

Inclusion of nano-silver compounds in RO membranes as solutions to fouling by microbes and natural organic matter during seawater desalination

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and Dr. P. Tetyana (MINTEK)

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Declaration

I declare that the work reported in this thesis is my independent work, submitted for the degree of Doctor of Philosophy to the School of Chemistry, Faculty of Science at Wits University, Johannesburg. This study has not been submitted to any other institution previously for examination.

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02/08/2023

Abstract

The access to safe and potable water has become a salient discussion for governments across the globe. This is due to pronounced levels of the decline in volumes of available freshwater. Attributions to this phenomenon are mainly climate change, eutrophication, discharge of untreated effluent, heightened irrigation, and industrialization. Currently exploited freshwater sources are rivers, lakes, dams, glaciers, and aquifers. However, inconsistent rainfall patterns have rendered some of these sources as 'stressed', which is exacerbated by exponential population growth and misallocation of available freshwater. In hindsight, seawater was identified as a possible source of potable water. However, the high levels of salinity and miscellaneous contaminants (i.e., pathogens and natural organic matter) necessitates treatment of seawater prior its usage. Therefore, the purpose of this work is to develop rugged polyamide thin film nanocomposite (TFN) reverse osmosis (RO) membranes with antifouling properties for seawater desalination.

TFN were fabricated by the inclusion of silver-based (i.e., silver sulfide) nanoparticles during interfacial polymerization of the polyamide active layer. Silver compounds are known to have superior antibacterial and photocatalytic properties, due to plasmonic and photoabsorption properties. For this reason, silver oxide (Ag_2O), silver sulfide (Ag_2S), and silver chloride (AgCl) nanoparticles (NPs) were colloiddally synthesized. These were then characterized and evaluated in photocatalytic and antibacterial applications. Cytotoxicity studies were also done to determine which of these NPs pose less risk to human health. The consolidation of data from these applications advised which of these NPs would be suitable for incorporation into the polyamide layer to produce fouling resistant TFN.

Microscopic analysis depicted well-defined shapes, with average sizes of 23.0 ± 5.7 (Ag_2O), 30.6 ± 7.4 (Ag_2S), and 10.6 ± 7.2 nm (AgCl). X-ray diffraction determined Ag_2O , Ag_2S , and AgCl NPs to have cubic, monoclinic, and cubic lattices, respectively. Optical spectroscopy determined Ag_2O , Ag_2S , and AgCl NPs to have band gap energies of 2.97, 3.11, and 3.05 eV, respectively. These observations inferred that crystalline NPs that exhibit surface plasmon resonance (SPR) in the visible region were successfully synthesized. SPR is a desired characteristic for photocatalysts, and indeed Ag_2O , Ag_2S , and AgCl NPs achieved humic acid degradation (HA) efficiencies of 86.2, 88.1, and 76.5%, respectively.

In antibacterial studies, the broth micro-dilution method indicated that the minimum inhibitory concentration (MIC) values against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) for Ag₂O, Ag₂S and AgCl NPs were 0.03125, 0.125, and 0.125 mg/mL, respectively. The well-diffusion tests showed that Ag₂O NPs had the largest zones of inhibition (ZOI), followed by Ag₂S, then AgCl NPs. These observations demonstrated the concentration-dependent mitigation of bacterial cell proliferation. The NPs were further tested for cytotoxicity against human embryotic kidney 293 (HEK 293) cells. It was found that the cytotoxic concentration that rendered 50 % viability (CC₅₀) were 0.0302, 0.3606 and 0.3419, and were obtained for Ag₂O, Ag₂S and AgCl NPs, respectively. This data implied that Ag₂O NPs were the most toxic, while Ag₂S and AgCl NPs were least toxic. In light of the above, Ag₂S NPs were selected to be incorporated into TFN RO membranes.

TFN RO membranes were fabricated by the addition of three different concentrations of Ag₂S NPs in the aqueous phase to form the active polyamide (PA) layer on a polysulphone (PSF) support, namely 20, 30, and 50 mg. Fourier transform infrared (FTIR) spectroscopy detected vibrational peaks at 1659 cm⁻¹ (amide I C=O stretch), 1542 cm⁻¹ (amide II C-N stretch), 1481 cm⁻¹ (C-H bend), 1385 cm⁻¹ (C-O stretch), 1242 cm⁻¹ (C-N stretch), and 779 cm⁻¹ (aromatic C-H and C=C wagging). The presence of aromatic and amide functional groups corroborated the formation of the TFN active layer, which is responsible for RO filtration of dissolved ions in water. Moreover, atomic force microscopy (AFM) revealed that average surface roughness decreased with increased Ag₂S NP loading. TFN loaded with 20, 30, and 50 mg Ag₂S NPs recorded water contact angles (WCA) of 54.1, 45.4, and 43.3°, respectively. The WCA of thin film composite membranes (TFC) without Ag₂S NPs was recorded to be 73.5°. This demonstrated that the inclusion of Ag₂S NPs increased surface hydrophilicity. In addition, salt rejection and water flux were higher for 30 mg loaded TFN (98 % and 32.7 L/m²h) compared to those of TFC (97% and 24.8 L/m²h). The bacterial growth inhibition was observed to be significantly high for 30 mg loaded TFN (80 %) compared to that of TFC (38 %). These observations indicate that the inclusion of Ag₂S NPs significantly enhanced the performance of RO membranes and cost effectiveness of desalination.

Dedication

This PhD thesis is dedicated to all my family members who perpetuated our lineage, demonstrated relentless determination to become perfect examples of virtue, as well as alleviated mediocrity in their generation and in generations to follow. Your legacy lives.

To my late paternal grandparents, Chrispus Mothelesi Nchoe and Mapule Anthens 'Oumie' Nchoe.

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List of oral presentations

- CoSAAMI 2021 virtual conference on Materials Science 21st September 2021: Coalescence of silver-based nanoparticles with polyamide thin film composite membrane for seawater desalination.
- University of the Witwatersrand 12th cross-faculty symposium, virtual meeting on 18th November 2021: Coalescence of silver-based nanoparticles with polyamide thin film composite membrane for seawater desalination.
- University of the Witwatersrand 13th cross-faculty symposium, virtual meeting on 29th September 2022: Fabrication of nano-enhanced polymeric membranes for fouling inhibition during seawater reverse osmosis.

List of poster presentations

- Catalysis South Africa (CATSA) 2022, Champagne sports resort, Drakensburg, KwaZulu Natal on 16 November 2022: Synthesis of silver-based nanoparticles for photocatalytic degradation of humic acid and rhodamine B.

Publications

- **Obakeng B Nchoe**, Obakeng B. Nchoe, Kabo Matshetshe, Muhammed As' Ballim, Phumlani Tetyana, Keneiloe Sikhwivhilu, Nosipho Moloto. Fabrication of Ag₂S incorporated Polyamide thin film nanocomposite reverse osmosis membranes with antifouling properties (manuscript submitted)
- **Obakeng B Nchoe**, Zakhele Ndala, Muhammed As' Ballim, Siyabonga Nkabinde, Nosipho Moloto. Synthesis of silver-based NPs for photocatalytic degradation of humic acid in aqueous solution (Manuscript submitted).
- **Obakeng B Nchoe**, Ndivhuwo Shumbula, Zakhele Ndala, Siyabonga Nkabinde, Tshwarela Kolokoto, Phumlani Tetyana, Keneiloe Sikhwivhilu, Nosipho Moloto, Facile synthesis of Ag₂O, Ag₂S and AgCl NPs for the photocatalytic degradation of rhodamine B dye (Submitted OM-D-23-00607, *Optical Materials*, 2023).

Research visits and summer school attendance

- MINTEK, advanced materials division, nanotechnology innovation center (NIC) 21 May – 24 October 2020: The purpose of the visit was to receive training on laboratory principles and techniques related to nanobiomedical technology. This was a form of preparation to carry out antibacterial studies using silver oxide, silver sulfide, and silver chloride nanoparticles. The findings positively confirmed the antibacterial activity of silver-based nanoparticles against Gram-positive and Gram-negative bacteria. The results are reported in the thesis.
- MINTEK, advanced materials division, nanotechnology innovation center (NIC) 16 March – 27 September 2021: The purpose of the visit was to fabricate polysulphone supported thin-film composite and thin-film nanocomposite membranes and evaluate their performance characteristics in terms of permeate flux, stability, salt rejection, as well as resistance towards organic fouling and biofouling. Fourier transform infrared spectroscopy analysis and atomic force spectroscopy of the membranes was also done. All these results are included in the thesis.
- European school on nanoscience and nanotechnology (ESONN), organised by Université Grenoble Alpes, France 28 August – 10 September 2022: The purpose of my visit to France was to participate in the ESONN programme. The first week of attendance was predominantly set out for master classes related to nanoscience and bionanotechnology, which included topics such as biosynthesis of nanomaterials as well as drug delivery. The second week entailed visits to the French national centre for scientific research, French alternative energies and atomic energy commission, Institute of structural biology, and the European neutron source. Here we had technicians who facilitated training workshops on state-of-the-art analytical and materials characterization techniques.

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Chapter 1: Background of research

1.1. Introduction

The desire for safe and consistent water supply has increased due to rapid population growth [1] and diminishing sources of water as dam levels drop annually [2]. Water scarcity can be defined as inadequate volumes of fresh water available to meet demands, which can be caused by inappropriate allocation of potable water, infrastructure mismanagement and contamination of natural water bodies [3]. In addition, unpredictable rainfall patterns contribute largely to fluctuating dam levels and water-use restrictions [4]. Access to safe water enables domestic, economic, and industrial activities of importance to take place, for which treatment methods such as desalination have been developed due to abundance of seawater on earth [5]. In South Africa, coastal cities such as Cape Town, Grahams Town and Richards Bay have experienced water shortages due to reasons formerly mentioned and have turned towards desalination [6]. One of the leading technologies for desalination is membrane technology, which is used for separation of salts and natural organic matter in brackish and/or seawater [7]. Reverse osmosis (RO) has become a leading tool for seawater desalination due to excellent physicochemical and separation properties. These include chemical stability, high salt rejection and good permeate flux [8]. In addition, the overall cost of desalination plant operation has been observed to drop by approximately ten folds over the past ten decades. This is mainly due to the implementation of hybrid conventional and renewable energy supply systems.

A challenge associated with seawater reverse osmosis (SWRO) is fouling, which deteriorates membrane integrity and efficiency, as well as quality of the permeate. Ultimately membrane life span is shortened, which increases operational costs due to frequent membrane replacement [9]. Membrane fouling is often caused by adsorption, accumulation and crystallisation of microbials, organic and inorganic constituents, respectively, found in feed water. [10]. Membrane fouling can be categorised as biofouling (microbials and extracellular compounds), organic fouling (natural organic matter) and scaling (calcium carbonate) [8]. Endeavours to mitigate membrane fouling include pre-treatment of the feed, surface modification and the development of nano-enhanced membranes (NEMs) [11]. NEMs have been developed by the coalescence of NPs such as graphene oxide (GO), carbon nanotubes (CNTs) [12], as well as metallic NPs such as

molybdenum disulfide (MoS_2) [13] with membrane thin film composites (TFC) to form thin film nanocomposites (TFN). Modern TFC membranes consist of a $\pm 20 \mu\text{m}$ thick PA layer while TFN membranes, of similar thickness, have nanostructured materials within the PA layer. Therefore, high levels of plant efficiency can be achieved by the integration of NEMs, which introduce robustness, high water throughput, and bestow antifouling properties to RO membranes [14]. Furthermore, research interest has grown around incorporation of metallic nanomaterials (i.e. silver) in SWRO membranes and has led to breakthroughs in desalination processes [15]. This creates a bacteriostatic TFN interface.

