ENVIRONMENTAL NANODETECTOR: DEVELOPMENT OF A NOVEL METHOD FOR THE DETECTION OF ENGINEERED NANOMATERIALS IN THE ENVIRONMENT

A THESIS SUBMITTED TO THE UNIVERSITY OF SURREY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Abstract

Airborne particulate matter, both in the workplace and the environment, has been linked to adverse health effects, this in turn has led to the establishment of legislation stipulating exposure limits. Advances in technology, and associated increased use of nanomaterials means that such regulations and associated monitoring remain highly relevant. Monitoring techniques used for airborne particulates are costly, bulky and insensitive to low to medium exposure to nanomaterials.

Capacitance based sensors, detecting changes in electrical impedance due to the presence of nanomaterials have been developed in this work. Capacitive interdigitated electrodes integrated with nanoparticulate trapping structures have been designed and manufacturing techniques suitable for mass manufacture have been evaluated and developed.

Photolithographic and inkjet printing based methods for manufacturing electrodes were evaluated, identifying inkjet printing as the most appropriate technique, providing good reproducibility, ease of fabrication and the ability to rapidly tailor electrode structures to provide different capabilities. It was found that higher sensitivities were obtained when gap widths between electrodes decreased.

Two trapping layers were evaluated, columnar Zinc oxide with pore sizes of 10nm to 170nm, and porous polystyrene with sizes of 10µm to 50µm. Whilst offering small pore sizes, potentially allowing the trapping and detecting of a smaller particle size distribution, under test conditions zinc oxide structures were shown to be too fragile to survive real life test events. Porous polystyrene structures were shown to have lower selectivity trapping all particles between 20-200nm, however these trapping structures were shown to withstand real life test events.

Analytical modelling has shown good agreement with experimental test results and has been used to predict the devices response to different nanomaterials offering the potential that the capacitance based sensors could also be used to differentiate between different nanomaterials.
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<td>Atomic Force Microscope</td>
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<tr>
<td>CLP</td>
<td>Classification, Labelling and Packaging framework</td>
</tr>
<tr>
<td>CNC</td>
<td>Condensation Nuclei Counter</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counters</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analysis</td>
</tr>
<tr>
<td>DMPS</td>
<td>Differential Mobility Particle Sizer</td>
</tr>
<tr>
<td>DOD</td>
<td>Drop On Demand</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EFSA</td>
<td>European Food Safety Agency</td>
</tr>
<tr>
<td>ELPI</td>
<td>Electrical Low Pressure Impactor</td>
</tr>
<tr>
<td>ENP</td>
<td>Engineered NanoParticles</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EST</td>
<td>Equivalent Sphere Theory</td>
</tr>
<tr>
<td>FDA</td>
<td>Food Drug Administration</td>
</tr>
<tr>
<td>IDT</td>
<td>InterDigiTated electrode</td>
</tr>
<tr>
<td>IPPC</td>
<td>Integrated Pollution Prevention and Control</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>NICNAS</td>
<td>National Industrial Chemicals Notification and Assessment Scheme</td>
</tr>
<tr>
<td>NSAM</td>
<td>Nanoparticle Surface Area Monitor</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorisation and restriction of Chemicals</td>
</tr>
<tr>
<td>RFID</td>
<td>Radio Frequency IDentification tags</td>
</tr>
<tr>
<td>ROHS</td>
<td>Restriction Of certain Hazardous Substances directive</td>
</tr>
<tr>
<td>SCHENIR</td>
<td>Scientific Committee on Emerging and Newly Identified Health Risks</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SES</td>
<td>Sequential Equilibration Systems</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizers</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TEOM</td>
<td>Tapered Element Oscillating Microbalance</td>
</tr>
<tr>
<td>WEEE</td>
<td>Waste Electrical and Electronic Equipment directive</td>
</tr>
<tr>
<td>WFD</td>
<td>Waste Framework Directive</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Background

The worldwide production of nanomaterials is approximately 11.5 million tonnes/year and is worth €20 billion/year (European Commission, 2014). This production includes a number of different substances, with novel materials being developed constantly. Applications for these materials are also widespread, with uses in areas such as medicine, electronics and cosmetics. As with all new chemicals and materials, appropriate regulation and control is imperative to maintain public health and wellbeing. However, a number of knowledge gaps exist in the area of nano-regulation that hinder the regulatory progress. One such problem is the agreed definition of a nanomaterial, with a number of different global regulatory bodies using different definitions (Table 1.1), obstructing international collaboration by the non-existence of an internationally recognised standard.

In addition to worldwide variance in definition, organisations within countries themselves provide different guidelines, with no overarching set of criteria for
nanomaterial assessment and control. For example, within the EU, both the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) regulations and the guidelines set by the European Food Safety Authority (EFSA) encompass nanomaterials as part of their assessment criteria, with guidelines differing between the two. In the USA, similar variance is demonstrated between the definitions used by the Environmental Protection Agency (EPA) and the Food Drug Administration (FDA).

Table 1.1 Examples of nanomaterial definitions used in different countries

<table>
<thead>
<tr>
<th>Regulatory Body</th>
<th>Origin</th>
<th>Definition</th>
<th>Identified Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Commission (European Commission, 2011)</td>
<td>EU</td>
<td>Natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate. For 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.</td>
<td>Includes aggregates and agglomerates which may be larger than the nanoscale</td>
</tr>
<tr>
<td>Environmental Protection Agency (EPA) (EPA,2011)*</td>
<td>USA</td>
<td>Material at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1-100 nanometre (nm) range in any direction.</td>
<td>Unclear whether agglomerates/aggregates are included</td>
</tr>
</tbody>
</table>

* No definition given. Guidelines in practice.
Table 1.1b Examples of nanomaterial definitions used in different countries (continued)

<table>
<thead>
<tr>
<th>Regulatory Body</th>
<th>Origin</th>
<th>Definition</th>
<th>Identified Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health Canada (Health Canada, 2011)</td>
<td>Canada</td>
<td>Any substance or product if it is at or within the nanoscale in at least one external dimension Has internal or surface structure at the nanoscale, or It is smaller or larger than the nanoscale in all dimensions and exhibits one or more nanoscale properties/phenomena.</td>
<td>Includes any size of material so long as it exhibits nano-behaviour.</td>
</tr>
<tr>
<td>National Industrial Chemicals Notification and Assessment Scheme (NICNAS) (NICNAS, 2013)</td>
<td>Australia</td>
<td>Intentionally produced, manufactured or engineered to have unique properties or specific composition at the nanoscale Size range typically between 1-100nm Either a nano-object (1-3 dimensions in the nanoscale) or nanostructured (internal or surface structure at the nanoscale)</td>
<td>Only refers to intentionally produced materials.</td>
</tr>
</tbody>
</table>

Within EU regulations (Regulation (EC) No. 1907/2006), it is observed that new substances are only assessed after passing a predetermined production threshold, however such regulatory guidelines place reliance upon limits used for bulk materials (Section 2.4), where particle size is not accounted for. This means that production of
nanomaterials may not elicit such assessment and a very high number of individual particulates can be produced before the threshold is reached.

Regulatory gaps are a consequence of the knowledge gaps associated with nanoparticle behaviour, with limited data being available to describe the effects of their physico-chemical properties where nanomaterials differ in comparison to their bulk counterparts. These changes can cause differences in their reactivity, toxicity and behaviour in the environment. The effectiveness of such frameworks are dependent on the understanding of behaviour produced by such changes in physico-chemical properties, however the current limited number of studies is not enough to alleviate concerns, particularly in the long term. In addition to this, potential adverse side effects of nanomaterial exposure and the levels at which they present must be identified.

With continued work on establishing the relevant regulations there exists a requirement for monitoring, both for ensuring that existing and future regulations are complied with, and when applying a precautionary approach in the absence of definitive nano-specific regulations. As a consequence current instrumentation is designed for stationary or laboratory-based use and is typically high cost, making it ill-suited for wide spread continuous compliance monitoring that would be of most benefit for the nano-sector.
1.2 Aims and objectives

Due to the limitations of current instruments, this project aims to develop an instrument capable of monitoring exposure to engineered nanoparticles, both occupationally and in the environment, in real time. The presence of nanomaterials can be detected in real time through changes in the capacitance of a capacitor due to the difference in relative permittivity of the nanoparticles with respect to the environment (i.e. air). In order to achieve the present aim, the following objectives were defined. The objectives include the design, fabrication and characterisation of sensor devices and trapping layers and are to:

1) Characterise the effect of nanoparticle inclusion on the impedance characteristics of planar capacitor type structures;

2) Evaluate the effect of the interdigitated electrode (IDT) dimensions on detection capability;

3) Develop a nanoparticle trapping layer and evaluate its size selectivity and collection efficiency; and

4) Evaluate the ability of an IDT electrode and trapping layer to collect, retain and detect nanoparticulates.
1.3 Thesis structure

This thesis is structured as seven chapters of which this is the first.

In Chapter 2 the background literature is reported. This is split into three parts, with the first section presenting information on nanoparticles, their behaviour, and current techniques available for detection and monitoring. In addition to this, this section identifies current gaps in legislation and instrumentation available. The second section of this review focuses on filtration theory, identifying key parameters affecting collection efficiency and the mechanisms which allow for size selection to occur. The final section details fabrication techniques for electrode structures identifying the advantages and disadvantages of these routes. Chapter 3, the methodology, contains a description of the generic experimental procedures used for fabrication and characterisation in this work. Chapter 4 presents the work undertaken with respect to the fabrication routes for both sensors and trapping layers. Particular attention is paid to identifying adequate fabrication routes for electrodes structures in order to produce reproducible, optimal dimension electrodes and for developing trapping layers with retention ability. Chapter 5 evaluates the trapping layers fabricated and identifies the most suitable trapping layer for sensor development based on retention efficiency and structural integrity. Chapter 6 demonstrates the development of theoretical model which may be used to identify important fabrication parameters and calculate the expected the behaviour of the device when exposed. The latter portion of this chapter
compares theoretical behaviour with experimental behaviour observed upon exposure.

This thesis concludes with Chapter 7 which presents the main conclusions and findings of this work in addition to identifying any future work.
2.1 Introduction

Nanomaterials can be defined as “those materials which contain unbound particles, agglomerates or aggregates where 50% of these have a size distribution in the range of 1-100nm” (European Commission, 2011; see Section 1.1). Airborne nanoparticles often reach concentrations of 10,000 to 500,000 particles/cm\(^3\). (Tardif. 2007) Nanoparticles are categorised as: engineered; incidental; or naturally-occurring. Engineered or incidental particulates are those which arise from man-made processes such as those for fabricating cosmetics (Lohani et al., 2014), automotive components (Coelho et al., 2012) and electronics (Fei et al., 2014) or particles occurring as products of combustion such as those emitted from diesel exhausts (Hesterberg et al., 2010) and cooking smoke (Kumar et al., 2013). Naturally-occurring nanoparticles include volcanic ash (Tepe and Bau, 2014), smoke from forest fires, and sea spray (Buseck and Adachi, 2008). This diversity results in a vast range of different material types and properties which would need to be detected by instrumentation for measurement or monitoring.
2.2 Monitoring nanoparticles

Atmospheric particulate matter in the environment has historically been linked to adverse health effects (Oberdörster et al., 2007). Regular monitoring of airborne particulates and accurate measurement techniques are required in order to enforce these limits effectively. Technological advances and the increased industrial use of nanomaterials in recent years have resulted in an increase in the number and range of nanoscale engineered particles in the atmosphere. These particulates (1-100nm in diameter) are at the limit of detection of currently available monitoring methods. In addition, such monitoring equipment has limited mobility and high procurement cost.

The functionality of engineered nanomaterials has led to a range of applications throughout industry and has provided consumers with numerous advantages such as medical care advances (Rijt et al., 2014), maintaining water quality (Li et al., 2008) and providing lightweight tougher materials for aircraft design (Ngô and Voorde, 2014). Concerns, however, arise from the knowledge gap in regards to the physiological consequences of exposure to these materials. This lack of knowledge has led to growing concern worldwide (Figure 2.1) regarding the potential adverse impacts of these materials on humans and the wider environment.
Chapter 2 Literature review

2.3 Exposure pathways

It is not possible to prevent human exposure to nanoparticles due to the proliferation of naturally occurring nanomaterials in addition to the occurrence of incidental and engineered nanoparticles. For engineered particulates, exposure is primarily through industrial production and formation. However, the general population is also exposed to nanomaterials through industrial release and use of consumer products (Figure 2.2).
There are multiple routes of entry into the human body following exposure to nanoparticles. (Figure 2.3). While occupational exposure studies have been conducted by multiple organisations (Schulte et al., 2013; Gordon et al., 2014; Brenner et al., 2015), many of these are focussed on larger particulates above 100nm and do not use particles in the nano size range. However, commonalities can be drawn to gain an appreciation of nanoparticle exposure. The most common entry route for nanoparticles into the body is through inhalation (Yah et al., 2012; Singh et al., 2014). Inhaled nanoparticles are of particular concern as they are less likely to be altered by the environment and are more easily able to enter the blood stream due to the structure of lungs, subsequently permeating cell barriers easily, reaching such organs as the brain, with potentially harmful effects on the blood brain barrier and its permeability (Borm et al., 2004; Lockman et al., 2004; Alessandrini et al., 2006).

Figure 2.2 Common exposure sources of nanoparticles likely to lead to exposure of receptors
2.4 Legislation

There are many different EU legislations (European Commission, 2008; EC) that apply to both nanoparticulates and larger particles (Figure 2.4). However, many do not currently identify nanoparticulates as separate entities from their bulk counterparts, thus newly observed behavioural and physico-chemical properties are not specifically accounted for. Revised legislation and standards are being developed to address this knowledge gap, with scientific bodies recommending that nanoscale materials are considered separately to their bulk counterparts. However, changes in
policy and the resultant regulations are normally retrospective and are generally implemented years after scenarios are encountered.

![Diagram of relevant EU documentation regarding nanomaterial regulation]

**Figure 2.4** Examples of relevant EU documentation regarding nanomaterial regulation
Numerous methods are employed to regulate nanomaterials throughout their life cycles (Figure 2.5). Production of nanomaterials is regulated under legislation such as the REACH (European Commission, 2006) which applies to the manufacturing, market placement and use of nanomaterials in the same way that they apply to bulk materials.

![Life cycle of a nanomaterial from extraction of the raw materials through to disposal or recycling](image)

**Figure 2.5** Life cycle of a nanomaterial from extraction of the raw materials through to disposal or recycling

Under the REACH regulatory framework, manufacturers are required to register anything produced or imported at 1 tonne/year or more unless they are identified as substances of very high concern (e.g. carcinogens, mutagens and reproductive toxins). Nanoparticles are not specifically mentioned but are included in the 2011 EC
recommendation that applies to both REACH and CLP, meaning the same restrictions, with regards to mass produced, still apply. A significant flaw when considering the number of nanoparticles needed to produce 1 tonne/year when compared to bulk materials.

In the case of nanomaterials identified as hazardous under Regulation (EC) No 1272/2008 of the CLP Framework which applies to substances and mixtures, restriction is independent of mass. However, the Framework itself makes no differentiation between nanoscale materials and bulk materials, despite inclusion in the 2011 EC recommendation. A lack of specific guidelines for nanomaterials presents many issues with using this framework. For example, nanomaterials may display hazardous properties which are not observed in bulk form, meaning they are exempt from those provisions which normally apply to hazardous materials. The implications of this oversight leads to the possibility that release into the environment may pose a greater risk than originally assumed.

Assessing the safety of hygiene products on the consumer market is covered by the Cosmetics Regulation (EU Regulation 1223/2009). This legislation takes a more direct approach to nanomaterials, with each material in its utilised form being assessed as a separate entity with restrictions being placed on preparation. Nanomaterials are discussed in this regulation, with new nanomaterials requiring authorisation by a committee before their use in products. Any products containing nanomaterials prior
to the implementation of this regulation can be subjected to full safety assessments if concerns are raised.

The Air Quality Directive 2008/50/EC was developed in order to prevent or reduce airborne nanomaterial exposure deemed harmful to humans and the environment. Again, the Directive does not directly reference nanomaterials, however, it does outline procedures for PM$_{10}$ (particulate matter $\leq 10\mu$m) and PM$_{2.5}$ ($\leq 2.5\mu$m) size fractions of airborne particulates, with nanomaterials making up a proportion of these size fractions. A framework of Air Quality Standards were published within this Directive detailing exposure limits for both PM$_{10}$ and PM$_{2.5}$ particulates (Table 2.1). Ultrafine particulates, those below 100nm (Andersen et al., 2008), are not yet regulated as a separate size class of particulate matter and are still included in PM$_{2.5}$ measurements, however, discussion as to whether a separate particle size class should be considered is currently ongoing.
Table 2.1 Comparison of Air Quality Standards applied in different countries

<table>
<thead>
<tr>
<th>Country/Area</th>
<th>Regulation</th>
<th>Statutory Limit (PM$_{2.5}$)</th>
<th>Statutory Limit (PM$_{10}$)</th>
<th>Relevant to Nanomaterials</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Union</td>
<td>Air Quality Directive 2008/50/EC</td>
<td>20µg/m$^3$ (3 year average)</td>
<td>40 µg/m$^3$ (1 year)</td>
<td>Inclusive of, but not directly mentioned.</td>
</tr>
<tr>
<td>United States</td>
<td>US Clean Air Act (1990) / National Ambient Air Quality Standards</td>
<td>35µg/m$^3$ (3 year average)</td>
<td>150 µg/m$^3$ (1 year)</td>
<td>Inclusive of, but not directly mentioned.</td>
</tr>
<tr>
<td>Australia</td>
<td>National Environment Protection Measure for Ambient Air Quality (1998)</td>
<td>8µg/m$^3$ (1 year)</td>
<td>50 µg/m$^3$ (1 day)*</td>
<td>Inclusive of, but not directly mentioned.</td>
</tr>
<tr>
<td>China</td>
<td>Ambient Air Quality Standards (GB 3095-2012)</td>
<td>35µg/m$^3$ (1 year)</td>
<td>70 µg/m$^3$ (1 year)</td>
<td>Inclusive of, but not directly mentioned.</td>
</tr>
</tbody>
</table>

* No more than five exceedances per year

End of life cycle regulatory legislation is also available, in the form of the Waste Framework Directive 2008/98/EC which was developed to protect the environment and humans by reducing and/or preventing the adverse effects associated with materials including nanomaterials used throughout industry. In addition to waste management, the European Commission has directives in place which specifically deal with airborne materials. The Waste Electrical and Electronic Equipment (WEEE) regulations also fall under end of life cycle legislation, with nanomaterials being
treated as their bulk counterparts unless a specific need for further review is deemed necessary (European Commission, 2008).

Lack of comparable toxicological and exposure data for nanomaterials, specifically long term exposure data, has meant that the establishment of legislation detailing nanoscale materials is a slow process, making identification of legislative gaps a significant challenge. Research suggests that behaviour of materials on the nanoscale often does not reflect that of the bulk material (Roduner, 2006). This behaviour, without the direct observation of long term studies, requires complex predictive modelling with well-defined conditions, a requirement that is difficult to accomplish when predicting behaviour within the human body or the surrounding environment. Another hurdle to overcome is the determination of which physico-chemical property is the most significant indicator of toxicity and therefore key for measurement regulation which should be agreed by all governing bodies. Pathways of exposure for nanomaterials are currently speculative instead of being based on expansive documented evidence (Ganzleben et al., 2011). Therefore the limitations of current legislation are as a result of lack of knowledge of nanomaterials and the uncertainty surrounding their behaviour within different systems.

