides in river water has been demonstrated, further research is required to enable more sensitive measurements to be obtained, as required to achieve the limits set in the WFD.

4 Recommendations for Implementation and Uptake of Research Findings

4.1 Identifying Pressures

One of the most important challenges of the 21st century is the ability to provide a clean and pollutant-free source of water for a wide variety of uses. In Ireland, the threats to water quality can arise from a variety of fields of use, including toxicity from pesticides used in agriculture, heavy metals from manufacturing and antibiotics from both human and animal consumption. Although the quality of water in Ireland is generally good, the EPA detected the herbicides MCPA in 55% of rivers monitored from 2013 to 2018 and 2,4-D in 29% of rivers monitored. Similarly, Pb was detected in 14 Irish public water supplies in 2018. Accurately monitoring the status of water bodies with respect to these contaminants is currently a huge challenge. With this in mind, the project aimed to develop electrochemical- and optical-based sensors for the detection of organic contaminants (herbicides) and heavy metals. While further research and development is needed to optimise the technologies developed, it is hoped that the data provided by the sensors can help to identify pollution sources rapidly and allow appropriate measures to be taken quickly to limit pollution events.

4.2 Informing Policy

The overarching legislation this project falls under is the WFD and the relevant follow-up recommendations from the European Commission to expand environmental monitoring. The WFD is supported by more targeted directives such as the Drinking Water Directive, which states that the limit for a single pesticide in drinking water is 0.1 μg/L and for the sum of all pesticides is 0.5 μg/L. The current statutory monitoring is based on discrete water sampling and might not provide a full picture of the status of water bodies. There is therefore a real need to develop and validate high-resolution monitoring solutions for pollutants. Such solutions can capture daily and seasonal variability in pollutant concentrations, and can greatly help the relevant stakeholders to assess, manage and monitor the state of water bodies and to ensure that the current policies are correctly implemented. In particular, they can detect repeated exceedances so that corrective measures can be undertaken. We believe that the UisceSense project has made significant strides in this context through the development and demonstration of proof of concept for several technology platforms and processes.

4.3 Developing Solutions

The UisceSense project resulted in a range of outputs and breakthroughs in the field, beyond the state of the art. The research carried out in this project shed light on the potential for the development and optimisation of novel environmental sensors and anti-biofouling strategies. In particular, it indicated the potential of electrochemical sensors for detection of heavy metals and of SERS surfaces for the detection of organic pesticides such as 2,4-D. To enable the deployment of such sensors, a number of anti-biofouling strategies were also explored. The first aspect was to develop atomistic modelling to understand the biofouling processes. The second was to experimentally study the anti-biofouling process. This was done both at the sensor level – by protecting the electrode surface with a sacrificial layer – and at the bulk surface level – by functionalising the whole surface of the chip with an adsorbate suitable for hindering or even prohibiting the growth of any potential biofouling organisms.

5 Research Outputs

UisceSense was an ambitious project aiming to develop highly novel sensors based on cutting-edge nanotechnology simulations, processes, technology and materials, with the aim of assisting Ireland to meet the requirements of the WFD. As a clear indicator that the UisceSense project surpassed the current state of the art we summarise the research outputs published and/or presented to the scientific community:

- Eight peer-reviewed publications have been prepared: five published, three submitted.
- Two PhD theses have been undertaken: one full thesis in preparation and contribution of one of the chapters in this report by a second student.
- Eight presentations have been made at international and national scientific conferences;
- Three official intellectual property submissions (potential patents) have been made.
- Two EU projects leveraged: one Horizon 2020 Marie Curie project, "AquaSense" 813680, successfully funded and one proposed project, "MINOAN", submitted to H2020-ICT37. Aquasense (https://www.aquasense-itn.com/) aims to develop innovative sensor networks for monitoring water and food quality. The research ranges from development of novel transducers and readout electronics to communications, drone deployment and artificial intelligence-based data analysis.