Gao et al., reported on the engineering of Ag-nanoparticle-encapsulated intermediate layer by tannic acid-inspired chemistry. Their aim was to fabricate TFN membranes of superior antibiofouling property. A water flux of $34.38 \pm 1.2 \text{ L/m}^2\text{h}$ and NaCl rejection of $98.12 \pm 0.3 \%$ were obtained at operating pressure of 224.8 Psi. The antibiofouling property was evaluated using the plate-counting method and revealed that proliferation of bacteria was significantly reduced with increased nanoparticle loading [16]. Related work was done by Bian et al., whereby polyamide TFN were fabricated using hollow phenolic resin nanospheres (HPS) and silver NPs immobilized HPS (Ag/HPS) as nanofillers. It was found that the water fluxes of TFN-HPS and TFN-Ag/HPS membranes were 80% higher than TFC membranes without nanofillers. Moreover, TFN-Ag/HPS demonstrated good long-term stability, achieved a flux recovery rate of 91.4%, and had resistance to biofouling of 96.7% against *Escherichia coli* [17].

Ahmed Al Mayyahi provided insights on thin film composite fabrication for enhanced performance. It was emphasized that the choice of monomers, surface modification of the PA layer, and the coalescence of NPs with the active TFC layer exhibited potential to significantly influence RO membrane performance [18]. A direct benefit observed from immobilization of NPs were the retardation of biofilm formation and deposition of dissolved organic matter on the membrane-water interface. [19]. Ideally, nanomaterials used in enhancing fouling resistance should be photoactive, bioactive and have low levels of cytotoxicity. In this study, TFC was coalesced with silver-based NPs to form TFN to improve water flux, salt rejection, fouling resistance and stability of the RO membrane. This innovative technology holds the potential to propagate efficiencies of water-cleaning process and contribute towards cost effective provision of global water security.

Silver and silver based (i.e. silver oxide, chalcogenide, and halide) NPs are known to have excellent antimicrobial properties, and have been proven to enhance performance characteristics of cosmetic and wound-healing products [20]. Silver-based NPs are semiconductors with good optoelectronic properties, are plasmonic, are stable, and have low cytotoxicity [21]. These properties make them useful in food safety technology, bionanotechnology and catalysis.

1.2. Problem statement

Seawater reverse osmosis (SWRO) has proved to be a viable method for desalination. A limitation to the sustainable use of this technology is membrane fouling by natural organic matter (i.e., humic substances), scaling (i.e., calcium carbonate) as well as microbials (i.e., *Pseudomonas*) found in seawater [22]. The observed fouling deteriorates membrane integrity, in which decreased permeate flux, salt rejection, permeate quality and membrane lifetime are apparent [15]. Moreover, membrane fouling increases the pressure and energy required to achieve targeted pure water throughput volume. Henceforth, the incorporation of nanomaterials offers the advantages of retarding the adverse effects of fouling, which in turn enhances membrane performance over time.

1.3. Rationale and motivation

Fluctuations in seasonal rainfall have been observed in South Africa and in surrounding regions, which contributes to water crises observed in recent years. Taking advantage of the vast coastline by tapping into seawater as a source for freshwater can provide more sustainable solutions to water shortages experienced in several residential and industrial areas. Therefore, the development/modification of RO membranes to enhance their efficacy can raise confidence in the desalination industry. Membrane technology has become a leading tool for seawater reverse osmosis (RO), aimed at curbing the dire effects of freshwater scarcity. RO membranes tend to suffer from fouling, a phenomenon where microbes and organic matter found in seawater adhere to the membrane surface. RO membranes have been modified to counteract fouling by moving away from cellulose-based membranes towards polyamide thin-film composite (TFC) membranes. The PA layer may be formed on a polysulfone or polyethersulfone support membrane. Polysulfone is a thermoplastic polymer consisting of repeating units with a sulfone group, while polyethersulfone is a thermoplastic polymer consisting of subunits of aryl-SO₂-aryl.

Due to the non-polarity of the aryl groups, polyethersulfone is relatively less polar compared to polysulfone. Therefore, polysulfone was selected as a suitable support for the active PA layer. However, TFC membranes do not fully address fouling and still require frequent replacement [8]. This in turn increases operational costs of desalination plants. The current work seeks to investigate the immobilization of silver sulfide nanoparticles on polyamide TFC membranes to form thin-film nanocomposites (TFN), with the intent to mitigate fouling, improve salt-separation and water through-put characteristics.

1.4. Aim and objectives

To synthesize nanoparticles of Ag_2S , Ag_2O and AgCl for photocatalytic and bacteriolytic studies, as well as their incorporation in polymeric membranes. To achieve the end-goal, the following objectives will be heeded to:

- Synthesis of size controlled Ag_2S , Ag_2O and AgCl nanoparticles via heat-up colloidal, hydrothermal, and hot-injection colloidal methods, respectively.
- Characterization of as-synthesized nanoparticles using X-ray, absorption, and emission spectroscopy, as well as microscopic techniques.
- Application of nanoparticles in the photocatalytic degradation of humic acid and antimicrobial studies against *Escherichia coli* and *Staphylococcus aureus*.
- Fabrication of TFC and TFN reverse RO membranes via interfacial polymerisation.
- Characterization of TFC and TFN reverse osmosis membranes using Fourier transform infrared spectroscopy, water contact angle analyser, as well as scanning electron and atomic force microscopy.
- Evaluation of permeate flux, salt separation, stability, and antifouling properties of membranes using a crossflow system at a pressure of 250 pounds/square inch.

1.5. Thesis outline

This thesis is presented in seven (8) chapters.

- Chapter 1 generally describes the focus of this study, the associated challenges, rationale and motivation for the study, the thesis outline, as well as the aim and objectives of the study.
- Chapter 2 highlights recent advances in membrane technology for desalination, and the properties of semiconducting nanoparticles that make them suitable for photocatalysis, antimicrobial studies, and their role in the development of fouling resistant reverse osmosis membranes. The fate of nanoparticles in the environment and their cytotoxicity are also discussed.

- Chapter 3 underscores the experimental and characterization techniques used for synthesis of Ag₂O, Ag₂S, and AgCl nanoparticles, as well their applications in photocatalytic degradation of humic acid and anti-microbial studies. The method used to determine cytotoxicity of nanoparticles was also outlined.
- Chapter 4 illustrates the characterization of Ag₂O, Ag₂S, and AgCl NPs. The optoelectronic properties, X-ray diffraction patterns, particle sizes, and presence of organic moieties on crystal facets emanating from capping agents used during synthesis were investigated. The conclusion on this section is also provided.
- Chapter 5 documents the results (efficiency %) obtained from applications of NPs in photocatalytic degradation of humic acid in aqueous solution. Solar simulated light was used as a source of photons for the generation of excitons. The conclusions deduced from this study are provided.
- Chapter 6 reports on observations made obtained from antibacterial studies, using Gram-positive and Gram-negative bacteria as specimen. Cytotoxicity studies of the as synthesized nanoparticles were also reported, where human embryonic kidney cells were used as specimen. Conclusions drawn from this chapter are included.
- Chapter 7 covers the fabrication method and characterization of TFC and TFN reverse osmosis membranes, as well as their performance characteristics in terms of salt rejection, permeate flux, stability, as well as fouling resistance against *Escherichia coli* (biological) and bovine serum albumin (organic). The conclusions made from reported investigations are also listed.
- Chapter 8 provides general conclusions drawn from investigations conducted throughout the study, coupled with some recommendations to improve and/or expand the study.

1.6. References

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Chapter 2: Literature review

2.1. Introduction

The dire effects of climate change have been observed over recent years, where deviations in rainfall patterns, increased number of non-perennial rivers and elevated surface temperatures were reported [1]. These factors result in reduced water tables and a limited number of perennial rivers as water sources for potable water [2]. Planet Earth is made up of 29% land, and 71% water. From the 71%, the oceans hold approximately 96.5% of all water on Earth. The remainder of the 3.5% is what constitutes freshwater. Freshwater is referred to as water that contains little to no dissolved salts, of which 70% exists as glaciers and icecaps, 29% as groundwater, and 1% as accessible freshwater from lakes, rivers, as well as in the form of soil moisture and water vapour [3]. A visual depiction of these statistics and locations of water sources can be observed in Fig. 2.1.

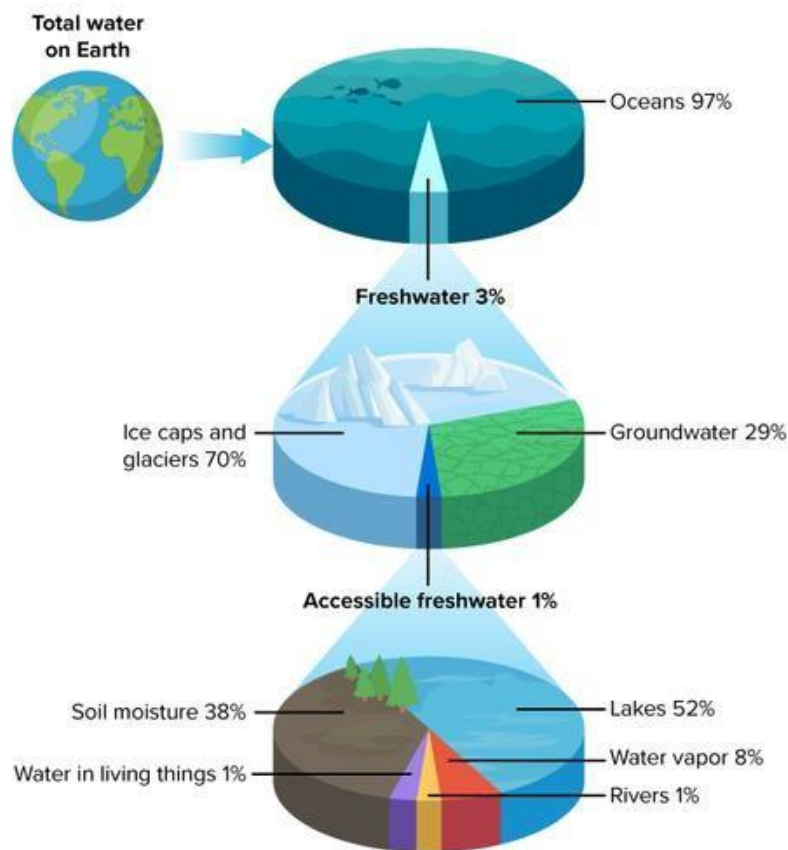


Figure 2.1. An illustration of global water storage and distribution locations [4].

Considering the impact of population growth, the demand for freshwater has immensely increased in order to meet socioeconomic needs. This has prompted the investigation of

alternative water sources, with brackish and seawater being the most promising [5]. However, these water source have high/toxic levels of salinity (10000-40000 mg/L) and cannot be directly used. Therefore, a desalination process should be applied prior consumption or industrial use. The two common methods for desalination are reported to be thermal, as well as membrane filtration or reverse osmosis (RO) methods. Both these methods are capable of producing potable water in large quantities. However, the rate of production, financial implications, and environmental impacts of these methods differ significantly [6]. The international desalination association (IDA) reported that there are approximately 18000 operational desalination plants globally, which collectively have a capacity to produce close to 96 million cubic meters of potable water per day (m^3/day). Despite this fact, and despite the enormous abundance of seawater, desalination accounts for just over 7-8% of the world's drinking water [7]. Nonetheless, these statistics are projected to double by the year 2035 as much research is invested in improving the efficiency, cost effectiveness, and environmental footprint of desalination.