Despite the lack of specific nanomaterial legislation, the availability of equipment capable of monitoring airborne nanomaterials is of great value for toxicological studies and the implementation of best practise guidelines, (e.g. the Scientific Committee on Emerging and Newly Identified Health Risks (SCHENIR)). It is also likely to be
required when legislation/regulation catches up with technology. For such monitoring, different physico-chemical characteristics of the nanoparticles including size, shape, surface area, charge and mass can be considered. Here the main types of measurement technique in common use are summarised alongside a critique of their use with nanoscale materials.

2.5 Materials and their physico-chemical properties

Engineered nanomaterials can be grouped as carbons, metallics, ceramics (including metal oxides, and nitrides) and intermetallics which are produced in varying quantities and purities in industry. In addition, these materials are known to have a variety of morphologies as shown in Table 2.2. Carbon-based nanomaterials include some of the most frequently reported nano-products in literature such as fullerenes, nanotubes, graphene and fibres. These materials exhibit electrical properties making them attractive for applications such as solar cells, super capacitors, and batteries (Landi et al., 2009; Hersam, 2011; Chen and Dai, 2014). Due to their open atomic structure they are also seen as potential gas storage media (Bekyarova et al., 2003).

Metal-based nanomaterials, including gold and silver, are used in a variety of applications such as medicines, drug delivery and water treatment (Salata, 2004; Qu et al., 2013) and can be coated or uncoated. The electrical conductivity of gold and silver nanoparticles also makes them attractive in the production of nano-electronic devices (Li et al., 2005). Metallic nanoparticles exhibiting magnetic properties are
also used in ferrofluids for applications such as audio speaker optimisation, chemotherapy and magnetic domain detection. Ceramic nanomaterials include oxides and nitrides of metals. Many of these, for example titanium dioxide and zinc oxide, exhibit behaviour that makes them attractive for UV protection for both humans and materials (Becheri et al., 2007). These materials in their macro, micro and nano forms are known to be bio-inert and are ubiquitous in medical and cosmetic products including toothpaste, face cream, and pharmaceutical drugs (Lohani et al., 2014).

Nanomaterials often display unique physico-chemical properties when compared to their micro and bulk counterparts (Stefanita, 2008). Firstly, as particle size decreases the relative surface area increases (Jiang et al., 2006; Sun and Simon, 2007), thereby increasing the relative proportion of reactive surface for a given mass of material and increasing the specific reactivity (Corma and Serna, 2006; Liu et al., 2012). Secondly, as particle size decreases below approximately 20 nm, distortions in the atomic structure of the particles give rise to quantum effects and changes in physical, thermal and electrical properties (Qi and Wang, 2002). Finally, as particle size approaches the wavelength of light there will be changes in the way light scattering occurs, rendering them less visible (Allen, 2013). In addition to individual particle characteristics, nanoparticles have a tendency to agglomerate, making it more difficult to distinguish between individual particles and those which have formed what appear to be “larger particulates” to monitoring instrumentation.
At the nanoscale, particle behaviour is often unpredictable when they are in contact with the human body or the surrounding environment due to the complex systems that they interact with. For example, nanoparticles can interact with other compounds in the environment, such as organic matter and proteins, which will change the behavioural properties of the nanoparticles complicating their behaviour within the environment. It is this unknown behaviour that causes the growing concern for safety and provides the main challenge for current instrumentation measurements.

2.6 Particle monitoring and characterisation

2.6.1 Measurement types and the techniques available

Physical characteristics of nanoparticles, including size, surface area and mass, can be measured along with particle number concentration when detecting and monitoring atmospheric nanoparticles.

There are a number of instruments that can be used for nanoparticle detection and measurement such as Scanning Mobility Particle Sizers (SMPS), microscopy instruments and Condensation Particle Counters (CPC). However, many of these instruments require a liquid media that may affect nanoparticles through such mechanisms as molecular adsorption onto the particle surface, which, if unaccounted for, may provide unreliable data.
Table 2.2 Non-exhaustive list of compositional categories of engineered nanoparticles and their potential applications

<table>
<thead>
<tr>
<th>Category</th>
<th>Material</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon nanotubes</td>
<td>Supercapacitors; gas storage</td>
</tr>
<tr>
<td></td>
<td>Carbon nanofibres</td>
<td>Catalytic media; gas storage</td>
</tr>
<tr>
<td></td>
<td>Carbon black</td>
<td>Rubber strengthening agents</td>
</tr>
<tr>
<td></td>
<td>Carbon nanofoams</td>
<td>Spintronic devices</td>
</tr>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gold</td>
<td>Conductive inks; electronics; colorimetric sensors; biomarkers</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>Conductive inks; molecular sensing; antimicrobial coatings</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>Antibiotics; antifungals; conductive inks</td>
</tr>
<tr>
<td></td>
<td>Platinum</td>
<td>Catalytic converters; cancer treatments</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td>Drug delivery; water treatment</td>
</tr>
<tr>
<td><strong>Ceramics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Titanium dioxide</td>
<td>Colour pigment; paints; dielectric mirrors; UV blocking pigment</td>
</tr>
<tr>
<td></td>
<td>Zinc oxide</td>
<td>Antibacterial; rubber vulcanisation; cigarette filters</td>
</tr>
<tr>
<td></td>
<td>Iron oxide</td>
<td>Magnetic resonance imagining; cell labelling; environmental clean-up</td>
</tr>
<tr>
<td></td>
<td>Tin oxide</td>
<td>LCD displays; magnetic data storage; energy saving; optoelectronic devices</td>
</tr>
<tr>
<td></td>
<td>Silicon nitride</td>
<td>Automobile pre-combustion chambers; spinal fusion devices; integrated circuit insulators</td>
</tr>
<tr>
<td><strong>Intermetallics</strong></td>
<td>Cadmium telluride</td>
<td>Solar cells; optical windows; lenses</td>
</tr>
<tr>
<td></td>
<td>Niobium -tin</td>
<td>Superconductor magnets</td>
</tr>
</tbody>
</table>
Ideally, particulate detection would be real time within the environment of study in order to assess any immediate exposure risks, however there are few instruments capable of this type of particle measurement and these measure at the microscale. Those that are able to detect particles that are in the nanoscale are even fewer (Figure 2.6). Other important considerations for real time measurement require that minimal sample preparation is required.

While instruments may report the size of the nanoparticles, this is rarely based on a direct measurement of the size and therefore subject to error, in particular when a particle exhibits different dimensions dependant on orientation. In addition, direct measurement of particle size distribution, as with liquid-based techniques such as dynamic light scattering, is rare with a more common route being the separation of particles into small size ranges (bins), with subsequent measurement being far more common.
2.6.2 Detection

2.6.2.1 Microscopy

Although excluded from real time particulate detection suitability based on the need for sample preparation and subsequent lack of real time information, instruments such as scanning electron microscopes (SEM), transmission electron microscopes (TEM)
and atomic force microscopes (AFM) can offer valuable information on nanoparticle morphology, topology and, in some cases, composition.

All three instrumentation types are commonly used for nanoparticle characterisation, both in isolation and in combination with other techniques. TEM analysis may provide both qualitative and quantitative sample information with resolution capabilities of approximately 0.2nm leading to its regular use in biological studies for example Lasagna-Reeves et al. (2010) used TEM to show gold nanoparticle accumulation in mice, and toxicity after repeated administration at different doses. SEM analysis has also been used in a number of studies with a resolution of approximately 0.4nm (Hitachi, 2015), for example to provide surface morphology information of the coatings added to polymeric nanoparticles for oral delivery of anticancer drugs (Yin-Win and Feng, 2005) and to determine the evaluate the antimicrobial properties of silver nanoparticles (Sondi and Salopek-Sondi, 2004).

There are significant limitations with regards to using microscopy to monitor airborne nanoparticles. Prior to analysis, appropriate sampling methods and sample preparation procedures are required making microscopy unsuited for real time detection of airborne nanoparticle samples. In addition, although quantitative information can be obtained, limited sample amounts can be visualised at any one time, thus providing a limited view with regards to exposure monitoring and uncertainty about the representativeness of the sample in addition to excessive time requirements.
2.6.2.2 Mass detection

Instrumentation that detects airborne particulates based on mass is also commercially available, an example of this includes the tapered element oscillating microbalances (TEOM). TEOM instruments are commonly used for mass concentration detection in the PM$_{10}$ range, particularly within the UK (Harrison and Allen, 2004) due to their capability for providing real-time continuous data. TEOM instruments contain a tapered tube with a filter situated at its tip which oscillates at a resonant frequency of several hundred Hertz. The resonant frequency is dependent on the physical characteristic of the tapered tube and filter, with instrumentation varying between manufacturers (Figure 2.7).

![Figure 2.7 Schematic of tapered element oscillating microbalance (TEOM) showing sample entry and collection filter](image-url)

Figure 2.7 Schematic of tapered element oscillating microbalance (TEOM) showing sample entry and collection filter
Particles entering the instrument collect on the filter where the mass change ($\Delta M$) can be calculated according to the change in the mechanical resonance frequency of the tip (Patashnick and Rupprecht, 1991).

$$\Delta M = K_0 \left( \frac{1}{F_i^2} - \frac{1}{F_f^2} \right)$$  \hspace{1cm} \text{Equation 2.1}

where $K_0$ is a calibration constant individual to the instrument, $F_i$ is the initial oscillation frequency and $F_f$ is the oscillation frequency after mass deposition.

Although TEOM instruments are used in many studies and for standardised detection throughout the world, they are particularly sensitive to humidity changes due to evaporation and condensation of water on the filter (Tortajada-Genaro and Borrás, 2011) which leads to fluctuations in the mass reading which are in the same range as the mass change caused by particles. In order to combat this sample filters are maintained at an elevated temperature, which in turn can lead to the loss of semi-volatile species, resulting in an underestimation of mass values. The loss of species is less likely to be an issue with engineered nanoparticles (ENP) as they are not typically semi-volatile materials. Developments have been made to target this disadvantage with the incorporation of sequential equilibration systems (SES) and Nafion® dryers (Lee et al., 2005) to reduce the relative humidity of the system, however their implementation is not simple and samples usually require further analysis for
confirmation. In addition to this, the incorporation of an electrostatic charge can cause a slight bias towards higher mass values when samples are charged.

2.6.2.3 Surface charge detection

Instrumentation based on surface charge detection provides surface area measurement. Such instruments include nanoparticle surface area monitors (NSAM). Aerosol samples are drawn through the NSAM with an initial 1µm cut off filter. Subsequently, the air is split into two streams with only one passing through further filters and an ioniser, resulting in positively charged ions and the other remaining untreated. The air with positively charged ions is then introduced into the mixing chamber with the untreated stream in order to promote diffusion charging of the aerosol sample. Charged aerosol samples are then moved into an ion trap, which acts as a size-selector for the instrument. Particles are size-selected based on their charged state, where particles with a charged state not corresponding to alveolar or tracheobronchial regions are collected and do not continue to the electrometer. Remaining particulates are then subjected to charge measurements at the electrometer where the charge measured is directly proportional to the surface area of the particles (Equations 2.2 to 2.4) (Ntziachristos et al., 2007).

For a monodisperse aerosol the filter current \(I\) is given by Equation 2.2.

\[
I = eQ\eta n_d
\]

Equation 2.2
Where \( e \) is the unit charge, \( Q \) is the flow rate of the sample with \( N \) as the number concentration, \( \eta \) is the particle penetration through the detector and \( n_q \) is the average number of elementary charges per particle. However, the majority of ambient air samples are not monodisperse. Thus, in order to account for polydispersity (Equation 2.3), number concentration is substituted for number size distribution as a function of particle diameter.

\[
\eta(d)\eta Q(D_p) = x d_p^{1.258}
\]

Equation 2.3

Where \( x d_p \) is the mobility equivalent in nm.

Total particle surface area \( (S_A) \) (Equation 2.4) can be determined where \( k \) is constant determined by the instrument’s calibration.

\[
S_A = k l
\]

Equation 2.4

The resulting size separation data from the instrument corresponds to the deposition size of particles in two regions of the lung, the tracheobronchial region or the alveolar region, with the assumption that inhalation is the primary source of exposure and that uptake of particulates into the body is dependent on the region of lung deposition.
2.6.2.4 Density

β-gauge particulate monitors are the most commonly used instruments to measure particulate density-based PM$_{10}$ concentration. These instruments work by measuring the attenuation of β-particles emitted by an external radioactive source by the studied environmental particles. Particles are deposited onto filter tape which passes between the β-source and detector. A separate reference chamber contains tape which has not been exposed to air samples. Measurements are taken over a fixed time period, where attenuation by both the exposed and unexposed tape is simultaneously measured by the device.

The β-particle flux is dependent on the mass of particles deposited on the filter tape. (Equations 2.5 to 2.7) (Gobeli et al., 2008);

\[ B = I_o e^{-\mu x} \]  \hspace{1cm} \text{Equation 2.5}

where \( B \) is the beta ray intensity of the attenuated beta ray, \( I_o \) is the non-attenuated beta ray intensity, \( \mu \) is the material dependant absorption coefficient and \( x \) is the mass density of the particulates;

The mass density, \( x \), can then be given by Equation 2.6;

\[ x = \frac{1}{\mu} \ln \left[ \frac{I_o}{I} \right] \]  \hspace{1cm} \text{Equation 2.6}
The particulate mass concentration, \( c \), can be determined (Equation 2.7) for a specified flow rate, \( Q \), and set time interval, \( t \).

\[
c = \frac{A}{Qt} \times \frac{A}{Qt} \ln \left[ \frac{I_0}{I} \right]
\]

Equation 2.7

Where \( A \) is the cross sectional area of the tape spot exposed to particles. Typically mass concentrations at \( \mu g/m^3 \) can be detected. \( \beta \)-attenuation devices can suffer from moisture condensation on the sample capture inlet, with the condensation trapping particles in the tubes before they reach the tape. Mixing samples with air prior to deposition can reduce this risk (Gobeli et al., 2008), in addition to reducing the likelihood of moisture affecting particle mass readings at the filter interface. As with the TEOM, a heated inlet may result in the loss of semi-volatiles. Whilst unheated inlets can be used, these are more susceptible to effects of changes in humidity.

2.6.2.5 Particle number detection

Traditional particle counting techniques used for number concentration, such as those based on light scattering, often struggle to count particles in the nanoscale. In such circumstances, condensation particle counters (CPC) can be used to enlarge the particles from the nanoscale to microscale, making them more easily detectable by optical instrumentation, most allowing detection of particles down to 10nm (Schmoll et al., 2010). CPCs work on the principle that the nanoparticles act as a nucleus for vapour condensation when in a supersaturated vapour, causing a liquid droplet to
grow around the particle. It is this droplet, as opposed to the particle, that is detected. Super-saturation can be achieved by diffusional thermal cooling, adiabatic expansion and mixing of cold/hot streams of air (Cheng, 2011).

In the case of thermal diffusion, particle/air samples enter the inlet and pass through a porous medium in contact with a working fluid, e.g. butanol. The air in close proximity to the medium becomes saturated with the vapour of the working fluid. Subsequently, the sample passes through a condenser where a temperature change is used to cause super-saturation of the vapour.

The particulates act as nucleation sites for the formation of droplets. The particle droplets then pass through a detector measuring the light scattered, allowing particle numbers to be determined. Particle number concentration is subsequently calculated for the particle count and volume of air sampled. These instruments are typically suited to indoor environments, being used for the monitoring of clean rooms and the
testing of other equipment. Outdoor applications have been studied but are more complicated in that the instruments measure particle numbers and cannot differentiate between particle types, a parameter more predictable in indoor conditions where there is a more limited initial range of size, sources and particle types. However some studies still utilise CPCs in order to take personal exposure measurements in specific environments (Ragettli et al., 2013).

2.6.2.6 Impedance detection

Impedance analysers are a group of instruments capable of measuring particulate concentration without the assumption of equivalent sphere diameter. Analysers detect particulates independent of their shape and size. The impedance is a function of the materials permittivity, which varies dependant on the material and the concentration or particle number present. Typically, analysers are attached to electrode structures where particles are able to land in the electrode gap (Figure 2.9). Changes in impedance are then measured by the analyser.

![Figure 2.9 Example of impedance analyser and electrode measurement instrumentation](image_url)
Studies, such as those conducted by Wu et al., 2006 and Yusof et al., 2012, have demonstrated the use of impedance analysis for particles and biological samples in liquid media, however it has not been possible to identify a published study that reports the airborne measurement of nanoparticles using this method. In addition to its independence from equivalent sphere diameter assumptions, impedance measurements have the advantage of being able to detect multiple properties, such as material type and concentration. However, in order to gain size information, instruments must be used in combination with size selection methods such as filter structures or size selection instrumentation.

2.6.2.7 Equivalent sphere diameter

In addition to technical limitations of the instrumentation discussed it is important to recognise the limitation of the assumptions made when the monitoring data is produced. One of the most significant assumptions of detection is the equivalent sphere theory (EST). Many instruments rely on EST to link the detected information to final measurement data (Figure 2.10).
The majority of particulates are non-spherical. As with all non-spherical objects, this means that the reported particle diameter will vary dependant on the measurement used. EST can be used in order to condense dimensions of a non-spherical object in order to provide a single measurement value; spheres being the only 3D shape which can be described accurately with a singular value (Figure 2.11).

Figure 2.10 Illustration of equivalent sphere theory (EST) use within particulate detection instrumentation where \( \rho \) is density

Figure 2.11 Example of non-spherical and spherical objects with multiple dimensions of measurement, where \( x/y \) are the length recorded of the object studied
There are a number of parameters that can be measured in the case of non-spherical objects in order to determine a single equivalent sphere diameter value. Industrially, there is no standard as to which parameter is utilised in instrumentation, meaning that measurement data from different instruments cannot be compared easily. A different equivalent diameter will be provided for any given non-spherical particle when different detection principles are employed (Figure 2.12).

Figure 2.12 Properties used to determine equivalent sphere diameter (Malvern, 2012) where D is diameter
2.6.3 Classification

2.6.3.1 Size selection

The accurate determination of airborne nanoparticle sizes in the environment is extremely challenging due their tendency to agglomerate. The presence of nanoparticulates can easily be masked by the presence of larger particles or they themselves can be mistaken for larger particles due to their propensity to agglomerate. For these reasons it is often necessary to filter or size-select particles in order to prevent nanoparticles from going undetected.

Particles can be size-selected by a number of techniques, including differential mobility analysis (DMA). Instruments capable of this size-selectivity include differential mobility particle sizers (DMPS) and scanning mobility particle sizers (SMPS).
When coupled to a suitable detector, DMA has an advantage when compared to optical techniques for particle size analysis as it is less sensitive to changes in the refractive index of the solvent. However, the temporal resolution of DMA techniques is reduced in comparison to optical counterparts due to the sequential nature of the analysis. Instruments using DMA have similar underlying working principles (Figure 2.13), which allow for the determination of particle size distribution information and, when coupled with other techniques, number concentration in predetermined size ranges.

![Diagram of working principles of differential mobility analysers](image)

**Figure 2.13** Working principles of differential mobility analysers
These instruments (Figure 2.14) operate by measuring the electrical mobility (Flagan, 2008) of the segregated particles.