5.1 Peer-reviewed Publications

1. Gutierrez Moreno, J.J., Fronzi, M., Lovera, P., O'Riordan, A., Ford, M., Li, W. and Nolan, M., 2019. Structure, stability and water adsorption on ultra-thin TiO_2 supported on TiN. *Physical Chemistry Chemical Physics* 21: 25344–25361. Available online: https://pubs.rsc.org/en/Content/ArticleLanding/2019/CP/C9CP04506F#!divAbstract
2. Robinson, C., Justice, J.. Petäjä, J., Karppinen, M., Corbett, B., O'Riordan, A. and Lovera, P., 2019. Nanoimprint lithography-based fabrication of plasmonic array of elliptical nanoholes for dual-wavelength, dual-polarisation refractive index sensing. *Plasmonics* 14(4): 951–959.
3. Gutiérrez Moreno, J.J., Fronzi, M., Lovera, P., O'Riordan, A. and Nolan, M., 2018. Stability of adsorbed water on TiO_2–tin interfaces. A first-principles and ab initio thermodynamics investigation. *Journal of Physical Chemistry C* 122(27): 15395–15408. Available online: https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.8b03520
4. Creedon, N.L.P., Gutierrez Moreno, J.J., Nolan, M., O'Riordan, A. ,2018. Characterization and detection of neonicotinoid pesticides using surface enhanced Raman spectroscopy and nano-electrochemistry. *ChemRxiv* (preprint), https://chemrxiv.org/articles/Characterization_and_Detection_of_Neonicotinoid_Pesticides_using_Surface_Enhanced_Raman_Spectroscopy_and_Nano-electrochemistry/7151924/1
5. Gutiérrez Moreno, J.J. and Nolan, M., 2017. Ab initio study of the atomic level structure of the rutile TiO_2 (110) – titanium nitride (TiN) interface. *ACS Applied Materials & Interfaces* 9(43): 38089–38100. Available online: https://pubs.acs.org/doi/abs/10.1021/acsami.7b08840

5.2 Planned Publications

1. Patella, B., O'Sullivan, B., Daly, R., Lovera, P., Inguanta, R. and O'Riordan, A. Reagent-free simultaneous detection of multiple metal contaminants in water using localised pH control. Submitted.
2. Daly, R., Poceviciute, E., O'Riordan, A. and Lovera, P. β-Cylodetxrin functionalised silver nanoparticles on microband electrode for sensitive detection of chlorophenoxy herbicides. In preparation.
3. Daly, R., O'Riordan, A. and Lovera, P. Electrochemical characterisation of titanium nitride microelectrodes. In preparation.

5.3 Conference Presentations – Posters

1. Eighth Conference on Analytical Sciences Ireland (CASi), 14 and 15 April 2016, Dublin City University (talk and poster).
2. International Water Association (IWA) regional conference, Dublin City University, 23–27 October 2016 (poster presentation and session chairing).
3. Autonomous Sensors & Earth Observation Conference, Dublin City University, 27 and 28 March 2017 (posters).

5.4 Conference Presentations – Talks

1. European Materials Research Society (EMRS) spring meeting, Strasbourg, France, 22–26 May 2017 (talk).
2. Deutsche Physikalische Gesellschaft – European Physics Society (DPG-EPS) Condensed Matter Divisions 2018, Berlin, 11–16 March 2018 (talk).
3. American Chemical Society (ACS) National Meeting, New Orleans, LA, 18–22 March 2018 (talk).
4. Institute of Electrical and Electronic Engineers, IEEE Nano, Cork, Ireland, 23–26 July 2018, chairing a session on SERS.
5. European Materials Research Society (E-MRS) autumn 2018 meeting, Warsaw, Poland, 17–19 September 2018 (talk).
6. IEEE Sensors, Montreal, 27–30 October 2019 (two talks).

5.5 Intellectual Property

In accordance with the national guidelines detailed in the National IP Protocol 2019 (https://www.knowledgetransferireland.com/ManagingIP/National-IP-Protocol/), all potential intellectual property developed at the Tyndall National Institute must be reported to the University College Cork Technology Transfer Office (TTO) through an official invention disclosure form (IDF), which is subsequently reviewed for patentability. From the research work performed in the UisceSense project, three IDFs have been officially submitted and reviewed by the TTO. All three IDFs have received a positive initial patentability assessment. Further research work will be required to submit a patent application.

Because of the sensitive nature of intellectual property (IP) protection, a non-confidential summary is presented for each IDF.

5.5.1 IDF#1: SERS monitoring of pesticides

Although the majority of the work in the UisceSense project focused on electrochemical monitoring of heavy metals, preliminary results have indicated that a novel process may allow the identification and monitoring of specific pesticides.

5.5.2 IDF#2: TiN functionalisation protocol

TiN was used early in the UisceSense project as a potential material for the nanoelectrodes and found to be unsuitable due to degradation (section 2.2.2). Further review of the results has uncovered a novel method for functionalising TiN for use in nanoelectrodes. Given that TiN also has significant anti-biofouling properties, this novel method has significant potential for environmental monitoring.

5.5.3 IDF#3: Novel anti-fouling materials

The use of atomistic and mathematical modelling to assist the development of biofouling resistance sensors in the UisceSense project is highly novel and represents fertile ground for further research and intellectual property. In addition to the work presented in Chapter 2, this modelling has identified a novel range of molecules that would potentially display resistance to biofouling. Given that this type of modelling correlates very well with experimental data, it is likely that these molecules will demonstrate the predicted anti-biofouling properties.

It should be noted that all three novel processes above have been assessed for patentability by the TTO. This initial assessment has confirmed that no other publications, disclosures, previous patents or data in the public domain are similar to these processes; i.e. there is high confidence that these IPs would be considered “novel” and “non-obvious” in terms of patentability criteria. The third requirement for patentability, “commercially useful”, is a given, as these processes have clear applications in environmental monitoring.