2.2. Desalination

The increase in global desalination capacity is inevitable, as more countries around the world ramp up their endeavours to avail more freshwater to their compatriots. These efforts will increase water security and alleviate competition which currently exists for this commodity. Desalination has developed and become adopted differentially across the globe as some regions experience water shortages variably due their hydrogeography and hydrologic cycles [8]. Moreover, this may also be influenced by a region's altitude, latitude, and longitude, as these factors significantly influence climate conditions. For instance, the Middle East region is a global leader (about 45% of total desalination) in implementing this technology as it is known to be arid. This has made it possible for this region to reduce food imports, as well as improve supply of potable water for its inhabitants. The second-leading region is North America (15%), followed by Europe (12%) and Asia (10%) [9]. To a certain extent, economic strength and political will can influence the earnestness to adopt desalination technology, as its implementation is still regarded as cost intensive. A graphical illustration of these statics is shown in Fig. 2.2.

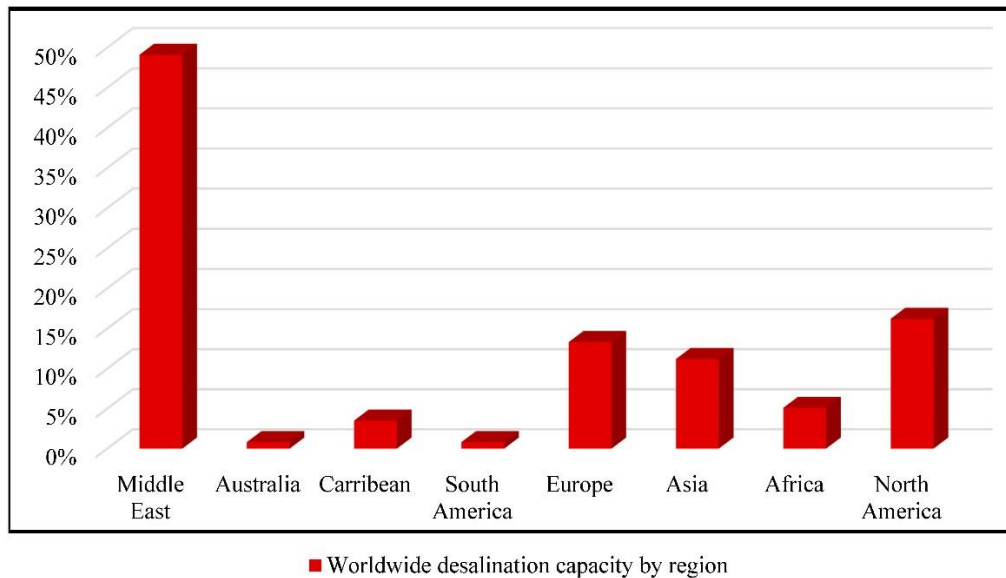


Figure 2.2 Regional desalination capacity of the world [10].

Notwithstanding that the African continent is 40% arid, the African region accounts for roughly 5% of the world's desalination capacity. About 50% of the population lives in water scarce areas, which debilitates them to thrive in socioeconomic development. Furthermore, the likelihood of malnutrition, viral transfer and high mortality rates among deprived societies is elevated [11]. Water obtained from desalination methods is of a superior quality because it simultaneously becomes disinfected. It is therefore empirical for the African region to prioritize desalination, which will relieve drought, improve food security, usher in opportunities for industrialization, and alleviate poverty.

2.2.1. Thermal desalination techniques

Thermal desalination technology is far older than desalination by membranes, with the first plant being commissioned during the year 1928 on the island of Curaçao in the Netherlands Antilles. In fact, the process of extracting salt from water dates from way back when the aim was recovering salt and not pure water [12]. In the current decade, thermal desalination processes account for 34.3% of the world's desalination capacity. This can be further divided into two main groups; (a) evaporation followed by condensation of the water vapour, and (b) freezing followed by the subsequent melting of water crystals. Group (a) was much more popular and comprises of multistage flash (MSF) distillation, humidification and dehumidification, mechanical vapour compression, and multiple effect distillation (MED) [13].

These processes require continuous heating of saline water, either through the combustion of fossil fuels or electrically heated coils and heat-transfer tubes. It is inevitable to have corrosion and scaling of the heated vessels containing feedwater, which increases the overall cost of operation. It is therefore evident that thermal desalination methods have a high carbon footprint and cannot be used as environmentally sustainable tools for the provision of large quantities of freshwater [14]. Despite MSF being a more common method, MED is expected to take over the market share. This is due to higher efficiencies and cost-effectiveness of MED, owed to the optimization of thermodynamic and mathematical models for plant operation [15]. Fundamentally the performance ratio in MED increases with the number of effects. The vapours produced in the first effect are used to heat up the evaporating tubes in the second effect, thus propagating condensation. A focus on desalination plant economics has led to the development of hybrid desalination systems that comprise of MED and membrane distillation. It was reported that the operating cost of the hybrid system was 17% lower than the standalone MED system and achieved a water recovery ratio of 52% [16]. A schematic diagram of the MED thermal desalination process is shown in Fig. 2.3.

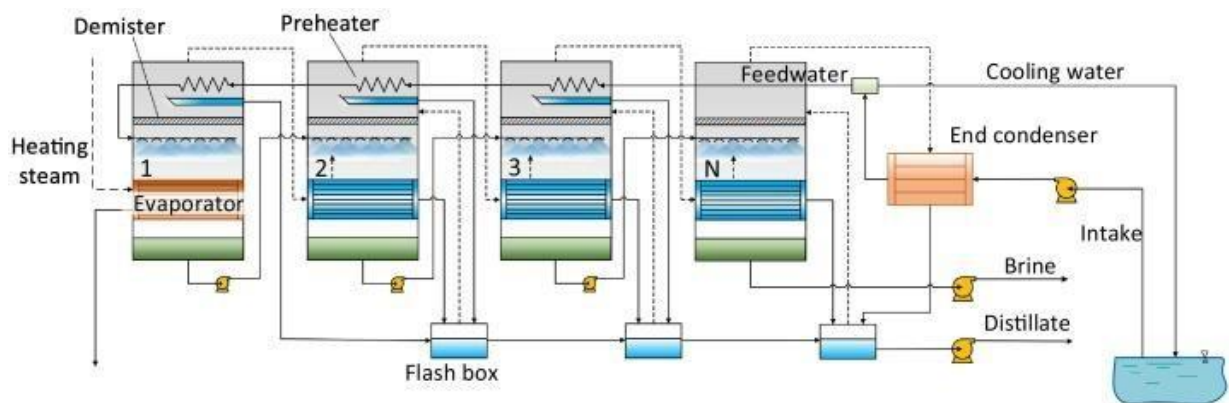


Figure 2.3 Schematic representation of the MED thermal desalination technique[16].

2.2.2. Desalination through membrane technology

Membrane technology for desalination purposes initially received attention in the early 1960's, where the first commercial desalination plant to use RO was commissioned in California at the Coalinga desalination plant in 1965 [17]. Membrane technology operates on the bases of a semipermeable barrier between two homogenous phases, which prevents solutes in the feed (i.e., dissolved ions) from passing through to the permeate.

The driving force for separation is usually an applied pressure [18], and this can also be assisted by an applied electrical current or temperature [19]. RO is predominantly inspired by the natural process of osmosis, where solutes migrate from a region of high concentration to a region of low concentration through a semipermeable membrane [20]. However, when the proportion of applied pressure exceeds the osmotic pressure the 'reverse' is achieved. RO systems are capable of purifying water to have total dissolved solids (TDS) of less than 50 ppm [21]. As per requirements from the world health organization (WHO), permissible levels of TDS in drinking water are 600-900 ppm. However, excellent water quality has TDS levels in the range 50-300 ppm [22].

Therefore, the RO desalination process is useful in producing high quality water for industries such as pharmaceuticals, food, and beverages, as well as biomedical technology [23]. Desalination membranes can be homogenous or heterogenous, symmetric, asymmetric and are usually polymerised on a support layer to form a thin-film composite (TFC). Examples of materials used to form TFC include cellulose acetate (CA) and polyamide (PA). CA is a synthetic compound that is made by acetylation of the natural polymer cellulose. These are what constitute the active boundary layer responsible for the restriction of dissolved ions. Commonly used supports are polyethersulfone (PES) [24], polyethylene (PE) [25], and polysulfone (PSF) membranes [26]. A few designs for desalination systems have been developed in the past decades, with electrodialysis processes [27], as well as the dead-end, and crossflow modules being most popular. In many instances, hybrid systems of dead-end and crossflow are utilized in desalination plants [28]. These two systems are discussed with more detail in the subsections below. In general, desalination membranes are required to have good mechanical strength, high water permeability, hydrophilicity, as well as fouling resistance towards dissolved organic matter and microbes [29].

2.2.2.1. Dead-end filtration systems

The dead-end system (also known as normal flow filtration) is regarded as the most basic filtration systems in operation. In this system, feed water is forced through membranes at an angle perpendicular to the membrane surface [30]. Nitrogen gas is usually used to create a pressure gradient within an airtight cell. The stirred cell is often equipped with a Teflon-coated magnetic stirrer to minimize concentration polymerization. Dissolved ions

in the feed are retained on the membrane surface by size exclusion, and to some extent by the Donnan exclusion effect. This subsequently leads to the accumulation of particles on the surface, also known as membrane caking or fouling [31]. The observed fouling is often exacerbated by the number and size of solutes present in the feed water. In addition, this leads to the clogging of membrane pores and reduces the transmembrane water flow. It is therefore necessary to place a feed pre-treatment system before allowing contact between the feed water-membrane interface [32]. This phenomenon is more prevalent with dead-end filtration systems compared to crossflow filtration systems because nearly 100% of dissolved solutes end up on the membrane surface. Thus, newly commissioned treatment plants are fitted with mechanical self-cleaning screens to restore membrane performance [33]. In the case of a crossflow filtration system, the flow of the feed and concentrate are parallel to the membrane surface. This acts as a 'cleaning mechanism' which slows the rate of fouling and gives longer intervals of good membrane performance. A schematic diagram of the dead-end filtration system is shown in Fig. 2.4.