![Schematic of a differential mobility analyser](image)

**Figure 2.14** Schematic of a differential mobility analyser where blue arrows show the air flow direction

For particles under 15µm in diameter, the electrical mobility can be determined using the inertia ($F_i$; Equation 2.9) and drag ($F_d$; Equation 2.8) due to the fact that the surrounding gas no longer behaves as a continuum fluid because the particles are sufficiently small relative to the mean free path of gas molecules;

$$\vec{F}_i = m \frac{d\vec{v}}{dt}$$

**Equation 2.9**

$$\vec{F}_d = 3\pi\mu D_p/C_c(Kn)$$

**Equation 2.8**

$$Kn = \frac{2\lambda}{D_p}$$

**Equation 2.10**
where $\mu$ is the gas viscosity and $D_p$ is particle diameter, $Kn$ is the Knudsen number (Equation 2.10) and $C_c$ is the slip correction factor given by (Equation 2.11). The values $A_1$ (0.257), $A_2$ (0.400) and $A_3$ (0.55) are experimentally derived values for air (Davies, 1945).

Electrical mobility (Equation 2.12), takes into account particle charge and the number of charges present and is thus calculated as:

$$Z = \frac{n e C_c}{3\pi \mu D_p}$$  \hspace{1cm} \text{Equation 2.12}$$

Where $Z$ is electrical mobility, $n$ is the number of charges present and $e$ is the elemental charge.

Cascade impactors such as electrical low pressure impactors (ELPI) are also used to physically size select particulates. In this case, samples are passed through a series of impaction stages (Figure 2.15) with a decreasing sized exit point into the next stage. It is the diameter of the exit point that controls the particulate size trapped by the impactor. Assuming that each stage is able to capture particles larger than its corresponding cut off size, a mass distribution of particles can determined based on their aerodynamic diameter by measuring the weight of the impactor before and after
sample exposure. Advantageously, particles impacted on each of the stages can be collected for further offline analysis such as compositional characterisation.

Figure 2.15 Schematic of a cascade impactor with red arrows identifying particles able to exit into the next impaction zone and green, those particles which are too large and impact onto the plate

2.6.3.2 Surface charge selection

Aerosol particle mass analysers (APM) generate mass distribution data. In this case, aerosols are passed through the annular gap of two rotating cylindrical electrodes (Figure 2.16). Particles rotate between the electrodes where a voltage is applied to the innermost electrode and the particles subsequently experience directly opposing
centrifugal and electrostatic forces. At this point, particles of a particular mass experience a balance in forces (Equation 2.13) and these particles can further traverse through the APM (Ehara et al., 1996).

\[ mr\omega^2 = q \frac{V}{r\ln\left(\frac{r_a}{r_b}\right)} \]  

Equation 2.13

Where \( m \) is the particles’ mass, \( \omega \) is the angular speed of the APM, \( r \) is the location of the particle relative to the rotational axis, \( q \) is the particle charge, \( r_a/r_b \) are the radii of the inner and outer electrodes respectively, and \( V \) is the applied voltage. Mass selected particles exiting the analyser can then be detected with an appropriate system.

Figure 2.16 Schematics of aerosol particle mass analyser instrumentation showing (A) particles between the electrodes and (B) the whole system.
2.6.3.3 Instrumentation suitability

Many of the instruments mentioned previously have limited capability, measuring only a single property (Table 2.3). In addition these instruments have their own limitations, being affected by environmental conditions including humidity and temperature. Many studies and monitoring plans use multiple techniques in combination at any one time, making the comparison of results difficult between different combinations. Many of the instruments available for particulate counting have a limit of detection above that of the nanoscale region, making them unsuitable for nanoparticle detection.

Table 2.3 Non-exhaustive summary of a selection of current air exposure monitoring instruments available

<table>
<thead>
<tr>
<th>Technique</th>
<th>Primary Data</th>
<th>Real time</th>
<th>Combination Technique</th>
<th>Nanoparticle measurement</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>β–Attenuation Analysers</td>
<td>Particle mass concentration</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>Radioactive source Humidity sensitive</td>
</tr>
<tr>
<td>Condensation particle counters</td>
<td>Particle number concentration</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Differential mobility analysers</td>
<td>Particle size selection number distribution</td>
<td></td>
<td></td>
<td></td>
<td>Small particle limitations due to charging probability</td>
</tr>
<tr>
<td>Electrical low pressure impactors</td>
<td>Surface area</td>
<td></td>
<td>✓</td>
<td></td>
<td>Small particle limitations due to charging probability</td>
</tr>
</tbody>
</table>
The systems mentioned do meet all the requirements needed for an airborne nanoparticle monitor and would not produce real time data needed for immediate hazard assessment. For this reason, a particle monitor capable of real time detection, independent of such assumptions as equivalent sphere theory is required.

### 2.7 Filtration

#### 2.7.1 Introduction

Instrumentation such as those discussed in Section 2.6 often contain a size selection step prior to the analysis stage in order to select the particulate range of interest. Filtration, being the removal of particles as they pass through a permeable material, is the most commonly utilised method of achieving this (Jennings et al., 2003). Filtering is also of interest in the current project in order to trap recovered materials for sensing, in particular using cross-flow and through-flow filtration.
Cross-flow filtration is achieved by positioning the filter parallel to the air flow in order to size separate particulates in contrast with through-flow filtration techniques that position the filter perpendicular to air flow (Figure 2.17). In cross-flow filtration, a pressure difference across the filter causes particles smaller than the pore size to pass through the filter. The advantages of cross-flow filtration compared to through-flow filtration include the reduction of the likelihood of particles building up on the surface of the filter, and therefore clogging of the device does not happen so readily. The most significant difference will be that the air speed will depend not on the macroscopic air velocity but rather the flow across the filter. The interaction mechanisms in both filter types are similar.

Figure 2.17 Illustration of cross-flow and through-flow filtration (*Speed depends on flow/pressure on permeate side of filter. It is typically less than slow flow with permeation tending to favour slower flow rates).
2.7.2 Filter types

2.7.2.1 Fibrous filters

A wide range of applications use fibrous filters (Figure 2.18) including respiratory protection, clean room filters and air sampling. Filters can be constructed from a number of fibrous materials, with cellulose (wood), glass and plastic commonly used. The individual fibres are typically placed in a random orientation. Airborne material is trapped as it flows through the structure. Most fibrous filters have a high level of porosity of between 70 and 99% (Crowe, 2005). Fibre length and diameter can range from the submicron scale to millimetres.

Figure 2.18 Micrograph of fibrous filter network (Whatman™ Filter, Analop 10, 0.2µm) Courtesy of David G. Jones, University of Surrey.
A number of advantages and disadvantages are associated within using fibrous filters (Table 2.4).

Table 2.4 Advantages and disadvantages of fibrous filters for aerosol sampling

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low cost</td>
<td>• Regular cleaning is needed – limiting geometry</td>
</tr>
<tr>
<td>• High particulate loading</td>
<td>(filtrate is trapped, building up in the filter)</td>
</tr>
<tr>
<td>• Large sample volume with low</td>
<td>• Humidity sensitive – may cause clogging of the</td>
</tr>
<tr>
<td>pressure drop</td>
<td>fibres and particle penetration is prevented</td>
</tr>
<tr>
<td></td>
<td>• Chemical resistance – material dependant (limits</td>
</tr>
<tr>
<td></td>
<td>material types that can be used, e.g. wood fibres</td>
</tr>
<tr>
<td></td>
<td>are less resistant than plastic based fibres.)</td>
</tr>
</tbody>
</table>

2.7.2.2 Membrane filters

Membrane filters (Figure 2.19) are typically used as cleaning filters and air sampling devices. Like fibrous filters they can be constructed from a number of different materials including Teflon™, polyvinyl chloride (PVC) and cellulose. Membrane filters are described by their pore rating, describing the particle size retained by the filter media to a specified degree of efficiency. The membranes will retain particles that
exceed the rating. Instead of being composed of individual fibres, membrane filters are a continuous material containing a high volume of interconnected pores of approximately equal size. The size of the pores and interconnecting channels define the filters’ pore rating.

Figure 2.19 Porous ceramic oxide membrane structure (Courtesy of Prof. R. Dorey)

Like fibrous filters, a number of advantages and disadvantages are associated with membrane filters (Table 2.5).
Table 2.5 Advantages and disadvantages of membrane filters for aerosol sampling

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low cost materials available</td>
<td>• Low particle loading capacity</td>
</tr>
<tr>
<td>• High collection efficiency</td>
<td>• Humidity susceptibility for some types dependent on material</td>
</tr>
<tr>
<td>• High mechanical strength</td>
<td>• High pressure drop</td>
</tr>
<tr>
<td></td>
<td>• Typically only operational in low temperature range</td>
</tr>
</tbody>
</table>

2.7.2.3 Capillary pore membrane filters

Capillary pore membrane filters (Figure 2.20) have applications in aerosol collection instrumentation construction. Materials used in these filters include polycarbonate and ceramics. Capillary pore membrane filters are formed of a continuous material containing a high volume of porous openings on the surface, like that of membrane filters. However, these filters contain multiple pathways through the material some of which extend through the thickness of the filter.
Advantages and disadvantages are associated with the use of capillary pore membrane filters and are shown in Table 2.6.

Figure 2.20 SEM micrograph alumina capillary pore membrane (courtesy of David G. Jones, University of Surrey)
Table 2.6 Advantages and disadvantages of capillary membrane filters for aerosol sampling

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Uniform surfaces</td>
<td>• High pressure drop, decreasing through the structure</td>
</tr>
<tr>
<td>• Humidity resistance</td>
<td>• Low particle loading capacity</td>
</tr>
<tr>
<td></td>
<td>• Issues with static charge build-up</td>
</tr>
</tbody>
</table>

2.7.3 Filter interaction mechanisms

2.7.3.1 Mechanisms

A number of different mechanisms occur simultaneously during filtering and then influence the collection efficiency of a filter. They include interception, inertial impaction, diffusion, gravitational settling and electrostatic deposition. The dominant mechanisms are affected by the physical characteristics of the filter such as fibre or pore diameter $D_f$, filter thickness $D_t$, and filter solidity $F_s$ (the volumetric ratio of fibres and the total volume of the filter) (Zhang, 2004).

2.7.3.2 Interception

Separation through interception occurs when particles in a gas stream come within one particle radius of the filter fibre or, in porous membrane structures, the outer edge of the pore (Xu, 2013; Figure 2.21). In this case only certain stream lines passing close enough to the fibre will allow for particle capturing in this manner. Particulates of
non-spherical geometry are especially affected by this mechanism as they have large surface areas and effective cross-sectional areas (Zhang, 2004) affecting particle bounce and subsequently collection efficiency (Boskovic et al., 2005)

Collection efficiency (Equation 2.14) for a single fibre ($FE_i$) through interception can be calculated as follows;

$$FE_i = \frac{(1 - F_s)D_p^2}{Ku(1 + \frac{D_p}{D_f})D_f^2}$$  \hspace{1cm} \text{Equation 2.14}

Where $F_s$ is filter solidity, $D_p$ is particle diameter, $D_f$ is fibre diameter and $Ku$ is the Kuwabara hydrodynamic factor (compensation for distortion effects of the flow around the fibre due to its proximity to other fibres). $Ku$ is dependent on both fibre diameter and filter solidity. In the case of particle diameters below 2µm, a slip correction factor is added, thus the calculation is as follows (Kirsch and Stechkina, 1978) (Equation 2.15 & Equation 2.16);
For particles 2µm and above;

\[
K_u = \frac{-\ln F_s}{2} - \frac{3}{4} + F_s - \frac{F_s^2}{4}
\]

\[\text{Equation 2.15}\]

For particles below 2µm;

\[
K_u = C_c - \frac{\ln F_s}{2} - \frac{3}{4} + F_s - \frac{F_s^2}{4}
\]

\[\text{Equation 2.16}\]

Where \(C_c\) is the Cunningham slip correction factor (Equation 2.11)

2.7.3.3 Impaction

Inertial impaction occurs when a particle of significantly large size is unable to adjust to the changes in airflow direction when in close proximity to the fibre or pore edge. Impaction is mostly attributed to larger or heavier particulates. As the air flow passes around the fibre/membrane structure the particle continues along its original path and hits the fibre directly, thus being captured. High gas velocities and dense fibre packing contribute to the frequency of this type of interaction.

![Diagram of particle filtration through impaction](image_url)

Figure 2.22 Illustration of particle filtration through impaction where the arrows show air flow direction
Collection efficiency for a single fibre through impaction \((FE_{im})\) can be calculated as through Equations 2.17 to 2.19.

\[
FE_{im} = \frac{(Stk)\alpha}{(2Ku)^2}
\]  
Equation 2.17

Where \(\alpha\) is given by Equation 2.19 and \(Stk\) is given by;

\[
Stk = \frac{P_PD_P^2C_CU_o}{18\eta D_F}
\]  
Equation 2.18

Where \(P_P\) is the particle density, \(C_C\) is the Cunningham slip correction factor and \(U_o\) is air velocity

For the ration of particle diameter to fibre diameter, where \(D_P/D_F < 0.4\) \(\alpha\) is given by;

\[
\alpha = (29.6 - 28F_S^{0.62})\left(\frac{D_P}{D_F}\right)^2 - 27.5\left(\frac{D_P}{D_F}\right)^{2.8}
\]  
Equation 2.19

For \(D_P/D_F \geq 0.4\), \(\alpha = 2.0\).

Unlike interception, efficiency decreases as a result of increasing pore diameter/fibre diameter ratio (Scott, 2005). However, this effect is less significant for larger particulates which are of comparable size to the fibre diameter (Zhang, 2004).

2.7.3.4 Diffusion

Diffusion of particles to the surface of filter fibres may also occur when smaller particles are subject to Brownian motion in slow moving the air streams, leaving more
time for the particles to move and hit the fibre. In this case efficiency is based on the ratio of the particle diameter/fibre diameter (Kulkarni et al., 2011).

Single fibre efficiency ($FE_d$) (Equation 2.20) can be described using the Peclet number ($Pe$) (Equation 2.21);

$$FE_d = 2Pe^{-\frac{2}{3}} + 1.24 \left(\frac{D_P}{D_d}\right)^{\frac{2}{3}} (KuPe)^{-\frac{1}{2}}$$  \hspace{1cm} \text{Equation 2.20}

$Pe$ is;

$$Pe = \frac{D_F U_0}{P_D}$$  \hspace{1cm} \text{Equation 2.21}

Where $U_0$ is air velocity and $P_D$ is the particle diffusion coefficient.
2.7.3.5 Gravitational settling

The gravitational settling of particulates on the surface of a filter occurs when particles deviate from their flow paths due to a sufficiently large settling velocity (Figure 2.24). The effect of this mechanism is more pronounced for large particles in lower air flow speeds (Liu and Liptak, 1997). The effectiveness of this mechanism is highly influenced by the position of the filter relative to the airflow. When the airflow is in a downwards direction, the mechanism is in effect, however with an upwards airflow, gravitational settling cannot occur. Above 0.01m/s air flow speed it is more likely that particle capture occurs as a result of impaction rather than settling (Zhang, 2004).

![Illustration of particle filtration through gravitational settling](image)

**Figure 2.24** Illustration of particle filtration through gravitational settling where the arrows show air flow direction

Filter efficiency proportioned to gravitational settling \((FE_g)\) (Equation 2.22) can be defined as;

\[
FE_g = Gf \left(1 + \frac{D_p}{D_f}\right) \sin \alpha
\]

**Equation 2.22**
Where $\alpha$ is the yaw angle (Figure 2.25) and $G_f$ is defined as (Flagan and Seinfeld, 1988); 

$$G_f = \frac{V_s}{U_0} = \frac{\rho_f D_f^2 C_c g}{18 \eta U_0}$$  

Equation 2.23

Where $V_s$ is terminal settling velocity, $U_0$ is air velocity and $g$ is the gravitational constant.

![Diagram](image)

Figure 2.25 Yaw angle ($\alpha$) between airflow and horizontal line affecting gravitational settling of particles where a yaw angle of 0 denotes gravitational settling.

2.7.3.6 Electrostatic forces

Electrostatic deposition on a filter surface occurs when the particles and the filter itself are charged (Figure 2.26). When the particle charge is known, using a suitable, oppositely, charged filter can greatly improve the capturing efficiency, however this mechanism is negligible in most circumstances.
Single fibre collection efficiency \((\text{FE}_e)\) can be calculated as \((\text{Brown, 1993})\) (Equation 2.24);

\[
\text{FE}_e = 1.5 \left( \frac{\varepsilon_f - 1}{\varepsilon_f + 1} \right) \frac{q^2}{(12\pi^2\eta U_0\varepsilon_0 D_p D_F^2)^{1/2}}
\]

Equation 2.24

Where \(\varepsilon_f\) is the relative permittivity of the fibre, \(\varepsilon_0\) is the relative permittivity of the vacuum and \(q\) is the electric charge of the particle (Coulombs).

2.7.4 Filter collection efficiency

Each of the interaction mechanisms affecting filter collection efficiency contribute to the total single fibre collection efficiency \((\text{FE}_T)\) which can be calculated using Equation 2.25;

\[
\text{FE}_T = 1 - (1 - \text{FE}_i)(1 - \text{FE}_{im})(1 - \text{FE}_d)(1 - \text{FE}_g)(1 - \text{FE}_e)
\]

Equation 2.25
For a given particle size, the proportion of particle capture due to a specific mechanism varies (Hinds, 1982) and is dependent on the geometry of the filter. The relative behaviour of each mechanism remains broadly consistent and can be seen in Figure 2.27.

\[
FE_0 = 1 - \left( \frac{N_{in}}{N_{out}} \right)
\]

Equation 2.26

Where \( N_{in} \) is the number of particles entering the filter and \( N_{out} \) is the number of particles leaving the filter.

The particle penetration, as a result of interaction mechanisms through the filter, is determined principally by particle size. However air flow rate has a significant effect on the proportion of particles filtered via each mechanism (Figure 2.28). Increasing
the flow rate increases particle penetration, but the efficiency of different interaction mechanisms is changed. For example, an increase in particle size leads to a consequential increase in the number of particles captured as a result of interception, yet changes in flow rate have no effect. Conversely, diffusion based capture has a larger effect at lower particle sizes, with increasing flow rate decreasing this efficiency. Impaction occurs more frequently at higher flow rates and larger particle sizes.

Under standard test conditions (approximately 2 m/s air flow), it is most likely that the mechanism of filtration for nanoparticulates (particles <100nm) would be interception. Gravitational settling is not possible if a sample is placed perpendicular to the airflow, with diffusion also unlikely to occur due to the fast flow rate. At lower air flow rates, those that the device is expected to experience in real environments, diffusion and interceptions are both likely candidates for the most significant contribution to nanoparticulate capture by the filter layer.

![Illustration showing the approximate effect of flow rate and particle size on the different interaction mechanisms and their relative dominance during particle capture](image)

**Figure 2.28** Illustration showing the approximate effect of flow rate and particle size on the different interaction mechanisms and their relative dominance during particle capture
2.8 Printed electronics

2.8.1 Introduction

Traditionally, photolithography is widely used for the fabrication of small, high resolution electronic components, however the equipment and materials used can be costly and time consuming. It is therefore advisable to evaluate alternatives to this method that would be suitable for printing on a bulk scale. There are a number of other printing techniques currently available.

Printed electronics refers to a group of printing methods utilised to fabricate small electrical devices, from circuits to individual components such as transistors and diodes. A number of different printing methods are available such as inkjet printing and screen printing. The versatility and variability of substrates and materials within the field of printed electronics affords many promising technological advances. Printed electronics are currently in use for a number of applications, these include: radio frequency identification (RFID) tags, where printed electronics allow for ultra-low cost tags that are used to track consumer goods amongst other purposes (Subramanian et al., 2005); printed transistors (Yan et al., 2009); printed sensors (Unander and Nilsson, 2009); and printed dielectrics (Mengel and Nikitin, 2010). Increasing interest has been given to printed electronics in recent years with an emphasis on more cost effective, environmentally friendly methods of fabricating electronic components.
2.8.2 Printing methods

2.8.2.1 Screen printing

Screen printing is a technique whereby ink is transferred onto a substrate through a wire mesh except in the areas protected by a blocking stencil (Figure 2.29). A blade is run along the surface of the mesh, filling the apertures with ink. A reverse stroke is then employed to cause the screen to make contact with the substrate and transfer the ink to the substrate. Printing can be done on a large range of materials such as plastics and fabrics meaning lower cost substrates can be used, however the feature sizes produced are greater than 75µm (Bao, 2000) making them inappropriate for small sensor devices such as the electrodes fabricated in this thesis. In addition to large feature sizes, replacement screens are required for each new pattern.