5.6 Education and Public Engagement

During the course of this project, a Lego farm was developed. The concept of Lego was selected to engage with the young generation and adults alike. This farm has been tremendously successful and provided an interface for the public to interact with the sensors. The Lego farm has been used in the following ways:

- presented at the National Ploughing Contest 2018 and 2019, visited by 5000 members of the public, including children, farmers and other stakeholders;
- presented to a range of government officials including (posts as at the time of the presentation) Leo Varadkar (Taoiseach), Phil Hogan (EU Commissioner), Mary-Mitchell O'Connor (Junior Minister for Jobs, Enterprise and Innovation), Francis Fitzgerald (Minister for Business, Enterprise and Innovation), Heather Humphreys (Minister for Business, Enterprise and Innovation), Simon Conveney (Tánaiste);
- in collaboration with Teagasc, presented to the King and Queen of the Netherlands in June 2019;
- borrowed by Teagasc for a host of events including Moorepark Open Day 2019, Oak Park Open Day 2018, etc.

Other outreach activities include:

- Science Week 2018 and 2019 – workshops organised by Tyndall National Institute and the French Embassy;
- Culture Night 2018 and 2019;
- Workshops organised as part of the native scientist programme (French language).

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Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
DFT	Density functional theory
DLC	Diamond-like carbon
EPA	Environmental Protection Agency
EU	European Union
GGA	Generalised gradient approximation
GC-MS	Gas chromatography–mass spectrometry
HPLC	High-performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
LC-MS	Liquid chromatography–mass spectrometry
MCPA	2-Methyl-4-chlorophenoxyacetic acid
PAH	Polycyclic aromatic hydrocarbons
ppb	Parts per billion
SERS	Surface-enhanced Raman spectroscopy
WFD	Water Framework Directive

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Development of Proof-of-concept Portable Sensors for Detection of Heavy Metals and Organic Pesticides and Investigation of Anti-biofouling Materials

Authors: Alan O'Riordan, Michael Nolan, Pierre Lovera,
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Identifying Pressures

One of the most important challenges in the 21st century is the ability to provide a clean and pollutant-free source of water for a wide variety of uses. In Ireland, the threat to water quality can arise from a variety of fields of use, including toxicity from pesticides used in agriculture, heavy metals from manufacturing and antibiotics from both human and animal consumption. Although the quality of water in Ireland is generally good, the Environmental Protection Agency detected the herbicides MCPA in 55% of rivers monitored from 2013 to 2018 and 2,4-D in 29% of rivers monitored. Similarly, lead was detected in 14 Irish public water supplies in 2018. Accurately monitoring the status of water bodies with respect to these contaminants is currently a huge challenge. With this in mind, the project aimed to develop electrochemical- and optical-based sensors for detection of organic contaminants (herbicides) and heavy metals. Although further research and development is needed to optimise the developed technologies, it is hoped that the data provided by the sensors can help to identify pollution sources rapidly and allow appropriate measures to be taken quickly to limit pollution events.

Informing Policy

The overarching legislation this project falls under is the Water Framework Directive (WFD) and the relevant follow-up recommendations from the European Commission to expand environmental monitoring. The WFD is supported by more targeted directives, such as the Drinking Water Directive, which states that the limit for a single pesticide in drinking water is 0.1 µg/L and for the sum of all pesticides is 0.5 µg/L. The current statutory monitoring is based on discrete water sampling and might not provide a full picture of the status of water bodies. Continuous, in *situ* sampling solutions can capture daily and seasonal variability of pollutant concentrations, and can greatly aid relevant stakeholders to assess, manage and monitor the state of water systems, and ensure that the current policies are correctly implemented. If analytically sensitive enough, they can inform when an exceedance is repeatedly observed so that corrective measures can be undertaken. We believe that the present project has made significant strides in this context through the development and demonstration of proof of concept of several technology platforms and processes.

Developing Solutions

The UisceSense project resulted in a range of outputs and breakthroughs in the field, beyond the state of the art. The research carried out in this project has shed light on the potential for the development and optimisation of novel environmental sensors and anti-biofouling strategies. In particular, it has indicated the potential of electrochemical sensors for detection of heavy metals as well as surface-enhanced Raman spectroscopy for the detection of organic pesticides such as 2,4-D. To enable the deployment of such sensors, a number of anti-biofouling strategies were also explored. The first aspect was to develop atomistic modelling to understand the biofouling processes. The second aspect was to experimentally study the anti-biofouling. This was done at both the sensor level – by protecting the electrode surface with a sacrificial layer – and the bulk surface level – by functionalising the whole surface of the chip with an adsorbate suitable for hindering or even prohibiting the growth of potential biofouling organisms.

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