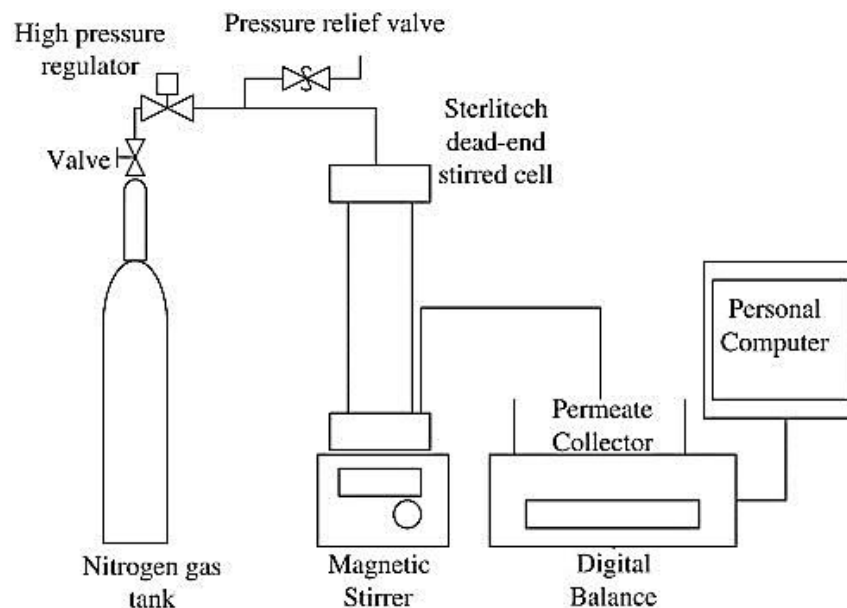


Figure 2.4 Schematic diagram showing the dead-end stirred cell system [28].

2.2.2.2. Crossflow filtration systems

Crossflow filtration systems (Fig. 2.5), alternatively known as tangential flow systems, have been extensively used for desalination, mainly due to the many advantages offered versus dead-end filtration systems. Crossflow filtration systems require less applied pressure and have a higher water recovery [34]. Moreover, the continuous circulation of feed water at high velocity significantly reduces concentration polarization and fouling

propensity at the water-membrane surface interface. In addition, this recirculation allows larger quantities of feed water to be processed per unit time [35]. The process is referred to as 'crossflow' because the feed water and concentrate (which flow parallel to the membrane surface) flow perpendicular to the permeate [36]. The most common applications of crossflow filtration systems for desalination are RO and nanofiltration (NF). The porosity of membranes used in these applications increases in the listed order of (0.1-1 nm) and (0.2-2 nm), respectively. Moreover, the required operational pressure is inversely proportional to increasing pore size [37]. RO membranes in crossflow systems are also prone to fouling, which leads to a decline in water flux. An attempt to restore water flux can be done by increasing the applied pressure. However, this poses a risk of collapsing the macrovoids of the PSF support layer and cause a further decline in membrane performance. Ultra-high pressure can lead to embossing, which leads to deformation of the active layer and a loss of salt rejection. It is therefore necessary to regulate the transmembrane pressure to maintain good RO membrane performance [38].

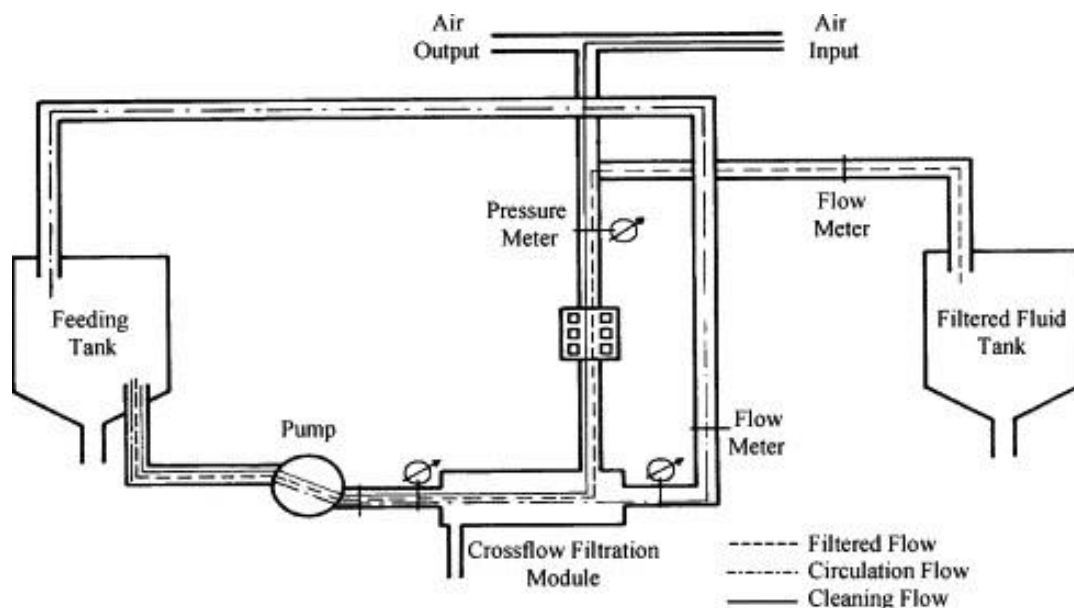


Figure 2.5 An illustration of a typical crossflow filtration process [39].

On an industrial scale, the most common crossflow filtration systems used for RO are hollow-fibre-based separation units [40] and spiral wound (SW) module [41]. However, the SW module is preferred because they are more resistant to fouling, have more tolerance to water pressure, and can handle larger quantities of water. The source of feed water is often brackish water or seawater, which have salinity levels of 500-3000 ppm and 33000-37000 ppm [42]. SW modules consist of several flat sheet TFC membranes stacked

with feed spacers in between and a permeate carrier, which are wrapped around a permeate-collecting tube. The feed spacers assist to create a turbulent flow between membrane sheets to minimize fouling, reduce resistance of water flow through the module, while the permeate-collecting tube ensures that the concentrate and permeate do not come into contact [43]. A schematic of a SW module compartment is on Fig. 2.6.

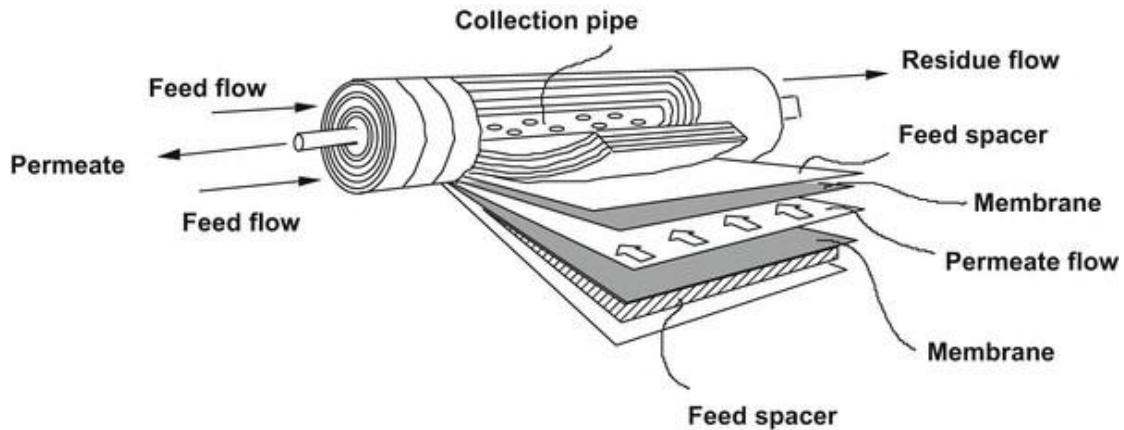


Figure 2.6 Schematic representation of a spiral wound SWRO module [44].

Nonetheless, seawater reverse osmosis (SWRO) membranes are still prone to fouling by particulate matter, NOM, and microbes found in seawater. The fouling reduces water flux, salt rejection, and necessitates higher operational pressure, which increases the required energy to perform adequate RO [45]. Several prefiltration methods (i.e., coagulation, microfiltration, and granular activated carbon filtration) have been incorporated into SWRO plants [46]. However, this precaution is not fully able to address the problem of membrane fouling. This has led to the re-evaluation of TFC membranes and development of TFN membranes, that have nanomaterials/nanofillers in the active layer. These nanofillers are usually photoactive and bacteriolytic, and have been reported to significantly improve membrane separation performance by minimizing fouling [47]. A few nanofillers that have previously been reported on are discussed in the next section.

2.3. Fouling

Membrane fouling in RO technology is a result of the deposition of particulate matter, solute macromolecules, and microbes on the surface of membranes or within the pores of diffusional pathways [48]. Following gradual deposition of foulants, the pore size becomes constricted and build resistance to water throughput. Fouling could be reversible or irreversible depending on if cleaning requires physical or chemical means, respectively. Physical cleaning methods include backwashing with air, backwashing without air, and relaxation. These are less complex than chemical cleaning and are less likely to cause membrane degradation. Chemical cleaning can be achieved by flushing the membrane module with a base (i.e., caustic soda), an acid (i.e., sulphuric acid), or an oxidant (i.e., hydrogen peroxide). Generally, chemical cleaning methods are more efficient as they can yield high flux recovery [49]. Biopolymers and particulate matter are reported to be behind reversible fouling, while low molecular weight molecules are mainly responsible for irreversible fouling. In addition, fouling creates a pressure drop across the membrane, which increases energy consumption of desalination plants required to meet targeted flux and deteriorates permeate quality over a period of time [50].

There are five main interactions that may either promote or minimize membrane fouling, namely, surface charge, surface roughness, hydrophilicity/hydrophobicity, feed water pH, and ionic strength. When solutes have similar charge to the membrane surface they are repelled by electrostatic forces. As observed on Pourbaix diagrams, solution pH affects the charge, thermodynamic stability, and speciation of solutes in aqueous media [51]. RO membranes are required to be hydrophilic to deter hydrophobic foulants from adhering to the surface. Moreover, it is necessary for the ionic strength of the feed to be low so that adsorbed molecules can repel each other at the surface [52]. Low average surface roughness has been reported to reduce the surface area on which foulants can foul the membrane [53]. Another contributor towards membrane fouling is concentration polarization. This is explained by the continuous transport of feed water to the membrane surface coupled with preferential/selective retention and accumulation of solutes (i.e., salts). The build-up of solutes creates a boundary layer of higher concentration. This occurs externally at the water-membrane interface, as well as internally between the thin-film composite layer and the porous support membrane [54].

The issue of membrane fouling during SWRO has prevailed for several years, which has severely impacted the economic viability of the process. However, this is a phenomenon as biofoulants and organic foulants are ubiquitous in seawater. Noteworthy strides in the improvement of membrane design have been made, as well as in the holistic desalination process. These include intrinsic properties of membranes (i.e., chemical composition and structure), optimization of membrane fabrication parameters, optimization filtration process parameters (i.e., feed flow rate), as well as the surface area of the membranes [55]. For the fabrication of TFN membranes, popular choices of nanofillers are carbonbased nano materials (i.e., graphene oxide and carbon nanotubes) as well as metallic NPs. Several researchers have reported on the coalescence of carbonaceous nanomaterial and metallic NPs, as well as their inclusion in the active layer for form TFN membranes [56].

2.3.1. Carbonaceous nanomaterials as nanofillers

Carbon-based nanomaterials such as graphene oxide (GO) and carbon nanotubes (CNTs) have been reported to have high thermal and electrical conductivity, good elasticity and flexibility, as well as high tensile strength. GO is an oxidized derivative of graphene, which is comprised of a single layer of graphene sheet. The edges of GO sheets are covalently bonded to oxygen-containing functional groups such as quinone, lactone, carbonyl, and carboxyl groups. Due to the structure of GO, it has been reported that the basal planes are attached to hydroxyl and epoxy groups. Like GO, CNTs are formed by a layer of carbon atoms that are bonded together in a honeycomb structure. The one-atom thick carbon layer has a cylindrical shape; hence it is termed to be a tube. CNTs can be single-walled or multi-walled, which have a size range of 0.5-2.5 nm and 7-100 nm, respectively. Due to their properties, these materials have featured in electrochemistry, corrosion inhibition, and separation applications. Moreover, their hydrophilicity and low cytotoxicity levels make them applicable in biotechnology, where they have been used for drug delivery, cell imaging, and cancer treatment. An illustration of how GO nanosheets are chemically derived from graphite and their appearance is presented in Fig 2.7. (a-b).