![Figure 2.29 Schematic of a screen printer showing working components and ink placement on substrate](image)

2.8.2.2 Flexographic printing

Flexographic printing involves the use of a number of different printing units, each representing a different ink type or colour. The substrate is fed into the press from
the first roll where it is then pulled through the different units (Figure 2.30). Each unit contains a printing plate, consisting of the pattern to be printed as the raised portion of the plate. These raised portions are coated in the ink which is transferred to the substrate when it is brought into contact in order for the pattern to be changed. The printing plate needs to be physically changed or altered. Flexographic equipment is low cost with fast drying ink. However, the feature size is too large for that required by IDT printing at greater than 80µm (Caironi and Noh, 2015).

![Figure 2.30 Schematic of a Flexograph](image)

2.8.2.3 Gravure printing

In the case of gravure printing, a plate or roller is first etched with the desired design with the recessed parts making up the image (Figure 2.31). These recesses are then filled with ink, whilst the rest of the surface is kept free from ink. The substrate is then pressed onto the plate where the image is then transferred. Advantageously, gravure printing is high speed, allowing for a large number of patterns to printed relatively quickly on a large range of different substrates however the equipment is
expensive and feature size is equal to that of screen printing at above 75µm (Caironi and Noh, 2015)

2.8.2.4 Pad printing

The pad printing process involves the transfer of an image from the cliché to a substrate via a pad. Initially, the image on the cliché is inked through a doctor blade process, where the pad then picks up the inked image. The pad moves to the substrate, where it makes contact and the image is transferred (Figure 2.32). Pad printing can be used on a large range of substrates with low equipment costs. Feature sizes however, are 100µm and above (Bansal and Boccaccini, 2012). In addition to this, pads must be replaced each time a new pattern is required.
2.8.3.5 Inkjet printing

Inkjet printing technology allows for significant cost reduction in printed electronic fabrication (Hayes et al., 2002). It is a non-contact process, allowing for ink to be printed only in desired locations with minimal fabrication steps (Davison, 2011). The technology itself is classified into two main categories, continuous inkjet printing and drop-on-demand printing.

2.8.3.5.1 Continuous Inkjet Printing

Continuous inkjet printing (CIP) involves the use of a high pressure pump, forcing the ink through an outlet. The continuous stream of ink is then broken into droplets through the vibrations of a piezoelectric crystal with droplets then being deposited on the surface of the substrate (Figure 2.33). Droplet deposition is controlled by the charge of both the ink itself, the charging electrode and the deflection electrodes (Martin et al., 2008). The droplet dimensions in continuous printing are typically
double that of the orifice diameter. An advantage of CIP over Drop-on-demand printing is the faster print speed (Wang & Derby, 2005).

![Diagram of continuous inkjet printer equipment]

**Figure 2.33** Schematic of continuous inkjet printer equipment

### 2.8.3.5.2 Drop-on Demand Inkjet Printing

Two types of drop-on-demand (DOD) inkjet printing exist (Figure 2.34). The first, thermal printing is achieved when a pulse of current is passed through the heating element causing a large pressure increase on vapourisation of the ink. This pressure increase causes a droplet to be propelled from the nozzle to the substrate. Piezoelectric printing works similarly, with a pulse of voltage being utilised. In this case, the change in voltage causes the piezoelectric material to change shape which generates a pressure pulse through the liquid, which subsequently propels a droplet from the nozzle (Bansal and Bocaccini, 2012).
The thermal and piezoelectric methods both have advantages and disadvantages dependant on their application. Thermal printheads are typically lower cost however the usage life is often shorter as a result of temperature damaged, in addition to limitations on materials that can be used as inks due to the temperature. Piezoelectric printheads offer a wider range of inks and a longer usage life. However, as a result, they are more expensive.

2.8.3 Comparison of techniques

A number of advantages and disadvantages have been identified for each of the printing methods above, making them suitable to different applications.

The low cost and ease of changing patterns makes inkjet printing well suited to the creation of electrode structures and thus shall be carried forward as a potential fabrication method for this thesis.
2.9 Materials

2.9.1 Introduction

Presented in this work are steps for the fabrication of interdigitated electrode structures. These structures allow nanoparticles to be monitored through the detection of impedance changes. In the case of these structures, it is known that the changes in the part of the structure that is between the electrodes result in the largest changes in electrical impedance (Terzic et al., 2012). As a result of this, the trapping layer and trapped particles will have the most influence on the impedance behaviour observed. It is therefore important to understand the impact of different materials on the system.

Based on the discussion of filter types and expected operation conditions, the filter layers required for this work should be designed to be effective for diffusion and/or interception based filtering. For this to be effective the filter should be characterised by small diameter fibres for diffusion.

Types of suitable structures have been reported in literature, with distinctly different structures. Sponge-like porous scaffold structures can be produced using sacrificial template, with both polymeric and ceramic structures being frequently reported in literature (Studart et al., 2006). In the case of ceramics, a high temperature process is used to burn off the sacrificial template. However, this would be unsuitable for the sensors reported here due to the damage that is liked to be caused to the electrode and substrate structure. Polymeric structures require much lower temperatures (if at
all) to be processed with, polystyrene being a cost effective, durable and water stable candidate material.

Alternative comb like structures, consisting of ZnO have been shown to be produced by low temperature hydrothermal routes that are compatible with substrate and electrode materials.

2.9.2 Trapping Materials

2.9.2.1 Polystyrene

Polystyrene is a water insoluble manmade aromatic polymer consisting of carbon and hydrogen (Figure 2.35). It is one of the mostly commonly used plastics worldwide (Maul et al., 2000). Polystyrene has a relatively low melting point at 240°C. Polystyrene is a non-polar plastic and exhibits good insulating behaviour with volume and surface resistance and dielectric strength being high (Wünsch, 2000). Its relative permittivity is approximately 2.5 between 0.1-1MHz.

![Chemical structure of polystyrene](image)

Figure 2.35 Chemical structure of polystyrene
2.9.2.2 Zinc oxide

Zinc oxide (ZnO) is a water insoluble, inorganic material which occurs naturally, however the main bulk of ZnO is manmade (Völz et al., 2000). The compound has many different applications including thin film transistors, laser diodes and photodetectors. Zinc oxide is known as a wide band gap semi-conductor, with the wide band gap permitting devices to work at higher frequencies, voltages and temperatures compared to other semi-conductors (U.S Department of Energy., 2013). ZnO is a polar crystalline structure (Figure 2.36). The relative permittivity of the compound is 8.5 and when undoped, ZnO exhibits insulating characteristics.

Figure 2.36 Crystalline wurtzite structure of zinc oxide (Niskanen et al., 2013)
2.9.3 Arizona Road Dust and its constituents

Arizona Road Dust (ARD) is a standardised test dust (ISO 12103-1) used for testing filtration throughout industry. However, the dust itself is made of a number of different materials (Table 2.7) in varying concentrations.

In this case, it is important to consider the dielectric properties of all the materials in the sample and, by taking the weighted average (by volume) of the individual permittivities of each of the components, the effective permittivity of the composite can be calculated ($\varepsilon_r = 4.9$).

Table 2.7 Composition of Arizona Road Dust standard test material (Powder Technology Inc, MSDS, 2014)

<table>
<thead>
<tr>
<th>Material</th>
<th>Typical Concentration (vol %)</th>
<th>Relative Permittivity($\varepsilon_r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide</td>
<td>68 – 76</td>
<td>3.9</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>10 – 15</td>
<td>9.1</td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>2 – 5</td>
<td>13.1</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>2 – 5</td>
<td>11.8</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>2 – 5</td>
<td>4.64</td>
</tr>
<tr>
<td>Sodium oxide</td>
<td>2 – 4</td>
<td>Not found</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>1 – 2</td>
<td>9.8</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>0.5 - 1</td>
<td>86</td>
</tr>
</tbody>
</table>

2.9.4 Relative permittivity

The permittivity of a material describes the degree to which it can be polarised on an electric field. The relative permittivity provides a measure of how much greater that degree of polarisation is with respect to a vacuum. When incorporated into a capacitor a material with a relative permittivity of 10 would allow the capacitor to store 10
times as much charge as an identically sized capacitor with nothing between the electrodes.

The resulting capacitance can be expressed by the following equation;

\[
C = \frac{\varepsilon_0 A \varepsilon}{D}
\]

Equation 2.27

where \( \varepsilon \) is the permittivity of the material, \( \varepsilon_0 \) is the permittivity of a vacuum (Figure 2.37), \( A \) is the area of the electrode surface and \( D \) is the distance between the electrodes (Figure 2.38).

![Vacuum Permittivity (\( \varepsilon_0 \))](image1)

![Material Permittivity (\( \varepsilon \))](image2)

Figure 2.37 Illustration of the permittivities of a vacuum and a material in a capacitor

![Illustration of a parallel plate capacitor](image3)

Figure 2.38 Illustration of a parallel plate capacitor
2.9.5 Impedance

Impedance is the alternating current analogy of resistance in a direct current electrical circuit and describes the resistance of a material to the flow of current through it. It consists of two phenomena: resistance and reactance.

Resistance is a measure of the resistance to the flow of electrons, with a low resistance material being one where electrons are able to flow easily, e.g. Copper.

Reactance describes the extent to which the material is able to store and release electrical energy as current changes in the AC circuit. Reactance is only observed for AC and not DC. Where energy is stored in the form of an electric field (e.g. in a dielectric capacitor) reactance is negative.

\[ Z = R - jX_c = R - \frac{j}{2\pi fC} \]  \hspace{1cm} \text{Equation 2.28}

Where \( X_c \) is the inductive reactance (\( \Omega \)), \( f \), the frequency and \( C \), capacitance.

While \( R \) is independent of frequency, \( X_c \) is a function of test frequency and capacitance of the capacitor.

It follows that in a purely capacitive system, with no electrical conductivity the impedance is given by;

\[ Z = \frac{j}{2\pi fC} \]
However, in real materials a degree of conduction does exist, such that impedance is given by:

\[ Z = R + \frac{j}{2\pi fC} \]

For the materials studied in this work DC resistivity is negligible, such that only capacitance need be considered. In these cases, the voltage and current are 90° out of phase with the current preceding voltage. Conversely, in a purely resistive system current and voltage are in phase.
Chapter 3 Experimental procedures

3.1 Introduction

The following Chapter describes the generic experimental procedures carried out throughout this project. Firstly, the fabrication of electrode structures by photolithography and inkjet printing is reported before presenting the fabrication methods used for particle trapping layers. The second section of this Chapter will illustrate exposure testing methods used to determine sensor suitability. The final section of this Chapter details the methods employed for characterisation of the sensing devices and their individual components.

3.2 Electrode fabrication

3.2.1 Photolithographic process

Patterned electrodes were deposited by a photolithographic lift-off technique. Mask templates were designed using computer aided design (CAD) software (AutoCAD
Chapter 3 Experimental procedures

2014, Autodesk Inc., U.S.). The pattern was designed for 40 x 40 mm$^2$ glass substrates.

A chrome photo mask was produced by Delta Mask BV, NL.

Microscope slides (75 x 25 mm, Fisher Scientific, UK) were cleaned with isopropyl alcohol (Fisher Scientific, UK, 99.5%) and acetone (Sigma Aldrich, UK, ≥99.8%) and subsequently plasma etched (Auto 306, Edwards, UK) for 3 minutes (Ar, 150 Watts) prior to the experimental procedure. Substrates were then processed according to the process illustrated in Figure 3.1.

Figure 3.1 Scheme of fabrication procedure for interdigitated electrode fabrication using photolithography

LOR 2A negative photoresist (Microchemicals, DE) was spun (3000 rpm, 45 seconds) onto the surface of each microscope slide producing a 10 μm thick layer of resist. The slides were subsequently baked on a hotplate for 5 minutes at 150°C. S1818 positive
photoresist (Microchemicals, DE) was spun over the slides (4000rpm, 45 seconds) which were then baked on a hotplate for 90 seconds at 115°C. The slides were then patterned using the chrome photomask and exposed to UV light (100mJ/cm²) with a mask aligner (Karl Suss MA56). After exposure, the photoresist was developed in MF319 developer (Microchemicals, DE) for 20 seconds before being washed in water. Patterned slides were plasma etched for 3 minutes (Argon, 50 watt) prior to deposition of conductive materials. All samples were sputter coated (Auto 306, Edwards, UK) first with a chrome layer (50nm), followed by a gold coating (Agar Scientific UK, 139nm). Samples were then washed in acetone to remove photoresist and any gold deposited on top of it until only the pattern remained.

3.2.2 Inkjet printing process

Interdigitated electrodes (IDT) were fabricated by printing silver nanoparticle ink (Sigma Aldrich, UK, <150nm, 20 wt. %) onto silicon wafers using a Dimatix Inkjet printer (DMP-2800, Fujifilm, U.S.). Ink temperature at the time of printing was 30°C, with a substrate temperature of 60°C in order to ensure optimal wetting characteristics and smooth electrodes. Electrodes were cured on a hotplate at 150°C for 10 minutes before being left to cool to room temperature. Each device was cleaned with isopropyl alcohol after cooling.


3.3 Trapping layer fabrication

3.3.1 Zinc oxide trapping structures

During fabrication (see Chapter 4), a seed layer was first deposited on the surface of the silicon wafer using zinc acetate dihydrate (0.005M, Sigma Aldrich, UK, ≥99.8%) in ethanol (Sigma Aldrich, UK, ≥99.8%). Droplets of the solution were added to the surface of each wafer until the surface was covered evenly. The film was allowed to dry for ten seconds in atmosphere before being blown with nitrogen gas until completely dry. The process was repeated 5 times. Samples were then heated for 25 mins at 350°C using a hotplate. This process was repeated three times.

After deposition of the seed layer, ZnO nanorods were grown via hydrothermal decomposition of zinc nitrate hexahydrate (Sigma Aldrich, UK, 98%, Zn(NO$_3$)$_2$·6H$_2$O) and hexamethylenediamine (Sigma Aldrich, UK, ≥99%, C$_6$H$_{12}$N$_4$) reagents (Equation 3.1 to Equation 3.3) (Breedon et al., 2008). An equimolar solution of the reagents was prepared with deionised water. Substrates were then submersed and heated in the solution for 2.5 hours at 90°C in a fan oven to allow for zinc oxide nanorod growth. After heating, samples were removed from the oven and allowed to cool to room temperature. Samples were then gently washed with deionised water and dried with nitrogen gas.
Hydrothermal decomposition

\[
C_6H_{12}N_4 + 6H_2O \xrightarrow{\text{heat}} 6CH_2O + 4NH_3
\]  
\text{Equation 3.1}

\[\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-\]

Metal origin

\[\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{Zn}^{2+} + 2\text{NO}_3^-\]
\text{Equation 3.2}

Zinc oxide deposition

\[\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2\]
\text{Equation 3.3}

\[\text{Zn(OH)}_2 \xrightarrow{\text{heat}} \text{ZnO} + \text{H}_2\text{O}\]

3.3.2 Polystyrene

Polystyrene trapping layers (Chapter 4) were fabricated using a sacrificial template technique. Polystyrene (molecular weight approximately 192,000, Sigma Aldrich, UK) and sodium chloride (Sigma Aldrich, UK, ≥99%) were added in varying amounts to butanone (Sigma Aldrich UK, ≥99.7%, 100ml) in a sealed container and ball milled for 48 hours. Pieces of silicon wafer (3 x 1 cm, Si-Mat, Germany) were washed with acetone and isopropyl alcohol prior to deposition of the trapping layer. The silicon wafers were placed on a hotplate at 70°C, droplets of the salt loaded polystyrene solutions were deposited on the wafers until the surface was covered. Once the butanone was evaporated, the wafers were removed from the hotplate and allowed to
cool to room temperature. Samples were then gently washed in distilled water in order to dissolve the sodium chloride revealing a highly porous polystyrene layer.

3.4 Exposure testing

3.4.1 Wind tunnel exposure

For the purpose of observing electrode response to particulate exposure, samples were tested in an industrial wind tunnel (Casella Measurement, Bedford, UK) (Figure 3.2). Untreated pieces of silicon wafer substrate (3x1cm) were exposed in a wind tunnel to Arizona Road Dust (ARD; ISO-12103-1, particle size 1-80µm; Particle Technology Ltd, Derbyshire, UK, see Appendix 1 for composition and size distribution) for periods of 0, 2, 5 or 10 minutes, at a wind velocity of 1.7m/s and an airborne particle density of 9.07mg/m³ for comparison purposes. Wafers were placed horizontally relative to the airflow.

![Wind Tunnel Diagram](image)

Figure 3.2 Schematic illustrating experimental set-up for wind tunnel exposure
IDT structures were exposed to ARD by placing them in the wind tunnel under identical conditions. Samples were exposed for a maximum duration of 10 minutes. Impedance and phase measurements were taken at 500 kHz at 30 second intervals using an impedance analyser (HP4192A, Hewlett Packard, US) recorded onto Microsoft Excel.

3.4.2 Nanoparticle exposure

In order to avoid the use of airborne nanomaterials, limiting exposure, trapping layers were exposed to titania particles (TiO$_2$, Sigma Aldrich UK, 0.15µg/ml, 20-200nm) suspended in water. Titania suspension (2.5ml) was passed across the surface of the trapping layer coated wafer at 2.5ml/hr and collected for particle size distribution analysis, as per the experimental set-up illustrated in Figure 3.3. Trapping layers were each exposed three times using virgin titania suspensions.

![Figure 3.3 Schematic illustrating the experimental set-up for filter testing](image-url)
3.5 Characterisation

3.5.1 Scanning electron microscopy and energy dispersive X-ray spectroscopy

3.5.1.1 Microscopy

Scanning electron microscopy was employed for structural examination at both micro and nanoscale. JEOL-7100F (JEOL, US) and FEI-XL30 SFEG (Philips, NL) microscopes were used to conduct studies in secondary electrode mode with a 5-15keV electron beam. Non-conductive samples were prepared by sputter coating with gold (Edwards S150B coating unit; 3nm coating, Edwards, UK) to prevent sample charging. The energy dispersive X-ray spectrocope (EDX) attached to the JEOL-7100F was used for elemental characterisation of samples.

3.5.1.2 Particle density analysis

SEM micrographs were analysed to determine the number of retained particles using ImageJ software (Version 1.49, National Institute of Health, US). Six areas of 4000 x 4000µm were used for each sample and averaged.

3.5.2 Particle size distribution analysis

Particle size distribution analysis was carried out using a Nanosizer LM10 (Malvern, UK). Samples were injected into the instrument, where 3x60 second video clips were recorded for each injected sample for particle detection through dynamic light
scattering. The procedure was repeated 4 times for each of the samples obtained and an averaged result was used for further analysis.

3.6 Summary

This Chapter has detailed the processes, methods and characterisation techniques that will be used to fabricate and characterise the devices made in the next chapter (Chapter 4).
Chapter 4 Design and fabrication of the device

4.1 Introduction

Sensing devices, developed as part of this thesis, consist of an interdigitated electrode array (Figure 4.1) for measuring the change in permittivity as particles become held in a surrounding trapping layer. In order to determine the optimum sensor design, a number of parameters such as electrode gap width and electrode size were modelled to determine their impact on the sensing capability of the device.

![Figure 4.1 Schematic of an interdigitated electrode array](image)

Interdigitated electrodes were then fabricated utilising two approaches described below; a photolithographic lift-off process, and an inkjet printing method. To evaluate the role of particle retention in sensing, two filtration layer materials, zinc oxide
nanorods and porous polystyrene, were compared. This chapter reviews the electrode and trapping layers produced.

4.2 Operational parameters affecting sensor behaviour

4.2.1 Impedance behaviour of non-exposed devices

As stated in Chapter 2, the impedance of a device can be calculated using a measured capacitance term. In order to calculate the capacitance ($C_s$) term for an IDT, the following was used (Webster et al., 2009):

$$C_s = (N - 1)L\varepsilon_0\varepsilon_r \frac{K[(1 - k^2)^{1/2}]}{2K(k)}$$  \hspace{1cm} \text{Equation 4.1}

where $N$ is the total number of electrode fingers, $L$ is the length of the electrode fingers, $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is the relative permittivity of the media between the electrodes. $K(k)$ is the complete elliptic integral of the first kind (Olthuis et al., 1995);

$$k = \cos\left(\frac{\pi E_w}{2(E_g + E_w)}\right)$$  \hspace{1cm} \text{Equation 4.2}

where $E_w$ is the electrode width, $E_g$ is the electrode gap width and;

$$K(k) = \int_0^1 \frac{dt}{\sqrt{(1 - t^2)(1 - k^2 t^2)^{1/2}}}$$  \hspace{1cm} \text{Equation 4.3}
4.2.2 Effect of electrode dimensions

During fabrication, dimensional variations in electrode gap and electrode width are possible due to the intrinsic nature of printing processes. In order to determine the effect of electrode gap width and electrode width, and their variation, on the responsivity of the sensor, theoretical values of impedance for different dimensions were calculated (Figure 4.2).

![Theoretical impedance between 0 and 0.25 IDT volume fraction as a function of gap width (100 and 500µm) with an electrode width of 400µm](image.png)

Figure 4.2 Theoretical impedance between 0 and 0.25 IDT volume fraction as a function of gap width (100 and 500µm) with an electrode width of 400µm

The model shows that a change in gap width between electrode fingers has a significant impact on the impedance behaviour predicted. Impedance is shown to increase as gap size decreases. In addition to this, smaller gap widths between electrodes have been shown to correlate with an increase in responsivity (Figure 4.3), similar to literature presented by Davidson, 2004 and Laconte et al., 2006, due to an
increase in the number of fingers in the same electrode area, maximising the sampling area.

![Graph showing theoretical responsivity between 0 and 0.25 IDT volume fraction as a function of gap width (100 and 500µm) with an electrode width of 400µm.](image)

**Figure 4.3** Theoretical responsivity between 0 and 0.25 IDT volume fraction as a function of gap width (100 and 500µm) with an electrode width of 400µm

In smaller structures, a similar gap width and particulate size has been shown to allow for detection of singular absorption events on the electrode surface as the proportionate change is larger (Malaquin et al., 2005). The model predicts that responsivity decreases from 40 Ω/Vf to 30 Ω/Vf when going from a gap width of 100µm to 500µm. Electrode widths were also modelled (Figure 4.4 & Figure 4.5).
This modelling suggests that variations in gap width effect smaller electrodes more significantly. With 100µm electrode gap, the initial electrode impedance may vary...
from 34.5Ω to 23Ω at 140µm and 60µm respectively, a difference of 11.5Ω between electrode structures as a result of dimensional differences. At an electrode gap of 400µm, this variation shows only a difference of 2.9Ω between 440µm (9.3Ω) and 360µm (36.4Ω). At 100µm this significant difference in impedance may lead to ambiguity in exposure testing results, as to whether or not the measured difference is due to dimensional differences or particulates.

In contrast to gap width, variation in electrode width has little effect on the impedance predicted, suggesting that impedance is independent of electrode width and only changes as a result of the electrode gap width present.

Predictive modelling of the electrode structures indicates that for a high responsivity, the best design would be one with a small electrode gap width, with no specific constraint for electrode size. However, smaller electrode widths would give more active sensor for a given footprint. Sensitivity should also be higher for a sensor with smaller gaps as a given particle entering the sensor would represent a larger volume fraction.

Small gaps can be realised using photolithography, however, this is expensive and presents difficulties when trying to change the design quickly. Inkjet printing offers an alternative method, allowing designs to be changed quickly and printed cost effectively. As responsivity is not affected to a large extent, inkjet printed electrodes are worthy of study.
4.3 Electrode fabrication

4.3.1 Photolithography

Chromium/gold electrode designs were fabricated on glass slides by using a photolithographic lift off process described in Section 3.1.1. Interdigitated electrodes (Figure 4.6) were fabricated with varying electrode width dimensions between 20µm and 40µm and gap sizes between 2µm and 25µm.

Prior to coating fabricated IDTs were examined under an optical microscope in order to evaluate the effectiveness of the photolithographic lift off process as a manufacturing route. Gold/chromium coating was then deposited according to the method in Section 3.1.1.

Although a small number of good quality electrodes were produced (Figure 4.7), a significant number of them displayed a lack of adhesion between the glass substrate...
and the chromium/gold coating, resulting in a peeling effect and loss of pattern (Figure 4.8).

![Image of microelectrodes](image)

**Figure 4.7** Example of chromium/gold microelectrodes on the surface of a glass substrate with an electrode width of 50µm and gap width of 5µm

![Image of faulty electrodes](image)

**Figure 4.8** Examples of faulty chromium/gold electrodes on glass substrate surface examined under an optical microscope where A) shows broken electrode structures and B) shows increased magnification sample of the peeling effect after coating

In order to combat the poor adhesion to the substrate, silicon wafers were used as an alternative substrate. Better adhesion was observed between coated electrodes and the silicon wafer surface with quality being more consistent (Figure 4.9).
In addition to better adhesion, smaller feature sizes were obtained when silicon wafers were used as a substitute. This is most likely due to the manufacturing process itself as the opaque nature of the wafers prevented the resist from absorbing additional UV light during processing contrary to the glass slides which both reflected and transmitted UV light leading to a poor quality pattern. An overview of the designs on a wafer is illustrated in Figure 4.10.

Figure 4.9 Example of chromium/gold interdigitated electrodes deposited onto a silicon wafer substrate.

Figure 4.10 Chromium/gold coated electrodes on silicon wafer substrate with electrode width dimensions between 20µm and 40µm and electrode sizes between 2µm and 25µm with each of the numbers corresponding to different dimensional layouts.
4.3.2 Inkjet printing

Using the same geometry as Section 4.2.1, IDT designs were fabricated by using an inkjet printing method (described in Section 3.2.2) onto silicon wafers, using silver nanoparticle conductive ink, with subsequent sintering. The electrodes produced had electrode gaps between 200-500µm and electrode widths between 200-500µm.

The fabricated electrodes were shown to exhibit unbroken electrode patterns (Figure 4.11). However, when observed under higher magnifications, differences in electrode width were observed due to manufacturing variances in dimensions (Figure 4.12). The predictive modelling chapter of this thesis (Section 6.2.5) presents an evaluation of the potential effects on measurement reliability of the observed variations in the manufacturing process.

Figure 4.11 Photograph of example inkjet printed microelectrodes. Design shows an electrode gap size of 400µm and electrode width of 400µm
After fabrication, samples of more than ±15% dimensional difference from the expected values of 400μm gap width and 400μm electrode width were rejected due to the changes observed in impedance (shown in Section 6.2.5) and the potential for unreliable measurement data. This threshold for process control was determined as a result of initial sensor impedance differences observed.

4.3.3 Comparison of fabrication techniques

A number of advantages and disadvantages have been observed with each of the processes examined for electrode fabrication (Table 4.1). The photolithographic process produces small electrode sizes down to 2μm, however consistency was shown
to be an issue. In addition to this, whilst many devices could be fabricated together using photolithography, the process itself was time consuming. Equipment considerations must also be taken into account with the cost of fabrication and of the processing of materials.

Table 4.1 Comparison of photolithographic and inkjet printing electrode fabrication processes

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolithography</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>Allows for bulk fabrication Small feature sizes</td>
<td>Expensive process and equipment</td>
</tr>
<tr>
<td>Glass Substrate</td>
<td>Low cost substrate</td>
<td>Quality continuity problems with peeling very common on smaller features</td>
</tr>
<tr>
<td>Silicon Substrate</td>
<td>Allows for smaller feature sizes than glass</td>
<td>Expensive substrate Peeling still occurs although significantly less on glass</td>
</tr>
<tr>
<td>Inkjet Printing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>Cheaper materials than photolithography</td>
<td>Larger feature sizes than photolithography Bulk scale still an option but slower than photolithography</td>
</tr>
<tr>
<td>Glass Substrate</td>
<td>Low cost substrate</td>
<td>Ink spreading problem, wetting properties not suitable. Patterns do not hold shape.</td>
</tr>
<tr>
<td>Silicon Substrate</td>
<td>Wetting properties significantly better than that of glass</td>
<td>Expensive substrate Some spreading of ink still occurs but less than 15% difference between expected and actual dimensions observed.</td>
</tr>
</tbody>
</table>

Inkjet printing offers a more cost effective method when compared to photolithography, with both materials and equipment lower in cost. Inkjet printing also offers bulk scale processing, although the final stages are slower than that of the
photolithographic process examined. A disadvantage in the case of printing is the inability to produce feature sizes below 10µm compared with those of the photolithographic process. Small dimensions are advantageous because size is related to sensitivity with smaller electrode gaps having been shown to have higher sensitivity (Tamaki et al., 2005). The quality of printing is higher in the case of inkjet printing. Due to higher process reliability, ease of fabrication, low cost of manufacture and potential to print onto low cost polymer substrates, inkjet printing was selected as the preferred manufacturing technique.

4.3.4 Evaluation of electrode fabrication

In order to verify model assumptions, the impedance of manufactured electrodes (Table 4.2) were measured for initial sensor impedance and then compared with predicted values calculated based on the average electrode gap and width observed (Figure 4.13). Comparison of theoretical and experimental values suggests that the model shows reasonable agreement with experimental values.

Table 4.2 Observed average dimensions of six different IDTs of nominal widths of 400µm for both gap size electrode width where n=6, with light microscope analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average electrode width (µm)/ ±Std dev</th>
<th>Average electrode gap (µm)/ ±Std dev</th>
<th>Measured Z(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>439(±3.6)</td>
<td>357(±4.7)</td>
<td>37.3</td>
</tr>
<tr>
<td>B</td>
<td>430(±9.7)</td>
<td>367(±9)</td>
<td>35.9</td>
</tr>
<tr>
<td>C</td>
<td>437(±4)</td>
<td>361(±4.8)</td>
<td>35.2</td>
</tr>
<tr>
<td>D</td>
<td>442(±2.4)</td>
<td>358(±3.3)</td>
<td>34.6</td>
</tr>
<tr>
<td>E</td>
<td>441(±1.2)</td>
<td>359(±1.2)</td>
<td>34.8</td>
</tr>
<tr>
<td>F</td>
<td>441(±1)</td>
<td>359(±1.4)</td>
<td>33.7</td>
</tr>
</tbody>
</table>
Figure 4.13 Comparison of initial impedance values for theoretical and experimental data at 0.5MHz. Impedance of IDTs with nominal electrode dimensions of 400µm electrode and gap width is shown by the solid red reference line. The dashed line shows where theoretical and experimental data are equal. Error bars represent standard deviations of experimental data.

Sample A (Electrode width 439µm and gap width 357µm) is shown to be an outlier. After further microscopic analysis, damage was found to the structure of the electrodes which may have caused the difference in initial impedance observed (Figure 4.14). All other electrodes showed good correlation between the predicted and experimental data.
The variation in electrode width and gap dimensions can also be observed within individual samples with electrode finger structures changing in dimension throughout their length. However, variation within the structure shows much smaller variance suggesting it is unlikely that impedance behaviour will be affected. Results have demonstrated that gap width is an important factor in choosing the optimum dimensions for electrode fabrication. However, a compromise must be made between attainable responsivity and reliability of results, with the model results indicating that smaller electrode dimensions allow for higher responsivity but they are also more susceptible to the impact of dimensional changes arising during manufacturing. At target dimensions of 400µm for both electrode width and gap, it has been observed that, although there are differences in dimension after fabrication, these differences
do not result in significant differences in the observed values of impedance and there is a good agreement between theoretical and measured impedance values.

4.3 Filter layer fabrication

4.3.1 Fabrication parameters

In order to design a suitable filter layer, parameters such as pore volume fraction, pore diameter ($D_p$), layer height ($H$) and uniformity must be taken into account (Figure 4.15). In the case of pore diameter, pores must be of adequate size to allow for nanoparticulate entry but must be small enough to filter out larger particle sizes (discussed in Section 2.7). In the case of a capillary type system, pores larger than the intended particle size range at the surface would allow for the translocation of particles throughout the layer, with smaller particles reaching the electric field or detection area closer to the electrode structures. The height of the trapping layer should be greater than half the gap width of the electrodes (Figure 4.15), which is the assumed height of the detection area or electric field height in order to prevent larger particulates at the surface being simultaneously detected with small particles within the structure.
The uniformity of the coating must also be considered, as non-uniform layers would result in some electrodes being coated with the trapping layer while others may not be coated. In addition, it is possible that larger particles may become trapped between the patches of trapping material, which would result in the detection and measurement of non-nanoscale particulates (Figure 4.16).

Figure 4.15 Important parameters for consideration on design of a filter layer where G is the electrode gap width (A), \( D_P \) is pore diameter, \( H \) is trapping layer height (B).

Figure 4.16 Illustration of plan view of a non-uniform filter layer and it’s trapping problems, showing (A) electrode gaps without uniform layer (B) large particulate trapping between clusters.
4.3.2 Zinc oxide

4.3.2.1 Porosity and uniformity

Zinc oxide nanorod trapping layers were grown according to the method detailed in Section 3.3.1. Layers were grown using different concentrations of equimolar growth solutions in order to prepare a range of porosities (Table 4.3), these were 8.3mM, 12.5mM, 16.7mM and 21.0mM (Table 4.3). Developed layers were observed using SEM (Figure 4.17).

Table 4.3 Zinc oxide nanorod preparations detailing concentrations of growth solution

<table>
<thead>
<tr>
<th>Final Concentration (mM) (Seed Layer Y/N)</th>
<th>Concentrations of solution constituents (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zinc Nitrate</td>
</tr>
<tr>
<td>8.3 (Y)</td>
<td>0.1</td>
</tr>
<tr>
<td>12.5 (Y)</td>
<td>0.15</td>
</tr>
<tr>
<td>16.7 (Y)</td>
<td>0.2</td>
</tr>
<tr>
<td>21.0 (Y)</td>
<td>0.25</td>
</tr>
<tr>
<td>8.3 (N)</td>
<td>0.1</td>
</tr>
<tr>
<td>12.5 (N)</td>
<td>0.15</td>
</tr>
<tr>
<td>16.7 (N)</td>
<td>0.2</td>
</tr>
<tr>
<td>21.0 (N)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Without the use of a seed layer, nanorods were not observed to have grown on the silicon wafer.
Films made using solutions of 16.7 and 21mM ZnO (Figure 4.17; C&D) revealed very few gaps between the rods suggesting that their filtering ability would be hindered and that the majority of particulates would not penetrate into the filter layer. The 8.3mM solution (Figure 4.17; A) concentration showed a sparsely covered substrate; it is unlikely that this rod distribution would provide an adequate filter layer due to the sparsity of nanorods on the substrate and the problems associated with non-uniformity as discussed. Films produced using 12.5 mM growth solution (Figure 4.17; B) exhibit both gaps and uniformity suggesting that this may be a suitable concentration for the filter fabrication. Further characterisation was carried out on each of the samples with the size distribution of gaps between the rods being measured in order to determine filter suitability (Figure 4.18).

Figure 4.17 Micrographs showing zinc oxide growth using growth solution concentrations of (A) 8.3mM (B) 12.5 mM (C) 16.7 mM and (D) 21 mM with zinc acetate seed layer on silicon wafer substrate, grown for 2.5 hours.
Figure 4.18 Distribution of nearest neighbour separation between zinc oxide nanorods grown in A) 8.3mM B) 12.5mM C) 16.7mM and D) 21mM growth solutions
Measurements of nearest neighbour separations (edge to edge) on the films showed that concentrations of 21mM and 16.7mM are mostly continuous layers with occasional gaps observed. At the highest concentration of 21mM, 100% of the gaps measured are in the nanoscale range (<100nm) (Figure 4.18; D). However 50% of these gaps were below 40nm and none of the gaps measured reached over 60nm, meaning almost 50% of the nanoscale size particles, those within the range of 50-100nm, would be unable to penetrate the layer. At 16.7mM (Figure 4.18; C), 100% of the gaps measured are within the nanoscale range, 50% of these are between 40 to 80nm. A larger range is covered at this synthesis concentration, however nanoparticles between 80 to 100nm would still be unable to penetrate the layer.

Synthesis at 12.5mM concentration (Figure 4.18; B) results in zinc oxide nanorods which show a significantly different size distribution with 50% of the gaps lying between 90 to 150nm. This film would cover the entire nanoscale range, however larger particulates above 100nm may also penetrate the layer. This may not cause a significant difference in results as many of the nanorods are not perpendicular to the wafer surface suggesting gap size changes with increasing depth into the filter layer, in this case larger particulates may not reach the depth required to be detected by the electrode structures below.

Using films made with 8.3mM (Figure 4.18; A) solutions the distance distribution of the rods reaches a maximum figure of 197nm with 50% of the gaps being larger than 150nm. As can be seen on the micrographs observations (Figure 4.17) it is likely that
this concentration results in too sparse a layer which would be inefficient for particle trapping with larger particulates also being retained within the layer. Particles smaller than the minimum gap sizes reported would be expected to be captured by the various filtering mechanisms discussed in Section 2.7.2.

Table 4.4 Summary of the nearest neighbour distribution measurements for zinc oxide nanorod concentrations grown using different growth solution concentrations

<table>
<thead>
<tr>
<th>Film concentration</th>
<th>Maximum Gap Size (nm)</th>
<th>Minimum Gap Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3mM</td>
<td>197</td>
<td>62</td>
</tr>
<tr>
<td>12.5mM</td>
<td>175</td>
<td>6</td>
</tr>
<tr>
<td>16.7mM</td>
<td>85</td>
<td>22</td>
</tr>
<tr>
<td>21.0mM</td>
<td>59</td>
<td>11</td>
</tr>
</tbody>
</table>

4.3.2.2 Thickness

In order to determine the thickness of zinc oxide nanorod layers, cross sections of samples were examined with SEM (Figure 4.19).

![SEM cross section micrograph of zinc oxide nanorod structures](image)

Figure 4.19 Example SEM cross section micrograph of zinc oxide nanorod structures
SEM characterisation of zinc oxide nanorod growth demonstrated that the density of nanorods changed as a function of growth concentration. An average layer height was calculated to be 304nm. This suggests that all captured particles will be within the detection volume of the electrodes beneath estimated at 200µm. Due to the small height of the trapping layer, with respect to the estimated detection volume, it is likely that larger particles on the surface of the ZnO would also be detected. So while the trapping layer would prevent the removal of previously detected materials, it may not be effective for size selection purposes. The maximum height of ZnO nanorods is limited by growth kinetics. Due to the restricted height of this ZnO trapping layer, an alternative trapping structure was explored.