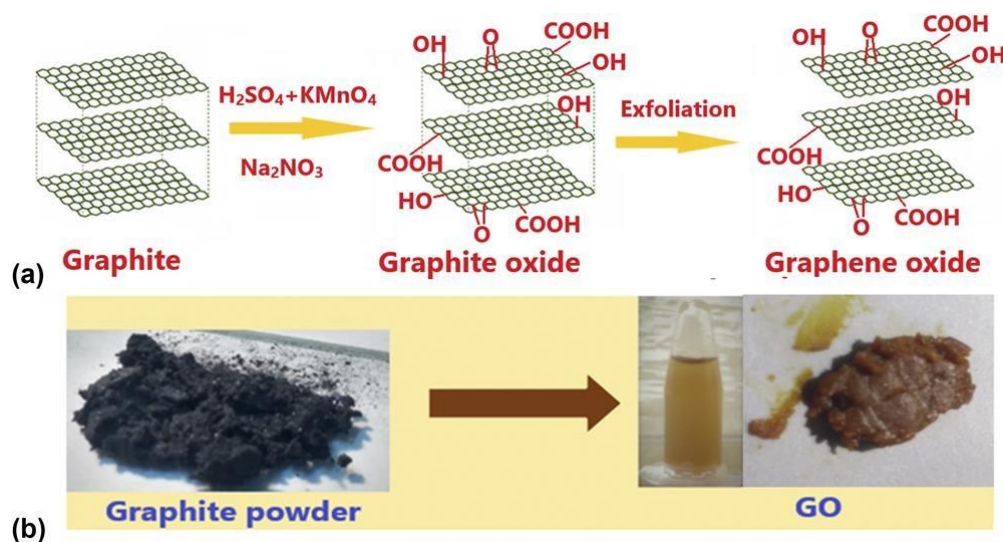


Figure 2.7 (a) Hummer's method for synthesis of GO nanosheets, (b) appearance of GO [57].

For separation processes in particular, the use of carbon-based materials has become popular in RO membrane modification to form TFN. Examples of such materials include single and multi-walled carbon nanotubes (CNTs) and (MWCNTs), zeolites, graphene and graphene oxide [58]. These types of TFN have been at the forefront of desalination membrane technology in recent years due to properties such as small pore size, good electrical conductivity, improved flux recovery, stability in acidic and alkaline conditions, high salt rejection, hydrophilicity, and mechanical stability over prolonged exposure to saline solutions [5]. A report demonstrating this feasibility was done by Ng et al., where a new interlayer-assisted interfacial polymerization method was adopted, and GO was incorporated in the polyamide layer. The polyethyleneimine (PEI) interlayered thin film composite (iTFC) membrane exhibited higher pure water permeance (PWP) of 1.76 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$ and salt rejection of 97.7%, compared to the conventional TFC (cTFC) membrane (1.34 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$; 96.9%). This was owed to the thin and compact PA layer formed. Furthermore, the performance of iTFC was observed to improve following the incorporation of 0.001 wt/v% of GO, producing PEI-interlayered thin film nanocomposite (iTfN-10) membranes with PWP of 2.66 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$. This was allotted to the enhanced surface roughness, hydrophilicity, and nanochannels created by GO within the PA layer. The antifouling property of iTfN-10 membrane was similar to that of commercial TFC but was better than that of the iTFC membrane. Moreover, iTfN membrane exhibited better antibacterial properties (*E. coli*: 44.3% and *S. aureus*: 77.6%) compared to commercial

TFC (*E. coli*: 24.7% and *S. aureus*: 50%) [59]. A theoretical schematic cross-sectional diagram of the three fabricated membranes is demonstrated in Fig. 2.8.

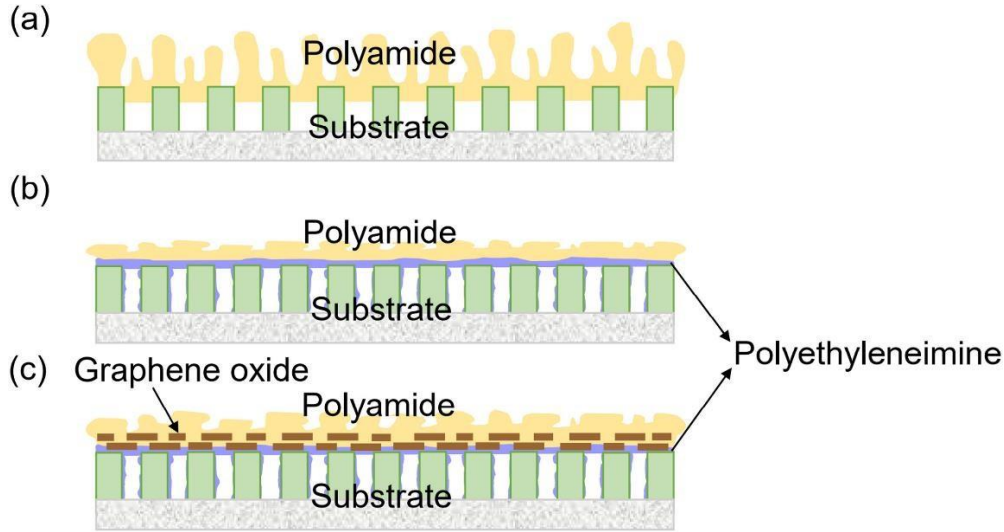


Figure 2.8 Cross-sectional schematic of (a) TFC, (b) iTFC, and (c) iTFN membranes [59].

In the context of coalescing GO with metallic NPs, El-Gendi et al., synthesized hydrophilic RO membranes from cellulose acetate/graphene oxide/AgNP (GO/AgNP) and cellulose acetate/graphene oxide/Ag-CuNP (GO/Ag-CuNP) for desalination applications. The biofouling inhibition on membrane surfaces was ascribed to the presence of nanoparticles [60]. The effect of applied pressure and saline (sodium chloride) concentration was varied between 0-35 bar and 5-10 g/L, respectively. It was observed that GO/AgNP and GO/Ag-CuNP loaded membranes were optimum at 15 and 35 bar, respectively. Salt rejection increased by $\pm 30\%$ for NP-loaded membranes compared to the unloaded membranes. Membrane flux also improved with NP loading, which was mainly dependent of the applied pressure. The total flux of the tested solutions was evaluated using equation (2.1)

$$J = Q(A \times T) \quad (2.1)$$

Where J denotes flux (kg/hrm²), Q, A and T represent the permeate mass (Kg), membrane area (m²) and time (hrs), respectively. On the other hand, salt rejection was determined using equation (2.2). Where C_f and C_p is the concentration of the feed and permeate, respectively.

$$R_s = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2.2)$$

Advantages have been offered by the inclusion of carbon-based materials in desalination membranes, however, limitations in membrane durability exist due to fouling propensity [11]. Moreover, the interlayer spacing of GO nanosheets can swell during dry and hydrated conditions from 7.7 Å to 17.7 Å, respectively. As a result, when salt ions dissociate the diameters of hydrated ions are smaller than 17.7 Å. This phenomenon causes a decline in salt rejection when TFN membranes are exposed to water for long periods of time [62].

2.3.2. Metallic nanoparticles as nanofillers

Nano-sized materials are known to have dimensions of 1-100 nm and have been reported to possess interesting crystallographic, optical, and electronic properties [63]. One of the best advantages of NPs is a high surface-to-volume ratio, which permits more contact with species within their environment per unit time. The engineering of nanostructures has enhanced efficiencies in a wide range of applications, which include bacteriolysis, catalysis, nanobiotechnology, water purification, and gas sensing. The potential for NPs to be used as bacteriolytic agents has been widely studied, with indications that metallic NPs significantly mitigate bacterial cell proliferation [64]. This creates an opportunity to deploy NPs on TFN membranes as nanofillers to counteract biofilm formation, and retard biofouling. Fig. 2.9. depicts the sequences of events leading to biofouling on membranes.

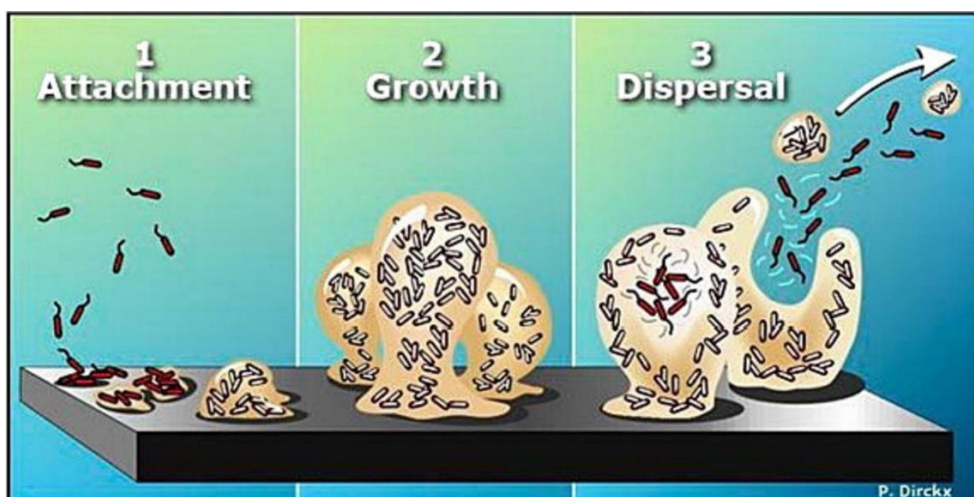


Figure 2.9 Proposed mechanism of biofilm formation on RO membrane surfaces [65].

Various mechanisms have been postulated for the pharmacokinetics of metallic NPs (i.e., silver or silver oxide) in microorganisms, which include; (i) the adhesion to and partial

destruction of the bacterial cell wall, (ii) gradual liberation of oxidative silver ions (Ag^+) from NPs leading to oxidative stress, and (iii) formation of reactive oxygen species (ROS) which disorientate regular DNA functions of the bacterial cell [66]. Considering the release of Ag^+ from NPs, which possibly leach into the permeate, the scientific community has raised concerns regarding cytotoxic effects. To address these concerns, Huo et al., reported on fabrication of TFN membranes with in-situ integration of functional NPs in the PA layer for high performance RO (Fig.2.10).

The nanofillers of choice were biomimetic nanoparticles (BNPs) and silver nanoparticles (AgNPs) to simultaneously optimize the membrane surface property and regulate its microstructure. The TFN membranes were fabricated through interfacial polymerization (IP), and the concentration of silver nitrate in the aqueous phase was varied between 210 mM. To assess the extent of Ag^+ liberation, a continuous examination was done over a 14-day period. The permeate was analysed using the inductively coupled plasma (ICP) technique. It was observed that the initial release rate (day 1-6) was directly proportional to AgNP loading, then a plateau was attained from day 7-14. The cumulative amount of Ag^+ detected in the permeate by the 14th day was $0.347 \mu\text{g/L}$ [67].