4.3.3 Polystyrene trapping layer

4.3.3.1 Porosity and uniformity

Polystyrene filters were deposited according to the method detailed in Section 3.3.2. Layers were deposited using different concentrations of polymer and sodium chloride (NaCl) in order to prepare a range of porosities (Table 4.5).
Table 4.5 Composition of polystyrene-NaCl mixes in 100ml butanone used to create polystyrene trapping layers and the resultant porosity.

<table>
<thead>
<tr>
<th>Constituents in Butanone (100ml)</th>
<th>Polystyrene (%w/v)</th>
<th>NaCl (%w/v)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>10</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>25</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>50</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>75</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>10</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>25</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>50</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>75</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>25</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>50</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>75</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>10</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>25</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>50</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>75</td>
<td>92</td>
<td></td>
</tr>
</tbody>
</table>

High NaCl concentrations (75%w/v) resulted in no porous structures being identified after the evaporation of butanone, the resultant layers crumbled immediately after cooling as the polystyrene was unable to form a sufficiently strong continuous network (Figure 4.20; A-D). Increasing the percentage of polystyrene resulted in a few smaller lumps of polystyrene/NaCl mix forming at 94% and 92% porosity, however a continuous film was not formed.

At 50%w/v NaCl porous structures were observed at all concentrations of polystyrene, (Figure 4.21).
Chapter 4 Fabrication of the device

Figure 4.20 Structures at 75%w/v NaCl with (A) 96% porosity; 1.5%w/v polystyrene (B) 95% porosity; 2%w/v polystyrene (C) 94% porosity; 2.5% w/v polystyrene and (D) 92% porosity; 3%w/v polystyrene structures

Figure 4.21 Structures at 50%w/v NaCl with (A) 94% porosity; 1.5%w/v polystyrene (B) 92% porosity; 2% w/v polystyrene (C) 91% porosity; 2.5% w/v polystyrene and (D) 89% porosity; 3%w/v polystyrene structures
At lower concentrations of 1.5-2% w/v polystyrene, a non-uniform distribution of the layer was observed with patches forming randomly across the substrate surface (Figure 4.21; A-B). At 2.5% w/v polystyrene a uniform structure was observed, however patches of silicon were still visible (Figure 4.21; C). As with the ZnO nanorods, the non-uniform distribution of the layer may result in non size specific trapping of particles, with either some electrodes having no layer or with larger particles being trapped between the patches affecting measurements. A 3% w/v polystyrene provided a uniform layer with an even distribution of polystyrene across suggesting that it would provide even coverage across the electrodes and avoid the patches as discussed in Section 4.3.1 (Figure 4.21; D).

At 25 %w/v of NaCl surface pores were observed, however, there were very few open pores with the majority of the structure being smooth and closed (Figure 4.22; A-D). Increasing the volume of polystyrene further decreased the amount of pores.

The lowest concentration of NaCl (10 %w/v) (Figure 4.23) resulted in small clusters of the porous polystyrene layer, randomly located on the surface of the silicon suggesting that particulates could not be trapped using this layer. Increasing the polystyrene concentration resulted in a smooth film across the surface of the substrate with no pores.
In order to further examine the suitability of this layer, the size distribution of the pores was measured for 94-89% porosity structures of polystyrene made with 50 w/v% of NaCl (Figure 4.24).

**Figure 4.22** Structures at 25% w/v NaCl with (A) 89% porosity; 1.5% w/v polystyrene (B) 86% porosity; 2% w/v polystyrene (C) 83% porosity; 2.5% w/v polystyrene and (D) 80% porosity; 3% w/v polystyrene trapping structures

**Figure 4.23** Structures at 10% w/v NaCl with (a) 66% porosity; 2.5% w/v polystyrene; (b) 62% porosity; 3% w/v polystyrene structures
Figure 4.24 Pore size distribution of polystyrene structures at A) 94%; 1.5% w/v polystyrene, B) 92%; 2% w/v polystyrene C) 91%; 2.5% w/v polystyrene and D) 89%; 3% w/v polystyrene porosities with 50% w/v NaCl.
Measurements of pore separations using SEM micrographs (Table 4.6) demonstrate that at porosities of 94% and 92%, gap sizes ranged from approximately 10µm to 48µm with the majority of pore sizes being greater than 25µm. The observations suggest that, although in the case of a porous membrane larger surface pore sizes are required in order for initial penetration with subsequent diffusion through the layers, in this case the pore sizes may allow for larger particulates outside the nanoscale range to diffuse through the layer. At porosities of 91% and 89% a small range of surface pore sizes can be observed with maximum and minimum sizes for both concentrations of 27µm and 6µm, respectively. In this case these pore sizes would be more suitable for initial penetration of particulates.

Table 4.6 Nearest neighbour distribution measurement summary of polystyrene concentrations

<table>
<thead>
<tr>
<th>Porosity</th>
<th>Minimum Gap Size (µm)</th>
<th>Maximum Gap Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94%</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>92%</td>
<td>16</td>
<td>49</td>
</tr>
<tr>
<td>91%</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td>89%</td>
<td>11</td>
<td>26</td>
</tr>
</tbody>
</table>

Further characterisation was conducted on the 89% porosity polystyrene structures in order to evaluate the structure fabricated (Figure 4.25). Analysis of the micrographs identified channels within the structure, potentially acting as pathways for diffusion of particulates throughout the layer. In addition to this, smaller sized structures below
the surface suggest a suitable filtration structure, with smaller nanoscale particles reaching the electrode structure below (Table 4.7).

![Example SEM cross section micrograph of polystyrene (89% porosity; 50%w/v NaCl; 3%w/v polystyrene)](image)

Table 4.7 Internal structure sizes at 89% porosity polystyrene layers made with 50%w/v NaCl; 3%w/v polystyrene with site numbers illustrated in Figure 4.26.

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>26</td>
</tr>
<tr>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>11</td>
<td>31</td>
</tr>
<tr>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>13</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>34</td>
</tr>
<tr>
<td>15</td>
<td>31</td>
</tr>
</tbody>
</table>
4.3.3.2 Thickness

In order to determine the thickness of polystyrene layers, 3%w/v polystyrene and 50%w/v NaCl (89% porosity) layers were examined using SEM (Figure 4.26).

Figure 4.26 SEM micrograph showing cross section of polystyrene layer with 89% porosity made with 50% w/v NaCl and 3% w/v polystyrene.

SEM characterisation of 89% porosity (3%w/v polystyrene/50%w/v NaCl) layers demonstrate a layer 50µm thick. This measurement suggests, as discussed at the beginning of this chapter, that the height of this layer will be suitable for particulate trapping and that particles captured will be within the detection volume/electric field of the electrodes beneath.

4.4 Summary

Advantages and disadvantages have been considered for each of the filter types and the production processes required to produce them. As discussed in Section 2.7.2, pore size affects the mechanisms through which particulates are filtered by the structure.
A structure with too large a number of pores would lead to decreasing efficiency of interception and diffusion mechanisms, the two mechanisms which at the targeted nanoscale range are most likely to affect filtration efficiency.

The zinc oxide nanorod filter layers were observed to most closely resemble a fibrous filter structure. A simple growth method was used, with materials obtained at low cost. However, the growth method is sensitive to contamination and even small amounts may cause structural changes to the layer. In addition to this, the raw materials themselves have a relatively short shelf life, which, on the bulk scale may add more time to the process.

The polystyrene scaffold was observed to most closely resemble a porous membrane structure. The fabrication process is also simple, with only few steps to consider, again with low cost raw materials. However NaCl can be left behind within the structure after processing leaving the structure with blocked pores, particularly those which may be too deep within the structure to be exposed to water during the washing stage.

Both zinc oxide and polystyrene layers showed porous structures which may be capable of trapping nanoparticulates. Zinc oxide structures provided smaller pore sizes which may influence size selectivity of the layer, in comparison with polystyrene where pore sizes are observed to be in the micron range.
In each case, concentrations were carried forward for further testing. Zinc oxide growth concentrations of 12.5mM and 16.7mM were identified in addition to polystyrene concentrations of 2.5%w/v and 3%w/v with 50%w/v of NaCl.
Chapter 5 Particle interactions with the trapping structure

5.1 Introduction

The following chapter describes the interactions observed between the trapping layers constructed using methods presented in Chapter 3, and particulates in order to explore the layer’s efficiency and suitability as particle trapping method.

5.1.1 Titania test solution

Prior to exposure, the titania (TiO$_2$) solution was filtered through a 200nm Whatmann filter (Fisher Scientific, UK) in order to control the particle size range detected before particle number size distribution analysis was undertaken (Figure 5.2). Particle number size distribution analysis of the stock 0.0015mg/ml titania solution showed a particle size range of 20-210 nm. A slight increase in size above 200nm filter is most probably due to the tendency of nanoparticles to agglomerate quickly (Jiang et al., 2008) or difference in filter size and particle size definitions.
Chapter 5 Particle interactions with the trapping structure

Figure 5.1 Micrograph of titania particles

Figure 5.2 Average particle number size distribution (n=6) of a 0.0015mg/ml titania particle solution prior to filtration with ZnO (12.5mM & 16.7mM) and polystyrene (91% & 89% porosity) trapping layers with standard deviation as error bars. Red bars indicate results representing the total particle count but without further evaluation.

Particles above 150nm show large error margins suggesting the particle sizing instrument is reaching its upper limit of detection. In addition to this, large agglomerates are the likely cause of such particle sizes rather than nanoparticulates. Therefore particles between 150 to 200nm are presented as part of the total particle count but are not evaluated further.
5.2 Evaluation of trapping layer in liquid media

5.2.1 Titania solution exposure

In order to assess the suitability of the layers, structures identified during the fabrication stage were exposed to titania particles (as described in Section 5.1.2) suspended in a water medium at a concentration of 0.0015mg/ml according to the method detailed in Section 3.3.2. After each exposure run the trapping layers were examined using SEM. The suspension before and after filtering was analysed using a Nanosight (LM10, Malvern UK) instrument, providing particle size distribution information and selectivity of the trapping structure.

Zinc oxide structures produced using growth concentrations of 12.5mM and 16.7mM (Section 4.3.2) and polystyrene structures with porosities of 91% and 89% with 50%w/v NaCl (Section 4.3.3) were selected for interaction evaluation as they demonstrated the most promising trapping layer structures based on pore size and homogeneity.

5.2.2 Elemental analysis

5.2.2.1 Zinc oxide trapping layers

Pre-exposure energy-dispersive x-ray spectroscopy (EDX) analysis (Section 3.4.1) of the ZnO nanorod trapping layers was undertaken with for the five expected elements: titanium; zinc; silicon; oxygen and carbon (Figure 5.3).
Carbon was observed to be similar for both the 12.5mM and 16.7mM ZnO structures. Carbon on the sample is mostly likely due to atmospheric contamination during handling or residual hexamethylenediamine. For 12.5mM and 16.7mM growth concentrations the average carbon present is below 5% at 4.7 at.% and 4.64 at.%, respectively. For the 16.7mM ZnO structure more zinc was observed compared to the 12.5mM system, due to higher ZnO coverage, with a 5 at.% difference between the two concentrations at 43 at.% and 38 at.%, respectively. In agreement with the observations made for zinc, a higher atomic percentage of silicon was observed at a concentration of 12.5mM, with a 5 at.% difference between the two concentrations due to less ZnO coverage on the surface. Oxygen was almost identical.
for both concentrations and is most likely to be due to an accumulation of zinc oxide, silica and atmospheric contamination. Titanium was not observed as would be expected of pre-exposure samples that have not been exposed to titania solution.

After the first exposure to a 0.0015mg/ml titania particle solution (Figure 5.4), carbon levels remained similar between the two samples with an overall increase between pre-exposed samples and exposed samples from less than 5 atomic percent (at.%) to 5-7 at.%, as would be expected with extended exposure to atmospheric conditions and sample handling.

Figure 5.4 Average atomic percentage for identified elements after first exposure to a 0.0015mg/ml titania particle solution for ZnO trapping layer growth concentrations of 12.5mM and 16.7mM with error bars of the standard deviation where n=6.
As with pre-exposure samples, zinc was identified at a higher percentage for 16.7mM samples. A decrease in ZnO amounts between pre-exposed and exposed samples is most likely due to the relative gain of titanium identified in the sample. Silicon remained at a higher percentage in the 12.5mM ZnO system. An increase in oxygen was identified within both samples. Titanium was identified in both samples following exposure suggesting that the trapping layer is capable of capturing titania particulates. A higher percentage of titanium was identified within 12.5mM layers (5 at.%) compared to 16.7mM layers (3 at.%), indicating that the 16.7mM structure may be too dense to capture particulates effectively. However this could also be an indication that the larger gap sizes found in the 12.5mM layers allow for a larger proportion of particles to be captured, some of which are outside the nano size range (100nm<x<200nm). In order to identify the source of titanium, particle size distribution measurements must be taken.

After a second exposure to a 0.0015mg/ml solution of titania particles (Figure 5.5), the amount of carbon remained similar between the samples with a slight increase from 5-7 at.% to 6-8 at.% when compared to the first exposure as a result of further exposure to the atmosphere and sample handling.
Figure 5.5 Average atomic percentage for identified elements after a second exposure to a 0.0015mg/ml titania particle solution for ZnO trapping layer growth concentrations of 12.5mM and 16.7mM with error bars of the standard deviation where n=6.

Zinc remains at a higher percentage for the 16.7mM structures at 27 at.% compared to 25 at.% for 12.5mM structures. A decrease in relative percentage of zinc is likely due to a further increase in titanium identified. Silicon is at a higher percentage for 12.5mM samples at 39 at.% compared to 37 at.% agreeing with zinc levels identified. Oxygen remains approximately the same for both samples compared with the previous exposure with less than a 1 at.% increase for both samples, likely due to titania capture. Titanium percentages have increased between exposures, with more titanium being identified in 12.5mM systems, increasing from 5 at.% to 6 at.% for this exposure compared to the second exposure. The 16.7mM systems also exhibited increases in titanium from 3 at.% to 3.5 at.% again suggesting that the
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16.7mM structure itself may be too dense for effective titania particle capture with only a small amount remaining in the sample.

A third exposure of the trapping layers to a 0.0015mg/ml solution of titania nanoparticles (Figure 5.6) shows that although carbon percentage remains similar between the two samples, there was an unexpected decrease in the amount identified. In previous exposures, the atomic percentages of carbon steadily increased with atmospheric exposure and handling.

![Graph showing atomic percentage for identified elements](image)

**Figure 5.6** Average atomic percentage for identified elements after a third exposure to a 0.0015mg/ml titania particle solution for ZnO trapping layer growth concentrations of 12.5mM and 16.7mM with error bars of the standard deviation where n=6.

Zinc atomic percentages show a decrease from 25 at.% to 11 at.% in 12.5mM systems and 27 at.% to 15 at.% in 16.7mM systems after three exposures to titania particles. This decrease suggests that destruction of the trapping layer has taken
place during exposure, which may be as a result of the water flow rate due to the structure weakening throughout exposure runs, or larger particles colliding with and damaging the structure during exposure. Large increases in silicon percentages were shown from 39 at.% to 48 at.% in 12.5mM systems and 37 at.% to 55 at.% in 16.7mM systems compared to second exposures again suggesting destruction of trapping layer leaving the silicon substrate surface exposed. Results suggest that damage to the trapping layer may be greater in the 16.7mM system with a larger proportion of the silica surface exposed compared to that of the 12.5mM system. However, a higher atomic percentage of zinc remaining present suggests that the ZnO nanorods may still be on the surface of the substrate. Further analysis by SEM (Figure 5.7) showed that the ZnO is still present in some cases, but the rods themselves have fallen over and are now lying horizontally on the surface rather than standing vertically as the structure was designed. This is most likely due to the pressure exerted by the flow rate of the solution on exposure.

Figure 5.7 SEM micrograph showing the destruction of a ZnO structure (16.7mM) after a third exposure to a 0.0015mg/ml solution of titania particles at a flow rate of 2.5ml/hr
5.2.2.2 Polystyrene trapping layers

Pre-exposure EDX analysis of the polystyrene trapping layers of 91% (2.5% w/v polystyrene, 50% w/v NaCl) and 89% (3% w/v polystyrene, 50% w/v NaCl) porosities was undertaken with four expected elements being identified; titanium, silicon, oxygen and carbon (Figure 5.8).

![Figure 5.8 Average atomic percentage for identified elements C, Si, Ti and O before exposure to a 0.0015mg/ml titania particle solution for polystyrene filter layer porosities of 91% (2.5% w/v polystyrene) and 89% (3% w/v polystyrene) with 50% w/v of NaCl, with error bars of the standard deviation with no titanium or oxygen detected where n=6.](image-url)

Carbon was observed to be higher in the polystyrene sample with 89% porosity with an atomic percentage of 70 at.% compared to 54 at.% at 91% porosity. A higher percentage was expected, with carbon being the main element of polystyrene.
As expected, no titanium was detected on the pre-exposure sample for either of the polystyrene trapping layers. In agreement with the concentrations for carbon, silicon is present in both layers and is inversely related to carbon with an atomic percentage of 45 at.% at 91% porosity and 30 at.% at 89% porosity.

After exposure to a 0.0015mg/ml titania particle solution (Figure 5.9), carbon remained at a similar level to that in the pre-exposure sample, suggesting, at this stage, that structural damage does not appear to have occurred.

![Graph showing atomic percentage for identified elements after first exposure](image)

**Figure 5.9** Average atomic percentage for identified elements after first exposure to a 0.0015mg/ml titania particle solution polystyrene filter layer porosities of 91% (2.5% w/v polystyrene) and 89% (3% w/v polystyrene) with 50% w/v of NaCl, with error bars of the standard deviation where n=6.

Titanium concentrations increased in comparison with non-exposed samples with atomic percentages at 3.5 at.% and 2.4 at.% for 89% and 91% porosity, respectively. Oxygen levels also increased in both samples between non-exposed and exposed; this is most likely due to either titania capture or atmospheric contamination. Silicon is
observed within both samples, with only a decrease from 45 at.% to 44 at.% at 91% porosity and 30 at.% to 24 at.% at 89% porosity, respectively. This decrease in silicon is mostly likely due to the gain of titanium within the sample.

After a second exposure to a 0.0015mg/ml of titania particle solution (Figure 5.10), carbon levels remained stable between the exposures.

![Average atomic percentage for identified elements](image)

**Figure 5.10** Average atomic percentage for identified elements after second exposure to a 0.0015mg/ml titania particle solution for polystyrene trapping layer porosities of 91% (2.5%w/v polystyrene) and 89% (3%w/v polystyrene) with 50%w/v of NaCl, with error bars of the standard deviation where n=6.

No change in titanium concentrations was observed when comparing first and second exposure samples with atomic percentages at 3.5 at.% and 2.4 at.% for 89% and 91% porosities, respectively. Titanium concentrations may have remained fairly constant between exposures due to the titania particles translocation through the
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EDX analysis at 5, 10 and 15keV gives penetration depths of 0.85µm, 4.0µm and 8.5µm, respectively (see Figure 5.11 to Figure 5.13).