This amount was far below the limit ($100 \mu\text{g/L}$) determined by WHO for Ag ions in drinking water [22]. In addition, TFN membranes fabricated using 10 mM AgNO_3 were determined to have enhanced hydrophilic, biofouling resistance, flux recovery against bovine serum albumin (BSA), and salt rejection properties compared to TFC. This observation demonstrates improved robustness of TFN, attributed to AgNPs.

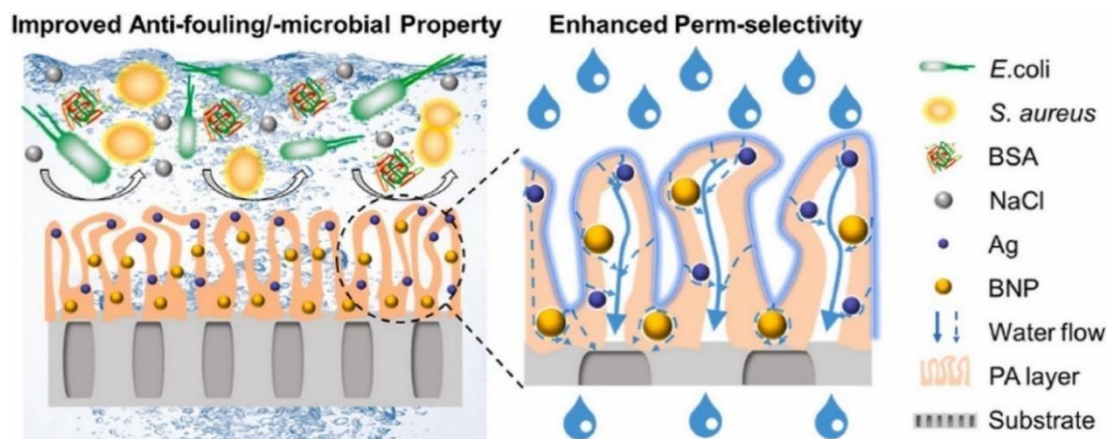


Figure 2.10 Hypothetical antifouling mechanism of AgNP loaded TFN membranes [67].

Bacteria is known as multicellular organisms which replicate in nutrient-rich environments to form a colony [68]. It is imperative to mitigate bacterial cell growth and inhibit potential spread of viruses and disease [69]. Moreover, microorganisms are known to secrete extracellular polymer substances (EPSs), which have been identified as contributors towards membrane fouling [70]. EPSs are high-molecular-weight natural polymers such as polysaccharides, lipids, nucleic acids and humic substances, which form part of natural organic matter (NOM) found in seawater [71]. Several pre-treatment methods such as chlorination, sand filtration, microfiltration (MF) and nanofiltration (NF) have been used to reduce levels of NOM in seawater prior (SWRO) to enhance their lifetime and permeate quality [72]. However, these methods were not able to sufficiently reduce NOM levels to quantities which decrease susceptibility to organic fouling. As a result, ultraviolet and visible light assisted photocatalysis using zinc oxide [73], titanium dioxide [74], copper oxide [75], silver oxide [76], zinc sulphide [77], silver sulphide [78], silver chloride [79] and non-valent silver NPs have emerged as useful tools of NOM degradation.

Some semiconductor NPs are known to have photocatalytic properties, capable of degradation of organic compounds in aqueous media through photodegradation. Photoexcitation is favoured when incident electromagnetic radiation has energy that is equal to or greater than the band gap energy (E_g) of the semiconductor [80]. When excited electrons lose energy and return to their ground state, photons are emitted as a form of fluorescence or photoluminescence. In semiconductor NPs, this observation is termed as electron-hole recombination. The charge carriers within semiconductors (photoelectron-hole pairs) permit discrete energy levels, also known as quantum confinement. The semiconducting properties and narrow band gap of nanoparticles permit facile electron transfer followed and radical (i.e., hydroxyl and superoxide ions) formation in during photodegradation [81]. Therefore, immobilization of metallic NPs on membranes to form TFN provides three advantages of enhanced resistance to biofouling, organic fouling, and mass transport of water [82]. An illustration of the photoelectron-hole pair formation and recombination leading to photocatalytic degradation of NOM is presented in Fig. 2. 11.

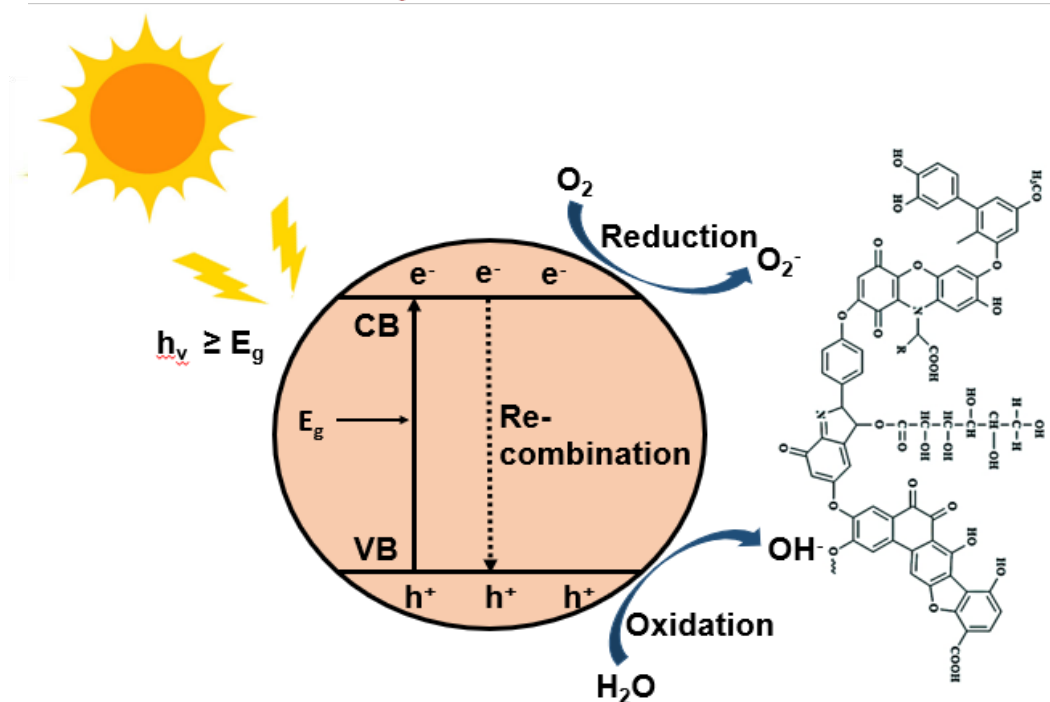


Figure 2.11. Schematic of NP charge carriers and photocatalytic degradation of humic acid

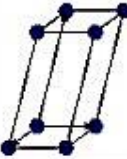
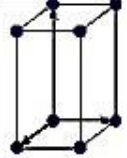
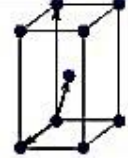
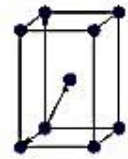
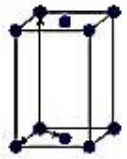
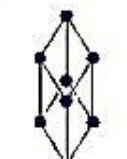
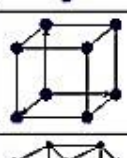
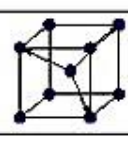
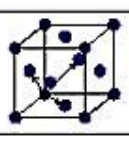
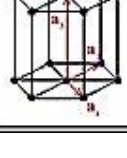
2.4. Nanoparticles

2.5.1. Properties

Nanoscience and nanotechnology have emerged as a significant research area of interest, mainly due to unique properties nanostructures have compared to their equivalent compound on a microscale or larger [83]. The engineering of nanostructures enables their utilization in a wide range of applications, which include bacteriolysis, catalysis, nanobiotechnology, water purification, and gas sensing. The synthesis of NPs can be achieved through physical (mechanical milling, chemical vapour deposition, spray pyrolysis, and inert gas condensation), as well as chemical (homogenous precipitation, thermal decomposition, colloidal synthesis, sol-gel, and microemulsion) methods [84]. Metallic NPs are highly crystalline, have crystal facets, and consist of one or more atoms (motifs) at each lattice point. Repetitive motifs in a crystal structure are referred to as unit cells, which are the smallest building blocks of a crystal system. Unit cells are classified as primitive and non-primitive. The former contains one lattice point, which is formed by lattice points at its corners. The latter consists of additional lattice points, positioned either on the face or within the unit cell [85]. The coordination numbers of motifs from primitive and non-primitive unit cells are six and eight, respectively. Motifs are also referred to as Bravais lattices, which are infinite arrays of discrete points generated by sets of discrete translational operations described in three dimensional spaces.

Bravais lattices are said to be equivalent in scenarios where they have isomorphous symmetry groups. There are fourteen possible Bravais lattices in a three-dimensional system, which emanate from two hundred and thirty (230) space groups. Space groups are mathematical derivations of ways in which crystals can be repeated through space (i.e., translation, rotation, gliding, and screwing) [86]. This implies that the orientation of a crystal can be alternated without changing the positions of the motifs. Table 2.1. depicts the Bravais lattices possible for three-dimensional systems.

Table 2.1. Bravais lattices of crystal systems [87].

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Silver based NPs (i.e. Ag₂O, Ag₂S and AgCl) have been widely synthesized using colloidal synthesis [88], homogenous precipitation [89] and thermal decomposition [90], [91] methods to produce well-dispersed NPs. Fakhri et al. [92] synthesized silver sulphide (Ag₂S) and copper-doped silver sulphide (Cu-Ag₂S) NPs by co-precipitation method in a 1:1 ratio of Na₂S and AgNO₃ at 0,001 M each. Characterization by XRD depicted sharp peaks with miller indices (111), (112), (121), (103), (031), (200) and (213). The crystalline diameter of the synthesized NPs was calculated using the Debye-Scherrer formula, represented in equation (2.3):

$$D = k\lambda/\beta \cos \theta \quad (2.3)$$

Where D is the crystalline to diameter, λ is the wavelength of incident X-rays, k is an integer, and θ is the diffraction angle. TEM micrographs showed ellipsoidal shaped NPs with particle size 30, 25 and 21 nm for Ag₂S, 6%Cu-Ag₂S and 10%Cu-Ag₂S NPs, respectively. Optical absorption spectroscopy determined band gap energy to be 3.38, 3.22 and 3.31 eV, in the same order as above, respectively. In another scenario, Patil et al., 2018. Biogenically synthesized silver-silver chloride (Ag-AgCl) NPs, using *A. Pilosa* extract as a stabilizing/capping agent. Diffractograms from powdered XRD showed sharp, well-defined peaks of AgCl at 2θ angles of 27.83°, 32.31°, 46.25°, 54.87° and 57.61° attributed to miller indices (111), (200), (220), (311) and (222) of face centred cubic (fcc) structure, respectively. Moreover, diffraction peaks of Ag NPs were found at 2θ values of 38.31°, 64.95° & 77.59° which correspond to (111), (220) and (311) fcc planes, respectively. UV-Vis spectrum showed a strong and narrow absorption peak at 454 nm, ascribed to small-sized Ag-AgCl NPs. EDX depicted peaks at 3 KeV and 2.7 KeV, which correspond to elemental silver and chlorine, respectively.