Figure 5.11 EDX simulation showing maximum penetration depth at 5keV with an estimated polystyrene layer density of 0.5g/cm³

Figure 5.12 EDX simulation showing maximum penetration depth at 10keV with an estimated polystyrene layer density of 0.5g/cm³
Figure 5.13 EDX simulation showing maximum penetration depth at 15keV with an estimated polystyrene layer density of 0.5g/cm³

The polymer layer is approximately 50µm thick suggesting that EDX cannot penetrate more than 17% of the layer’s depth, therefore any titania particulates located deeper than this penetration depth would not be detected. Analysis using up to 30keV can be for EDX analysis (Figure 5.14), which would allow for a penetration depth of 30µm, or 60% of the total layer thickness. However, prolonged exposure to 15keV or higher leads to destruction of the polymer layer itself (Figure 5.15) and unreliable measurements.
Figure 5.14 EDX simulation showing maximum penetration depth at 30keV with a polystyrene layer density of 0.5g/cm³

Figure 5.15 SEM micrograph showing damage to polyvinyl chloride following EDX at 15keV (Courtesy of David G. Jones, University of Surrey)

The atomic percentage of oxygen increased by less than 1% for both 91% and 89% porosities, from 1.5 at.% to 1.7 at.% and 2.1 at.% to 2.3 at.% after a second exposure, respectively (see Figure 5.10). This increase in atomic percentage reflects the addition of titania particles into the system, in addition to any atmospheric contamination. Silicon values remained constant and proportional to the carbon detected.
After a third exposure to titania nanoparticles (Figure 5.16) carbon levels remained stable between second and third exposures at levels of 71 at.% and 53 at.% at 89% and 91% porosities, respectively. The small differences are most likely due to weighted percentage with the addition of titania and possible contamination of the sample from handling and the atmosphere. Titanium levels increased by 1 at.% for both samples, suggesting that titania particle capture was still possible. Silicon levels remained stable as expected between exposures with only weighted proportion adjustments being accounted for.

![Diagram](image)

Figure 5.16 Average atomic percentage for identified elements after third exposure to a 0.0015mg/ml titania particle solution polystyrene filter layer concentrations of 91% and 89% with error bars of the standard deviation where n=6.
5.2.2.3 Summary

After EDX analysis of ZnO and polystyrene trapping layers after exposure to titania nanoparticles it was observed that both layers are capable of trapping titania particulates (Figure 5.17).

![Graph showing titanium atomic percentage in different layers after exposures](image)

**Figure 5.17** Average titania particle capture variation in observed samples of ZnO (12.5mM and 16.7mM) and polystyrene (91% and 89% porosities) layers after three exposures to a 0.0015mg/ml solution of titania particles

Zinc oxide layers displayed structural damage after use when examined by SEM, correlating with EDX results showing a significant increase in silicon after three exposures to 0.0015mg/ml titania solution. Atomic percentages of titanium identified in polystyrene samples were low (see Section 5.2.2.1) and could be as a result of the layer depth and EDX penetration capabilities making it difficult to obtain a more reliable estimate of titania captured. However, it is not possible to look at absolute variation in titanium levels, only the general trend due to other
elements, such as carbon masking the absolute values. In order to further investigate the interactions of both layers with titania, analysis of particle number size distribution was simultaneously undertaken to identify the size range of particles being filtered and the trapping efficiency (Section 5.2.2).

EDX analysis is limited in its ability to quantify elements which means that results gained are an approximation although trends can be observed. Lighter elements such as Oxygen and Carbon can be difficult to quantify, in the case of oxygen, an element present in the filter structures and TiO\textsubscript{2} particles, quantitative analysis is affected by the valency of the cations and stoichiometry. In order to further verify the effectiveness of the trapping layers to capture and retain particles, particle size analysis was carried out in liquid media.

5.2.3 Particle number size distribution analysis

5.2.3.1 Zinc oxide layers

5.2.3.1.1 Zinc oxide 12.5mM structures

ZnO layers, produced using growth medium at concentrations of 12.5mM (Figure 5.18 to Figure 5.20), were exposed to titania solution with three repetitions and the particle size distribution of the resultant filtrate solutions compared with that of the pre-exposure solution (Figure 5.21).
Figure 5.18 Average particle number size distribution of a 0.0015mg/ml titania particle solution after first filtration with ZnO (12.5mM growth media) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

Figure 5.19 Average particle number size distribution of a 0.0015mg/ml titania particle solution after second filtration with ZnO (12.5mM growth media) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.
The particle number size distribution analysis demonstrates that the 12.5mM ZnO trapping layer has a significant trapping impact on particles within the 20-70nm range for the first two exposures to the titania solution, with a trapping efficiency...
ranging from 62% at 20-30nm to 20% at 50-60nm (Table 5.1). Between 60-150nm the efficiency of the trapping layer is lower, with increasing particle size contributing to smaller percentage decreases in the total number decrease between exposures. Above 170nm, both first and second exposures show an increase in particulates within this size range. The increase in particulates may be due to agglomeration of particles within the solution. This size range is outside the gap distribution sizes measured in Section 4.4.1.1 suggesting that, instead of being trapped, the particles may be settling on the surface of the trapping layer.

Table 5.1 Change in average particle number after 0.0015mg/ml titania particle solution filtration with 12.5mM zinc oxide at a flow rate of 2.5ml/hr where white shows a loss in in particle number and black, a gain.

<table>
<thead>
<tr>
<th>Particulate size range (nm)</th>
<th>Exposure One</th>
<th>Exposure Two</th>
<th>Exposure Three</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>No particles</td>
<td>No particles</td>
<td>No particles</td>
</tr>
<tr>
<td>10-20</td>
<td>No particles</td>
<td>No particles</td>
<td>No particles</td>
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<tr>
<td>20-30</td>
<td>-62.20</td>
<td>-66.66</td>
<td>-0.74</td>
</tr>
<tr>
<td>30-40</td>
<td>-53.30</td>
<td>-34.18</td>
<td>+6.31</td>
</tr>
<tr>
<td>40-50</td>
<td>-42.53</td>
<td>-42.56</td>
<td>-31.66</td>
</tr>
<tr>
<td>50-60</td>
<td>-20.78</td>
<td>-16.23</td>
<td>+1.07</td>
</tr>
<tr>
<td>60-70</td>
<td>-30.00</td>
<td>-30.10</td>
<td>-17.73</td>
</tr>
<tr>
<td>70-80</td>
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<td>-6.12</td>
<td>-11.33</td>
<td>-2.35</td>
</tr>
<tr>
<td>90-100</td>
<td>-0.90</td>
<td>-4.68</td>
<td>-3.48</td>
</tr>
<tr>
<td>100-110</td>
<td>-12.85</td>
<td>-13.40</td>
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</tr>
<tr>
<td>110-120</td>
<td>-3.60</td>
<td>-5.29</td>
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<td>130-140</td>
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<td>-5.67</td>
<td>-5.67</td>
</tr>
<tr>
<td>140-150</td>
<td>-16.47</td>
<td>-20.50</td>
<td>+77.36</td>
</tr>
</tbody>
</table>
A third exposure demonstrated a substantial drop in filter efficiency with the highest percentage decrease being 32% at 40-50nm. In correlation with EDX analysis, which suggested that the trapping layer itself was being damaged, it is possible that the increases in larger particulates measured are due to parts of the ZnO trapping layer collecting in the solution rather than titania particles. In addition, a re-release of trapped particles upon trapping layer destruction may also result in an increase.

5.2.3.1.2 Zinc oxide 16.7mM structures

ZnO layers, produced using growth medium at concentrations of 16.7mM (Figure 5.22 to Figure 5.24), were exposed to titania solution with three repetitions and the particle size distribution of the resultant filtrate solutions compared with that of the pre-exposure solution (Figure 5.25).

Figure 5.22 Average particle number size distribution of a 0.0015mg/ml titania particle solution after first filtration with ZnO (16.7mM growth media) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.
Figure 5.23 Average particle number size distribution of a 0.0015mg/ml titania particle solution after second filtration with ZnO (16.7mM growth media) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

Figure 5.24 Average particle number size distribution of a 0.0015mg/ml titania particle solution after third filtration with ZnO (16.7mM growth media) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.
Chapter 5 Particle interactions with the trapping structure

With a 16.7mM ZnO trapping layer, particle number size distribution analysis demonstrates that the trapping layer has a much lower trapping potential than the 12.5mM ZnO filter with filter efficiency reaching a maximum of 26% between 30-40nm during exposure two. The filter demonstrates that particles between 20-50nm for two exposures to titania solution are the most efficiently trapped particles, which agrees with the nearest neighbour distribution within the structure (see Section 4.2.1.1).

Trapping efficiency decreases with increasing particle sizes and, as with the 12.5mM ZnO layers. Agreement is also observed when referring to EDX analysis which
suggested that, as with the 12.5mM concentration, the trapping layer itself was damaged during exposure, making it possible that the larger particulate increases measured are due to parts of the trapping layer collecting in the solution or re-suspended particulates are being detected. Again, trapping has occurred in some ranges, but particulates may have become trapped within the damaged structure, therefore a lack of discernible particle size trapping pattern is observed.

Table 5.2 Change in average particle number after 0.0015mg/ml titania particle solution filtration with 16.7mM zinc oxide at a flow rate of 2.5ml/hr where white shows a loss in in particle number and black, a gain.

<table>
<thead>
<tr>
<th>Bin Size</th>
<th>Exposure One</th>
<th>Exposure Two</th>
<th>Exposure Three</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>No particles</td>
<td>No particles</td>
<td>No particles</td>
</tr>
<tr>
<td>10-20</td>
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<td>No particles</td>
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</tr>
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<td>60-70</td>
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<td>-16.38</td>
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<td>-5.32</td>
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<td>80-90</td>
<td>+1.16</td>
<td>-4.40</td>
<td>-1.62</td>
</tr>
<tr>
<td>90-100</td>
<td>-3.66</td>
<td>-4.27</td>
<td>-3.96</td>
</tr>
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<td>100-110</td>
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<td>-11.92</td>
<td>+15.61</td>
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</tr>
</tbody>
</table>

5.2.3.1.3 Zinc oxide comparison

Filter growth concentrations were compared by efficiency (Figure 5.26). Comparing trapping efficiencies of 12.5mM and 16.7mM ZnO structures shows that the 12.5mM
structure is more efficient at trapping nanoscale particles with both first and second exposures trapping a higher percentage of particles between 20 – 100nm compared with the 16.7mM structure. However, 16.7mM structures demonstrated less variance in trapping efficiency than 12.5mM with both exposure one and two demonstrating very little difference in efficiency. 12.5mM and 16.7mM ZnO structures both showed a negative efficiency after 130nm after a third exposure suggesting both layers were damaged which correlate with the EDX results.

Figure 5.26 Comparison of filter efficiency during exposure testing of a 0.015mg/ml titania particle solution with 12.5mM and 16.7mM ZnO layer growth solutions at a flow rate of 2.5ml/hr where (x) is the exposure run number.

5.2.3.2 Polystyrene layers

5.2.3.2.1 Polystyrene 91% porosity structures
Polystyrene trapping layers with porosities of 91% (Figure 5.27 Figure 5.29) were exposed to a 0.0015mg/ml titania particle solution with three repetitions and then compared with the pre-exposure solution (Figure 5.30).

**Figure 5.27** Average particle number size distribution of a 0.0015mg/ml titania particle solution after first filtration with polystyrene (91% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

**Figure 5.28** Average particle number size distribution of a 0.0015mg/ml titania particle solution after second filtration with polystyrene (91% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.
Figure 5.29 Average particle number size distribution of a 0.0015mg/ml titania particle solution after third filtration with polystyrene (91% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

Figure 5.30 Comparison of particle number size distribution after filtrations of a 0.015mg/ml titania particle solution through a polystyrene (91% porosity and 50w/v% NaCl) trapping layer at a flow rate of 2.5ml/hr
Particle number size analysis demonstrates that the 91% porosity trapping layer has a significant trapping impact in two ranges, between 20-70nm and between 100-150nm throughout all three exposures to titania solution (Table 5.3). Trapping behaviour demonstrated an 86% particle number reduction for particles between 20-30nm. In addition to trapping between these ranges trapping occurs for particles within every size range and that larger particles are also trapped within the layer or on the surface of the layer with larger particles being trapped with up to 50% efficiency. The gap size analysis undertaken in Section 4.4.3.1 showed the surface pores are microns in size allowing for all particulate sizes tested to penetrate the layer however the decrease in trapping efficiency for larger particulates compared with the nanoscale range (20-100nm) suggest that at least some of the particles do not penetrate or are re-entrained into the titania solution. In agreement with EDX analysis (Section 5.2.1.1), particle number size distribution suggests that no structural damage occurred and that comparison of exposures show there was little variance in trapping efficiency.
Table 5.3 Change in average particle number of titania particles in solution after filtration through a 91% porosity polystyrene trapping layer (50g NaCl) at a flow rate of 2.5ml/hr where white shows a loss in in particle number and black, a gain.

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<th>Exposure Two</th>
<th>Exposure Three</th>
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</tr>
</tbody>
</table>

5.2.3.2.2 Polystyrene 89% porosity structures

Polystyrene trapping layers with porosities of 89% (Figure 5.31 to Figure 5.33) were exposed to a 0.0015mg/ml titania particle solution with three repetitions and then compared with the pre-exposure solution (Figure 5.34).
Figure 5.31 Average particle number size distribution of a 0.0015mg/ml titania particle solution after first filtration with polystyrene (89% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

Figure 5.32 Average particle number size distribution of a 0.0015mg/ml titania particle solution after second filtration with polystyrene (89% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.
Figure 5.33 Average particle number size distribution of a 0.0015mg/ml titania particle solution after third filtration with polystyrene (89% porosity and 50w/v% NaCl) trapping layers at a flow rate of 2.5ml/hr with standard deviation as error bars where n=6. Red bars indicate results representing the total particle count but without further evaluation.

Figure 5.34 Comparison of particle number size distribution after filtrations of a 0.0015mg/ml titania particle solution with polystyrene (89% porosity and 50% w/v NaCl) trapping layers at a flow rate of 2.5ml/hr with pre-exposure particle number size distribution where n=6.
Particle number size analysis demonstrates that the 89% porosity trapping layer has a significant trapping impact between 20-80nm throughout all three exposures to the titania solution (Table 5.4). Trapping efficiency was shown to be as high as 85% for particles between 30-40nm. Overall observation suggests that the layer traps particles within all size ranges. The first and second exposures show an increase in particulates between 170-180nm, however this is not reflected in the third exposure. An increase in this range may be due to the surface pores being micron size (Section 4.4.3.1) which would allow for all particulate sizes tested to penetrate the layer, however the decrease in trapping for larger particulates compared with the nanoscale range (20-100nm) suggest that at least some of the particles do not penetrate or are re-entrained into the titania solution. Little variance was observed in trapping efficiency.
Table 5.4 Change in average particle number of titania solution after filtration through a 89% porosity polystyrene trapping layer (50%w/v NaCl) at a flow rate of 2.5ml/hr where white shows a loss in in particle number and black, a gain.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>Exposure One</th>
<th>Exposure Two</th>
<th>Exposure Three</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>No particles</td>
<td>No particles</td>
<td>No particles</td>
</tr>
<tr>
<td>10-20</td>
<td>No particles</td>
<td>-80.37</td>
<td>-81.12</td>
</tr>
<tr>
<td>20-30</td>
<td>No particles</td>
<td>-82.80</td>
<td>-84.42</td>
</tr>
<tr>
<td>30-40</td>
<td>-66.10</td>
<td>-68.51</td>
<td>-72.13</td>
</tr>
<tr>
<td>40-50</td>
<td>-31.99</td>
<td>-37.44</td>
<td>-40.45</td>
</tr>
<tr>
<td>50-60</td>
<td>-64.42</td>
<td>-52.06</td>
<td>-52.75</td>
</tr>
<tr>
<td>70-80</td>
<td>-22.96</td>
<td>-27.80</td>
<td>-31.31</td>
</tr>
<tr>
<td>80-90</td>
<td>-18.27</td>
<td>-22.35</td>
<td>-24.28</td>
</tr>
<tr>
<td>90-100</td>
<td>-11.09</td>
<td>-22.61</td>
<td>-28.20</td>
</tr>
<tr>
<td>100-110</td>
<td>-42.39</td>
<td>-30.58</td>
<td>-31.24</td>
</tr>
<tr>
<td>120-130</td>
<td>-10.56</td>
<td>-1.37</td>
<td>-16.04</td>
</tr>
<tr>
<td>130-140</td>
<td>-19.21</td>
<td>-19.95</td>
<td>-20.71</td>
</tr>
<tr>
<td>140-150</td>
<td>-34.53</td>
<td>-35.81</td>
<td>-37.17</td>
</tr>
</tbody>
</table>

5.2.3.2.3 Polystyrene comparisons

Comparing trapping efficiencies of 91% (2.5%w/v polystyrene; 50%w/v NaCl) and 89% (3% w/v polystyrene; 50%w/v NaCl) porosity polystyrene structures shows that the 91% structure is more efficient at trapping nanoscale particles between 20-50nm with both first and second exposures compared with the 89% structure. This is most likely due to the larger pore sizes identified in this structure (see Section 4.4.3.1).
Filter growth concentrations were compared by efficiency (Figure 5.35).

![Graph showing comparison of filter efficiency during exposure testing for 99% and 89% porosity polystyrene structures at a flow rate of 2.5ml/hr.](image)

5.2.4 Conclusions

ZnO and polystyrene trapping layers both showed the capability to trap titania particulates suspended in water. A comparison was made of two concentrations identified from each filter type as the most efficient (Figure 5.36). A film formed of 12.5mM ZnO was identified as showing the highest trapping efficiency in the nanoparticle range. A polystyrene porosity of 89% was observed to have more selectivity compared with 91% porosity concentration, which trapped increased numbers of the larger particulate size range.
Comparisons of the ZnO and polystyrene trapping layers suggest that polystyrene has the highest trapping efficiency between the two filters. In addition to this, the variation in trapping efficiency between exposures is much lower compared with that of the ZnO filter. ZnO layers also exhibit structural damage during the third exposure showing that the structural integrity of this trapping layer is not suitable sufficient and thus ZnO is no longer considered for further work.
5.3 Evaluation of trapping layers in an airborne scenario

5.3.1 Introduction

In order to evaluate the trapping layer structures and the effect of their particle retention on impedance behaviour, the model developed in Chapter 4 was used to predict the changes in impedance under wind tunnel conditions when exposed to Arizona Road Dust. Theoretical behaviour was then compared with the experimental data obtained for validation purposes.

5.3.2 Relative permittivity model

In the case of the interdigitated electrode structures in this study, the media between the electrodes can be considered as a composite, consisting of air and particulates. At low volume fractions the relative permittivity of a randomly distributed particulate composite can be calculated as a function of volume fraction of the two phases and their respective dielectric properties, where the effective relative permittivity is given using the Maxwell-Garnett mixing rule (Jamnik et al., 2006);

\[
\varepsilon_{\text{eff}} = \varepsilon_{\text{air}} \left(1 + 3V_{np} \frac{\varepsilon_{np} - 1}{\varepsilon_{air} - 1} \right)
\]

Equation 5.1
where $\varepsilon_{\text{eff}}$ is the effective relative permittivity, $\varepsilon_{\text{np}}$ is relative permittivity of the nanoparticles, $\varepsilon_{\text{air}}$ is the permittivity of air and $V_{\text{np}}$ is the volume fraction of nanoparticles.

Practically, unless under laboratory conditions, it is unlikely that one will find monophasic media in environmental samples. The presence of multiphasic samples is a much more likely scenario, e.g. ARD (Section 2.9.3).

![Figure 5.37](image)

**Figure 5.37** Calculated relative permittivity of an Arizona Road Dust (ARD)-air composite using the Maxwell-Garnett formula and a volume weighted average of the dielectric behaviour of the individual components of Arizona Road Dust where relative permittivity of ARD

### 5.3.3 Assessment of the range of validity

The Maxwell-Garnett model is only valid at low volume fractions as it assumes percolation pathways are unlikely to occur (Moiseev, 2010). Furthermore, at low volume fractions, it is most probable that captured particles will assemble as a monolayer on the sensor, thereby interacting with the electric field between the
interdigitated electrodes. To assess the stage at which percolation would occur and the model would cease being valid, a 2D structure was simulated and populated with randomly placed particles in multiple simulations. In reality, it is unlikely that particles will be truly isolated due to the nature of particulates and the tendency of nanoparticulates to agglomerate under environmental conditions. However, such an approach is likely to estimate the maximum powder loading that could be tolerated under ideal conditions.

Within a square array, particle-particle interaction was considered to occur when neighbouring particles shared an edge or a corner (Figure 5.38). Using, 10,000 simulations of a 10 x 10 array (Figure 5.39), the particle volume fraction at which there was a 50% chance of particle-particle interaction occurring was found to be 0.214 (Figure 5.40). A more appropriate limit to be confident that the model was valid would be 10% or 1% probability of interaction which corresponds to 0.195 and 0.18 volume fraction exposures, respectively. For this study an upper working particle concentration was then taken to be a volume fraction of 0.18. This is also within the linear region of the Maxwell-Garnett model (Figure 5.37).

![No Interaction](image1.png) ![Interaction](image2.png) ![Interaction](image3.png)

Figure 5.38 Particle interaction model conditions illustrating interaction and non-interaction scenarios
Figure 5.39 Illustration of particle volume fractions within the system and the likelihood of interaction between particulates

Figure 5.40 Probability of particle-particle interaction occurrences as a function of IDT volume fraction of occupied by particles
5.3.4 Effects of frequency on detection and measurement

In order to determine the most appropriate working frequency of the IDT sensor, modelling was used to predict the frequency at which a higher responsivity can be gained. Using the operating parameters of the HP4192A impedance analyser (Hewlett-Packard, UK), frequencies between 0.5 MHz and 5 MHz were chosen as a suitable range for modelling conditions (Figure 5.41).

![Graph showing predicted variation in impedance as a function of volume fraction of Arizona Road Dust at frequencies between 0.5 MHz and 5 MHz with electrode dimensions of 400 µm for both electrode gap and width.]

The model demonstrates that all the frequencies examined tend to show similar responsivity as a function of volume fraction, demonstrated by comparing the slope of the curves. However, a frequency of 0.5 MHz would be easier to reproduce in a
smaller sensor, requiring simpler electrodes and less power to achieve. A steep slope indicates that there will be a large change in impedance for a given change in particle loading. In addition to a steep slope, it is also important that the rate of change of impedance with volume fraction of particles is approximately constant so that the sensor exhibits linear behaviour across the detection range making the results easier to validate.

5.3.5 Material interactions

Using the major components of ARD as examples of typical exposure materials, the theoretical model was used to predict likely differences in impedance that would occur as a result of exposure to each of the different materials found in ARD, based on their relative permittivity (Figure 5.42). These predictions were then compared with experimental observations in order to determine the capabilities of the model and system in addition to the model’s reliability and thus usefulness.
Following the simulation, it is apparent that materials can be distinguished based on their relative permittivity. However, in addition to this it also suggests that it may be difficult to differentiate between materials with values of permittivity which are close to each other. In order to examine this observation further, the effective permittivities of air-particle composites containing particles of increasing relative permittivities and their effect on impedance were plotted as a function of volume fraction of particles (Figure 5.43).
Figure 5.43 Effective permittivities of air-particle composites as a function of different relative permittivity of particulate phase

Plotted effective permittivities of increasing values as a function of IDT volume fraction suggest that as the value of relative permittivity increases away from the relative permittivity of air (1.000589) absolute differences between relative permittivity of materials produce less of an effect on impedance behaviour. At higher values of relative permittivity a greater difference is required to differentiate between materials. This means that it will be easier to differentiate between materials with low relative permittivities than those with higher relative permittivities. This can be seen in the ARD data which shows that the effective permittivity of silicon dioxide and aluminium oxide can be differentiated relatively
easily ($\varepsilon_r$ values are 3.9 and 9.1, respectively) whilst calcium oxide and ferric oxide ($\varepsilon_r$ values are 11.8 and 86, respectively) are likely to be difficult to differentiate using their permittivities.

5.4 Experimental verification

5.4.1 Mass prediction

Bare silicon samples exposed to ARD for 10 minutes were analysed in order to determine the number density of adhered particles (Figure 5.44 and Figure 5.45). This verification was conducted on samples without a trapping layer in order to allow an accurate particle count to be obtained.

![SEM micrographs](image)

Figure 5.44 SEM micrographs of silicon wafer substrates after (A) 0 mins, (B) 2 mins (C) 5 mins and (D) 10 mins of Arizona Road Dust exposure at a wind velocity of 1.7m/s and an airborne particle density of 9.07mg/m$^3$. 

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Increased exposure time correlated with an increase in the number density of particles on the substrate surface during the 10 minute exposure. Particles within a narrow size range were trapped on the silicon surface over 10 minutes with an average particle size of 3.2μm. The size selectivity that occurred without a filter is most likely due to the fact that the smallest particles either do not interact with the surface or are re-entrained back into the air flow across the sample. In addition to this the largest particles may also suffer a similar fate, they may be removed by the airflow or through collisions with other large particles both on the surface, knocking off the particulates, and in the air, diverting their course meaning some never reach the sample. Examination of the micrographs also suggests that some of the particulates are agglomerated smaller particles which have not broken apart within

Figure 5.45 Plot showing average number density of particles ± stdev deposited on silicon test wafer as a function of time of exposure to Arizona Road Dust with an airborne particle density of 9.07mg/m³ at a velocity of 1.7m/s after 6 repetitions.
the wind tunnel or on impact with the silica surface. Particles are likely to interact with the surface through the interception mechanism as particles approach within one particle radius of the substrate.

A capturing efficiency estimate can be calculated by considering the collection area as a fraction of the whole wind tunnel cross-sectional area. Sample area is given by the sample width and a sampling height which is dependent on the boundary layer thickness. The boundary layer thickness (where flow is 99% that of the bulk flow rate), assuming a laminar flow (Figure 5.46), is given by Equation 5.2 (Bansal, 2005).

\[ \frac{4.91 \times x}{\sqrt{Re_x}} \]

Equation 5.2

Where \( x \) is the distance from the sample’s leading edge and \( Re \) is the calculated Reynold’s number. The maximum thickness of this layer at \( x=3 \text{ cm} \) was used as the sampling height as a first approximation.
Predicted mass exposures, based on particle loading in the airflow and the percentage of the wind tunnel cross sectional area occupied by the sampling area, were then compared with the mass calculated based on observations of the number of trapped particles (and average density of ARD) seen at each of the exposure times tested and are presented in (Table 5.5).

**Table 5.5 Calculated percentage capturing efficiency for bare silicon samples**

<table>
<thead>
<tr>
<th>Exposure time (minutes)</th>
<th>Predicted mass (ng)</th>
<th>Experimental mass (ng)</th>
<th>Capture efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.76</td>
<td>0.35</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>1.90</td>
<td>0.58</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>3.80</td>
<td>0.68</td>
<td>18</td>
</tr>
</tbody>
</table>
Based on particle counting of SEM micrographs of substrates after exposure at each exposure time, capturing efficiency of 47% was observed after 2 minutes with efficiencies at 5 and 10 minutes decreasing to 30 and 18% respectively. These observations suggest that without a filter layer the majority of particulates did not adhere to the blank surface of the silicon wafer. The boundary thickness, and sampling height, had a maximum value of 210µm at 3cm from the leading edge. This sampling height was calculated to be less than a percent of the total area of the wind tunnels cross-sectional area through which particles were able to flow. The boundary layer is defined as the point where flow velocity is 99% of that of the bulk, however at this speed many particles would fail to decrease in velocity to a speed that would allow them to settle on the sample surface therefore a lower speed may be more relevant meaning that the sampling height would be lower and capturing efficiency would increase. Irrespective of this, surface phenomena effects such as re-entrainment, re-suspension, particle bounce and impaction can be also assumed as the likely causes of the less than 100% capturing efficiencies in addition the efficiency decrease over time. Such phenomena are also likely to explain the decrease in observed capturing efficiency at longer times as a steady state surface coverage is approached. Such an observation confirms the need for a trapping layer that is able to retain the particles that have adhered to the surface. However, as the predicted mass results are within an order of magnitude of those determined experimentally, it
suggests that a prediction of particle loading in air could be determined using the model provided an equipment correlation factor is known.

6.4.2 Impedance behaviour prediction

The predicted impedance model values calculated using device dimensions of 400µm for electrode width and gap, observed volume fractions of particles, and was compared to the experimental particle retention data obtained during wind tunnel exposure to ARD (Figure 5.47).

Figure 5.47 Comparison of average normalised theoretical and experimental impedance for an IDT without a trapping layer as a function of IDT volume fraction of Arizona Road Dust. Dimensions of 400µm for both gap width and electrode width (n=6) and error bars demonstrating standard deviation

Comparison of experimental and predicted values for an IDT with dimensions of 400µm for both gap and electrode width without a trapping layer show good correlation. Experimental results show a response of 42.5Ω/Vf higher than that of
the predicted data at 31.5Ω/Vf, most likely due to the differences in electrode dimensions of the actual devices.

It was found that after 10 minutes of exposure particulates occupied only 2% of the sampling area. However, air particulate density levels found inside the wind tunnel are unlikely to occur in environmental exposure scenarios as they are more concentrated and are regarded as extreme, meaning that in real life such exposures would take significantly longer to accumulate providing long sensor lifetimes. In addition to particulate density, air flow speed in real life environmental scenarios is likely to be much lower than 1.5 m/s upon entering the device and contacting the sample surface. In this case higher speeds increase the frequency of particle collisions and occurrence of particle impaction on the sample surface leading to a reduction in the number of particles able to settle on the sampling area.

In order to further examine the validity of the model, devices with polystyrene trapping layers as described in Section 4.3.2, were also exposed to ARD in the wind tunnel and compared with model predictions in order to identify any differences in behaviour (Figure 5.48). ZnO trapping layer devices could not be tested in this way due to the destruction of the ZnO layer during exposure to ARD in the wind tunnel.
Figure 5.48 Comparison of normalised theoretical and experimental impedance as a function of volume fraction with Arizona road dust and dimensions of 400µm for both gap width and electrode width with n = 6 and error bars demonstrating standard deviation with a polystyrene trapping layer.

The experimental and predicted data values for samples with a polystyrene filter layer show good correlation between the two data sets. A straight line is produced as a result of the small volume fraction range measured. Over a wider range the theoretical graph is shown to produce exponential decay. Experimental results show a response of 30Ω/Vf compared with a response value of 31.5Ω/Vf for theoretical values. The results suggest that the addition of a polymer layer can be easily accounted for by the theoretical model allowing it to be used for future device design and selection of appropriate filter layers. The responsivity of the polystyrene system is comparable to the bare substrates indicating that the trapping layer plays no role in collection efficiency.
5.5 Conclusions

Agreement was observed between the model and the experimental data for impedance behaviour of printed electrodes with and without a trapping layer. This provides validation for the model assumptions and shows that by combining experimental results and model predictions that the impedance based sensor, coupled with an appropriate trapping layer, could be used to detect the presence of nanoscale materials in airborne or liquid environments as well as provide an indication of size and type of the material. Data obtained from both data sets suggests that dimensional variations due to manufacturing have little impact on the impedance values measured as the small differences observed are significantly lower than the response of both the model and the experimental data.

Differentiation between materials based on their relative permittivities is achievable, however those materials with similar permittivities are more difficult to differentiate between particularly when the permittivity moves further away from that of air. In some cases, where the values differ by less than that of the device responsivity, the materials are indistinguishable from each other at this point.

The addition of a porous polystyrene layer to the device is easily accounted for by the model, with results still in good agreement with experimental data which suggests that polystyrene would make an efficient trapping layer. As discussed in
earlier in Chapter 5, ZnO trapping layer damage suggests that the layer would not
be suitable as a trapping structure due to its low mechanical strength.
Chapter 6 Conclusions and further work

6.1 Summary of findings

The work presented in this thesis focuses on the development of a novel sensor for airborne nanoparticulate monitoring suitable for both environmental and occupational applications. The following chapter illustrates the main conclusions drawn from the work and identifies potential future work which could be implemented.

Engineered nanoparticles were detected using interdigitated arrays with 400µm electrode widths and 400µm gap widths between the electrodes with a responsivity of 42.5Ω/V for TiO$_2$. 400µm dimensions provide a balance between measurement sensitivity, reproducibility and ease of fabrication using inkjet printing. In order to retain a particulate material, and hence measure exposure, a polystyrene trapping layer was deposited over the electrode surface. The polystyrene structure proved to be robust under both liquid flow and wind tunnel experiments, showing retention of the particulates within the structure.

Over an exposure time of ten minutes, the volume fraction of particles deposited was found to be at 2% coverage of the device, suggesting that continuous monitoring for longer periods of time can be conducted before replacement or cleaning of the sensor devices is required.
The device developed provides a suitable alternative to particulate monitoring methods currently employed. Instead of using methods based on the equivalent sphere diameter assumption, a method independent of size and shape has been developed, based on the relative permittivity of the materials. Concentration measurements, rather than size provide an alternative to the mass-based regulations in effect, where nanoparticle production is overlooked in favour of bulk material related mass restrictions. Using concentration-based, size-independent monitoring, as described in this thesis, could provide a method which is suitable for international implementation and a single parameter which can be compared across instrumentation.

In addition to legislation related benefits, the device is easy to use, robust and portable with the ability to function as a real time monitoring instrument.

6.2 Conclusions

The work in this thesis demonstrated that it was possible to measure changes in impedance behaviour of the capacitor type structure developed, during nanoparticle inclusion into the system. Observed impedance agreed with predicted values with the model indicating that it is possible to differentiate different particles based on their relative permittivity.

Dimensions of the IDT structure affected the sensitivity of the device, with smaller gap width between electrodes achieving a higher sensitivity than those further apart, as demonstrated by the predictive model developed in Chapter 6 of this thesis.
However manufacturing methods limited the size resolution of the features that could be achieved and thus, a compromise of 400µm for both gap width and electrode width was determined.

In order to retain the particles for exposure monitoring, a trapping layer was developed. Zinc oxide and polystyrene trapping layers were examined, where pore sizes of between 10nm to 170nm and 10µm to 50µm were achieved, respectively. Under exposure conditions zinc oxide structures were unable to withstand the conditions and were damaged, resulting in a structure that could not retain particulates. Polystyrene layers were found to withstand exposure scenarios, with particles between 20-200nm being retained within the structures.

When the sensors with trapping layers were exposed to airborne particulates a change in impedance behaviour was observed over time demonstrating that the sensor is capable of particulate detection and real time monitoring. Theoretical modelling and experimental results showed good agreement with responsivitites of 30Ω/Vf and 31.5Ω/Vf respectively.

### 6.3 Future work

#### 6.3.1 Introduction

This thesis has demonstrated that it is possible to detect engineered nanomaterials in airborne and liquid environments using interdigitated electrode sensor structures based on changes in impedance of a particle trapping layer due to the incorporation
of nanoparticles. Further development of sensor structures will require investigation of the manufacturing techniques and sensor materials, to yield cost effective platforms, further validation studies to understand real life behaviour, as well as integration with suitable electronics for portable applications.

6.3.2 Manufacturing and materials

6.3.2.1 Substrates

Silicon wafers provided a suitable substrate material for electrode structure mounting compared to the glass substrates tested in this thesis, however these substrates are costly and ill-suited to high throughput ink jet printing based manufacturing routes which would prove economically unsound for bulk production of the devices. Instead, low cost polymeric materials for long term use would be beneficial.

Polymer materials offer the advantage of lower cost but are more challenging to print on due to their inherent surface properties that affect wetting and print resolution/quality. Suitable surface treatments such as plasma or chemical washes, should be explored as routes to achieving high quality printed features.

6.3.2.2 Inks

For similar sustainability reasons the use of different inks, based on lower cost materials such as copper should be explored as the current method (silver) would prove costly on an industrial scale.
Particulate based inks using conductive materials such as copper offer a lower cost alternative to silver, however ink formulation requires a number of steps during manufacture to ensure small particulate sizes capable of being inkjet printed (less than 200nm) in addition to manipulation of carrier fluids in order to provide suitable viscosity and surface tension. Lastly, particle loading within the ink is an important parameter of design, ensuring that enough material is present to produce a conductive response.

In addition, the adaptation of environmentally friendly carrier fluids such as water would enforce the eco-awareness of the fabrication in line with the project.

Aligned to this would be the study of ink spreading to minimise manufacturing variances and provide the means to create smaller, higher sensitivity devices. This would involve the use of different solvents and/or additives to the solvent in order to manipulate the viscosity of the ink. In addition to this, different temperatures of both inks and substrates would be of interest in order to determine optimal wetting characteristics.

6.3.2.3 Trapping structure fabrication

Polystyrene trapping layer structures provided a good filtration efficiency for nano size particulates however, due to the size of the pores, larger particulates were also retained within the structure. In order to combat this, it would be necessary to reduce the salt crystal size further, (e.g. to the nanoscale) using further ball milling,
electrospray or direct synthesis. Polystyrene/salt solutions could then be deposited onto the substrates using spin or spray coating in order to produce a uniformly thick layer across the surface, where salt could then be removed from the polystyrene structure. Salt crystals less than 200nm would result in pores which would allow for the size selection of nanoscale particulates less than 100nm in size.

6.3.3 Validation studies

6.3.3.1 Airborne nanomaterial exposure

Testing nanoparticulate exposure in airborne samples is required in the development of this sensor in order to identify behaviour under the intended use conditions of the instrument. The following test chamber has been designed in order to take into consideration safety concerns (Figure 7.1) around creating airborne nanomaterials.

![Figure 6.1 Schematic for airborne nanoparticle exposure testing apparatus](image)

The testing apparatus illustrated would allow for the contained exposure of devices with nanoparticles, providing a fixed air flow rate and airborne particle concentration which would
vary dependant on the scenario being simulated, for example, an indoor exposure testing scenario would have a low air velocity of approximately 0.15m/s (Orosa J & Oliveira A.C, 2012). An advantage of such testing would be the ability to relate actual air testing concentrations to the trapping layers’ effectiveness where actual particle concentrations can range from 4,000 and 25,000 particles/cm$^3$ (Santern et al., 2009) in domestic households, dependant on influencing factors such as location and ventilation.

6.3.3.2 Long term exposure studies

Current devices were tested over an exposure time of 10 minutes, however, it would be beneficial to observe the lifetime of a sensor in terms of exposure. Sensors will, at some point, retain an adequate volume fraction where particles can no longer be trapped and impedance behaviour remains constant. Long term exposure testing would ensure that maintenance of such a sensor was carried out within a suitable time frame in order to maintain accuracy of the measurements. However, it would be advantageous for sensors to have longer life spans. Longer life spans would limit the requirement for regular replacement of the sensor.

In addition to the filling of a specific volume fraction, degradation of the electrodes would be an important observation. Degradation of electrodes, due to particulate exposure or other environmental factors could lead to changes in impedance behaviour not due to the particles themselves, affecting the reliability of the data recorded.
6.3.3.3 Electronics

In order for the system to be portable, an alternative measurement system is required. Currently the sensor is connected to an impedance analyser, however such instruments are costly and bulky, which makes them inadequate for portable monitoring devices. At its heart, the system works by detecting a change in capacitance of the IDT structure. This is a similar approach employed by portable humidity sensors. An alternative route would therefore be to take such an existing electronic system, and adapt it to the sensor developed in this thesis to yield a portable nanoparticle monitoring system.
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