2.5.2. Size and shape engineering

The control of nanoparticle size and shape is influenced by several factors, which include precursor concentration, reaction temperature, time, and intensity of agitation. Formation of NPs involves nucleic kinetics in which growth is directed by the type of capping agents and their concentration [93]. In addition, the use of a mixture of two-to-three capping agents at different ratios can influence size and shape of NPs [91]. Semiconductor nanomaterials have inherent optoelectronic properties that differ from their bulk materials, where their absorption maxima ($\lambda_{\max}$) are blue shifted (hypsochromic). As illustrated in Fig. 2.12. (a), the energy difference between the valence band and conduction band is inversely proportional to the size of NPs. This implies that more energy is required to excite an electron as NP size decreases. Therefore, photoabsorption is favoured when incident electromagnetic radiation has energy that is equal to or greater than the band gap energy (E_g). When excited electrons lose energy and return to their ground state, photons are emitted as a form of fluorescence or photoluminescence. In semiconductor NPs, this observation is termed as electron-hole recombination. The charge carriers within semiconductors (photoelectron-hole pairs) permit discrete energy levels, also known as quantum confinement.

This quantum confinement deliberates that electrons become trapped to certain densities of states (DOS), determined by characteristic spatial dimensions. The free motion of carriers is limited to two, one, and zero spatial dimensions. This function describes the number of states at a particular energy level that electrons may occupy, essential for determining the carrier concentrations and energy carriers within semiconductor materials [94].

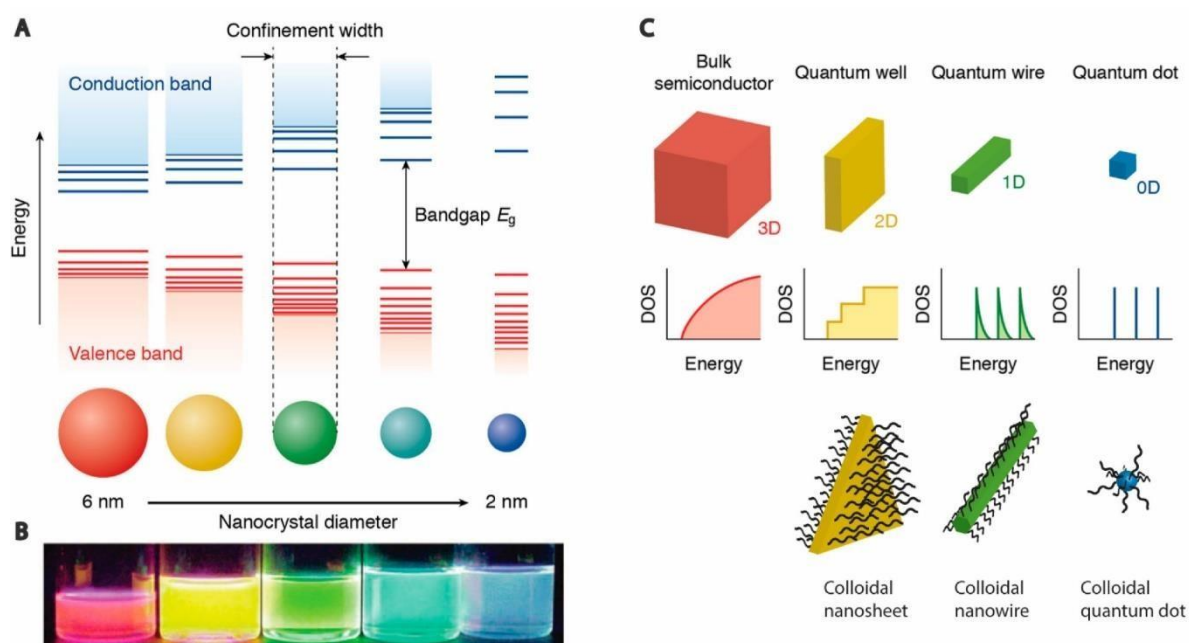


Figure 2.12 (a) Quantum confinement of NPs with respect to their, (b) their photoemission spectra, and (c) density of states of semiconductor NPs [95].

2.5.3. Cytotoxicity

A knowledge gap continues to exist in understanding fate of NPs on the environment and biotic species. Ample research and applications of NPs is perpetually done, which may lead to uncontrolled release of nanomaterials into the environment. A wide range of NPs have been reported to be cytotoxic towards living organisms in a dose-dependent manner. The cytotoxicity of NPs vary depending on their physicochemical properties such as size, shape, surface charge, as well as photolytic and oxidative characteristics [96]. Cytotoxicity can be termed as the toxicity induced by the action of chemotherapeutic agents on viable cells. Cytotoxicity of NPs arises from oxidative stress induced on cells, which compromises cell viability. Oxidative stress is ascribed to an imbalance in the accumulation of reactive oxidative species (ROS) within cells or tissues and their ability to detoxify these reactive species [97]. ROS can be in the form of superoxide, hydroxyl, and hydride anions. It can be measured via high-content analysis (HCA), [3-(4,5dimethylthiazol-2-yl)-2,5 diphenyl

tetrazolium bromide] (MTT) assay, as well as neutral red uptake (NRU) techniques. Common human cell lines used for cytotoxicity studies include T98G and HeLa, which are found in the cerebrum and epithelium, respectively [97].

The generation of ROS was observed to increase with longer contact time between NPs and microorganisms. Moreover, it was reported that uncapped NPs were less stable than capped NPs where a decrease in absorbance was monitored via UV-Vis spectroscopy [98]. Several studies have reported on cytotoxicity evaluations of nanomaterials *in vitro* and *in vivo*, bringing forth remarkable insights. Fig. 2.13. illustrates a suggested mechanism of NP cytotoxicity on mammalian cells. Ozkan Vardar et al. 2018. investigated the cytotoxicity of Ag₂S NPs *in vitro*, using Chinese hamster lung fibroblast (V79) cell specimens. It was determined by MTT and NRU that cell viability was significantly compromised at Ag₂S NP concentrations above 100 µg/mL. Therefore, Ag₂S NPs were observed to have relatively low cytotoxicity towards V79 cells. The genotoxicity of Ag₂S was studied by the alkaline comet assay to determine DNA strand breakage at unicellular level. It was found that no cell proliferation nor mutation occurred on the V79 cells at concentration range of 5-200 µg/mL, which indicates biocompatibility of Ag₂S NPs [99].

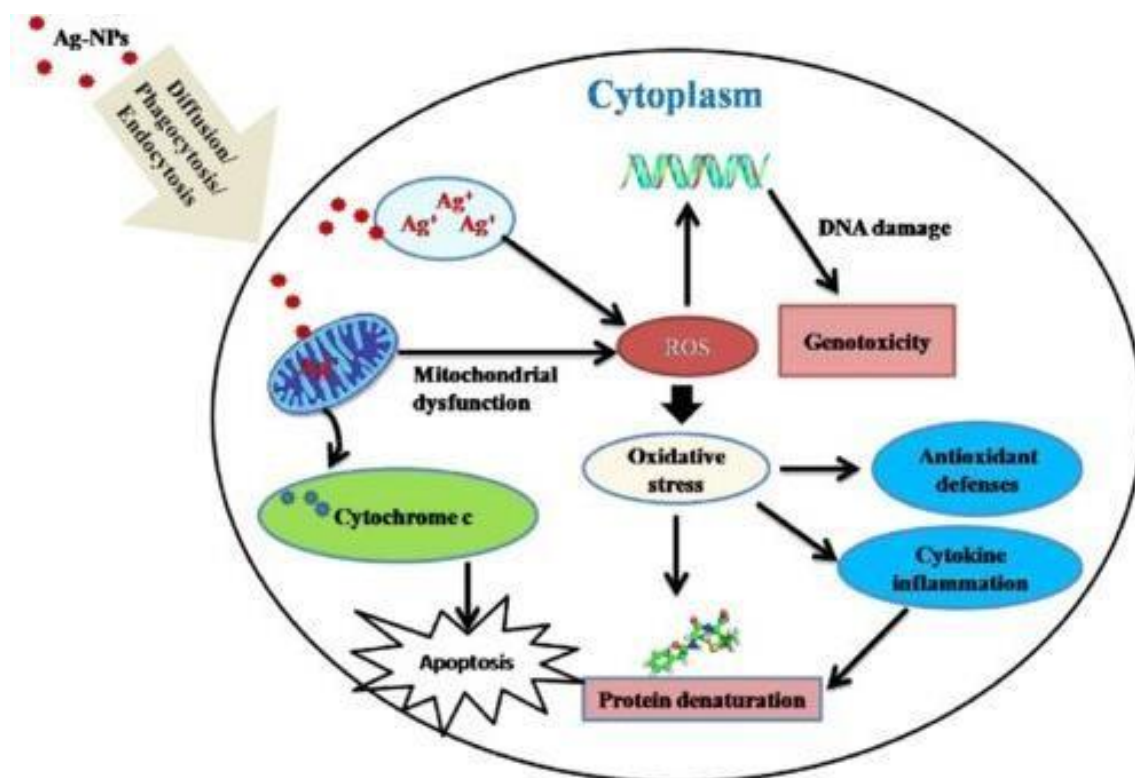


Figure 2.13 Proposed mechanism of cytotoxic effects of silver NPs on mammalian cell [100].

In another study conducted by Dhamaraj et al., 2021, an investigation on the antibacterial and cytotoxicity activities of biosynthesized Ag₂O NPs using culture supernatant *Bacillus paramycoids* was done. The synthesized NPs had a characteristic UV-vis absorption peak at 420 (2,95 eV). XRD analysis revealed a face centered cubic crystallographic structure, while TEM showed the NPs to have a diameter in the range of 20-70 nm. Ag₂O NPs demonstrated significant antibacterial activity against biofilm forming bacteria. The zone of inhibition observed against *Vibrio parahaemolyticus*, *Salmonella* species, *Enterobacter* species, and *Micrococcus* species were 32 mm, 30 mm, 28 mm and 30 mm respectively at 100 µg/mL. Moreover, a MTT cytotoxicity assay was done *in vitro* on A549 cancer cell line over a concentration range of 0-100 µg/mL. It was found that cytotoxicity was directly proportion to NP concentration, where the half-maximal inhibitory (IC₅₀) concentration was found to be 58.5 µg/mL [101]. Considering evidence obtained from previous work done, the use of silver-based NPs as antibacterial and anticancer agents is highly feasible due to relatively low cytotoxicity towards mammalian cells and aquatic species [102].

2.5. Silver-based nanoparticles

Silver (Ag) and silver-based NPs have been identified as useful semiconductor nanomaterials due to remarkable properties they possess. These include a narrow band gap energy (E_g), as well as good optical and emission properties due to quantization [103]. Consequently, what arises is quantum confinement, which is when the particle diameter is the same magnitude as the de Broglie wavelength of the electron wavefunction [104]. These properties position silver-based NPs as good light-harvesting materials and has charted a path for them being utilized in applications such as solar cells [89], colorimetric sensors [105], photocatalysis and bacteriolysis [76]. The photocatalytic and antibacterial properties of Ag and silver-based NPs have made them eligible to be used as nanofillers in TFN membranes to inhibit the phenomenon of fouling [106].

2.5.1. Synthesis methods for silver based NPs

Silver based NPs such as silver oxide (Ag₂O), silver sulfide (Ag₂S), and silver chloride (AgCl) NPs have been synthesized and used due to their photoluminescent and antimicrobial properties. The reported synthetic methods for silver-based NPs are the simple chemical method [107], organometallic method [108], the green synthetic method [109], solvothermal method [90], chemical co-precipitation method [110], and the

aqueous synthetic method [111]. The simple chemical method involves the production of new chemical compounds from simpler materials, whose form is changed as the reaction is propagated. An organic, non-polar solvent is often used as a supernatant for the dissolution of precursors and suspension of NPs. The size and shape of the NPs are controlled using surfactant molecules. The organometallic method consists of three main components, namely, precursor, organic solvent, and a surfactant. This method uses high temperatures and non-polar solvents (i.e., trioctylphosphine) [112]. The green synthetic method involves the production of Ag₂O NPs using naturally derived stabilizing agents such as bacteria, fungi, or plant extracts to control NP growth [113]. This method has become popular as it is associated with less toxic and environmentally friendly means of NP synthesis. However, NPs produced using this method have been reported to have high polydispersity and a mixed morphology. The aqueous synthetic route, solvothermal method, and chemical co-precipitation method will be discussed in detail below as they were used in the current study to synthesize Ag₂O, Ag₂S, and AgCl NPs, respectively.

2.5.1.1. Aqueous synthetic route

The aqueous synthetic method is regarded as a less toxic and environmentally friendly method because water is used as a solvent. The control of NP nucleation and growth is often done by the addition of small-sized and water-soluble organic molecules or surfactants, which binds to NP facets through its nucleophilic functional groups (i.e., amine or hydroxyl). The aliphatic chains of the surfactant form a monolayer around individual NPs, which provide stability and mitigate agglomeration [114]. Surfactants are known to decrease the interfacial tension between a liquid and solid NPs, as they can function as wetting agents, emulsifiers, or dispersants [115]. Silver nitrate (AgNO₃) is often used as a precursor due to it having a high solubility product constant (K_{sp}), which is reported to be 256 grams (g) per 100 millilitres (mL) of water at 25 °C and 912 g per 100 mL water at 100 °C. Moreover, AgNO₃ is relatively less expensive compared to other salts of silver, it is also less photosensitive and non-hygroscopic compared to silver fluoroborate (AgBF₄) or silver perchlorate (AgClO₄) precursors [116]. AgNO₃ is often combined with alkali hydroxide to form Ag₂O solid particles. NPs produced through this method have been reported to have a low quantum yield, mixed-morphology, and tend to have a broad size-distribution. However, endeavours have been made to improve uniform morphology, narrow size distribution, and photoactivity of NPs produced using this technique [117].

2.5.1.2. Solvothermal method

The solvothermal method has been spotlighted as an effective technique for the synthesis of NPs which are homogenous in composition, morphology, and geometry. Moreover, NPs produced using this method have a narrow size distribution and thermodynamic stability, which makes them desirable for industrial biomedical applications [118]. It involves the use of an aqueous or non-aqueous solvent in which precursors are dispersed, followed by an application of moderate-to-high temperature (100-1000 °C) and pressure (1-10 000 atm) to propagate nucleation reactions [119]. The growth kinetics, crystal phase, and morphology of obtained NPs are controlled by the capping ligands used, reaction temperature, and molar ratio of precursors. Due to temperature and pressure conditions, the formed product is expelled from the liquid phase by crystallization [120]. It is noteworthy that solvent temperature and pressure influences characteristics such as density, viscosity, thermal conductivity, heat capacity, and dielectric constant (ϵ). ϵ expresses the solvent polarity, which may be defined as the ratio of the absolute permittivity of a substance to the absolute permittivity of free space. Thus, establishing a sheer balance of these parameters can induce unique properties of the solvent [121]. The ϵ of solvents decreases dramatically when temperature increases and can help predict how well a solute can dissolve in it. A solvent with low ϵ is more suited to dissolve non-polar and non-ionic compounds [122]. When the ϵ of a solvent is high, it is better suited to dissolve polar and ionic compounds. Therefore, elevated temperatures promote the precipitation of ionic species from the liquid phase to the solid phase [123].

2.5.1.3. Chemical co-precipitation method

The co-precipitation technique involves the precipitation of silver metal ions in the form of metal hydroxide from a salt precursor (AgNO_3) with the help of a Lewis base (chloride anions) in an organic solvent. The controlled release of silver cations (Ag^+) and chlorine anions (Cl^-) aids to regulate the kinetics of nucleation and nanoparticle growth [124]. This controlled release increases the propensity of forming monodispersed NPs with a well-defined shape as the amount (mol/L) of cationic and anionic precursors diminish in the organic solvent [125]. The nucleation process forms many tiny (less than nanometric) particles in the supernatant solution, followed by controlled growth of the tiny particles into nano-sized particles due to Ostwald ripening and aggregation. The NPs obtained are insoluble in the supernatant solution under high supersaturation conditions, which helps

induce precipitation [126]. Nanomaterials obtained through this method are reported to have a degree of crystallinity, whose crystallite size and morphology can be controlled by capping agents. This method is a common technique for facile and cost-effective synthesis of homogenous NPs, which can easily be transposed on a large scale for industrial purposes [127]. Co-precipitation has also been reported to be useful for the formation of core-shell nanostructured materials. In this instance, two or more metal salt precursors with varied K_{sp} values are reacted together in the solvent of choice at a predetermined molar ratio and temperature [128]. The precursor with the higher K_{sp} value will be first to undergo nucleation and growth processes, which will serve as the core. The second precursor with a lower K_{sp} value will undergo nucleation, followed by growth and aggregation on the surface of the core when its concentration crosses the solubility product value in the supernatant medium [129].

2.5.2. Structural properties

Silver and silver-based NPs are renowned solid-state materials with a broad range of applications, due to their unique physical and chemical properties. As particle size decreases, the density of edge surface sites increases, which yields highly crystalline NPs. Silver-based NPs display high structural/mechanical stability when they have low surface free energy. Surface free energy, which significantly influences NP size and shape, is defined as a physical phenomenon induced by intermolecular interactions such as Keesom orientational forces, Debye inductive force, London dispersion, Lewis acid-base interactions, energetically homogenous and heterogenous interactions, and hydrogen bonding. Therefore, silver-based NPs with high surface free energy are considered thermodynamically unstable and are susceptible to disintegration upon interaction with their surrounding environment [130]. Surface capping agents are often used to control the transformation of NP seeds from precursors as well as lower the surface free energy of NPs, thus promoting thermodynamic stability and well-defined shapes. The shape of silver-based NPs has a strong association with their photonic and catalytic character. A good example is surface plasmon resonance (SPR), which is brought about by the collective oscillation of conduction electrons upon interaction with incident electromagnetic radiation (EMR). Therefore, NP shape determines the polarization of conduction electrons and surface distribution of charges, and thus determines the

amount, intensity, and wavelength of SPR absorption peaks, as well as the ratio between absorption and scattering of EMR [131].

2.5.2.1. Silver oxide nanoparticles

Silver oxide can exist as AgO, Ag₂O, Ag₃O₄, Ag₄O₃, and Ag₂O₃, which have different crystal phases. However, the most stable forms are AgO and Ag₂O, with Ag₂O NPs being more prominent [132]. The crystal structure of Ag₂O NPs is usually based on a compact array of oxygen anions, with silver cations positioned on the interstices. The crystal lattice parameter of Ag₂O NPs is usually denoted by $a = 4.0862 \text{ \AA}$ and assumes a face centred cubic crystal (FCC) crystallographic geometry [133]. Ag⁺ atoms are bonded in a linear geometry to two equivalent O²⁻ atoms, where both bond lengths are 2.06 Å. Moreover, O²⁻ atoms are bonded to four equivalent Ag⁺ atoms, forming a corner-sharing OAg₄ tetrahedra. Crystal lattices are 3-dimensional [134] (crystal planes). The 3 sets of parallel planes are used to define the structure and shape of the unit cell and crystal lattice by making axes visible. These are the basis on which Miller indices are calculated [135]. Miller indices are a group of three integers (h, k, ℓ) that indicate the orientation of a plane or a set of parallel planes of atoms in a crystal. These are the reciprocals of the fractional intercepts that the plane makes with the crystallographic axes. Moreover, Ag₂O NPs have been reported to have intense peaks at 2θ values of 37.7°, 43.9°, 64.1°, and 77.1° which are indexed at crystallographic reflection planes {111}, {200}, {220}, and {311}, respectively [136]. With regards to morphology, the type of solvent and capping agents used during synthesis is a significant determinant. However, Ag₂O NPs are often reported to acquire spherical and ellipsoidal shapes. In many instances the green synthetic method is used to produce Ag₂O NPs, which appear to be agglomerated and do not assume a well-defined shape. Thus, when aiming to mitigate agglomeration and control the shape of NPs, it is best to use capping ligands with known structure and properties [137].

2.5.2.2. Silver sulfide nanoparticles

Silver sulfide has three known forms that have varied thermodynamic stability based on temperature. The monoclinic acanthite (β -form) is stable below 173 °C, the body centred argentite (α -form) is stable above 180 °C (also known as silver glance), while the face centred cubic (γ -form) is stable above 586 °C [138]. When Ag₂S is crystallized above a temperature of 173 °C, solid crystals with cubic morphology and symmetry are formed.

When cooling occurs, a single crystal of argentite inverts to a polycrystalline nature and retains a cubic morphology [134]. Both acanthite and argentite share a similarity of having a body-centred arrangement of sulphur atoms, however, the arrangement of silver atoms is different, which exhibits crystal polymorphism. The structure of Ag₂S NPs is two-dimensional (layered), with one Ag₂S sheet oriented in the (1, 0, 0) direction [139].

There are two inequivalent Ag⁺ sites, where both are bonded in a distorted linear geometry to two equivalent S²⁻ atoms. With the only difference in the two sites being the lengths of the Ag-S bonds, which have been computed to be 2.44 Å and 2.43 Å. Therefore, S²⁻ is bonded in a four-coordinate geometry to four Ag⁺ atoms [140]. Generally, Ag₂S NPs have distinct peaks observed at two theta (2θ) angles of 22.3°, 26.4°, 29.7°, 37.2°, 43.1°, and 54.1°; which are attributed to *hkl* values of {-101}, {021}, {111}, {112}, {200}, and {041}, respectively. Considering the shape of Ag₂S NPs, several research has demonstrated that the hexagonal shape is common for these NPs [141], [142], [143].

However, as previously mentioned, the choice of capping agents as well as the solvent used has a significant influence on NP shape [91].

2.5.2.3. Silver chloride nanoparticles

Silver chloride is a naturally occurring mineral called chlorargyrite. Nanoparticles of AgCl are reported to assume a cubic crystal structure with the space group *Fm* $\bar{3}$ *m*, in which each silver ion is surrounded by an octahedron of six chloride ligands to form a mixture of edge and corner-sharing AgCl₆ octahedra. Analogously, each chloride atom is bonded to six equivalent silver ions to form a mixture of edge and corner-sharing ClAg₆ octahedra [144]. The main contributor of the crystallization mechanism of AgCl NPs is the concentration of free silver ions in the reaction medium [145]. X-ray diffraction characterization of AgCl NPs has demonstrated prominent peaks observed at 2θ values of 28.1°, 33.5°, 46.1°, 57.4°, and 56.1°, which were assigned to {111}, {200}, {220}, {211}, and {222} miller indices [146]. AgCl is typically insoluble in water, dilute acids, and alcohol. This is due to the ionic bond between silver cations and chlorine being stronger than the forces that promote the formation of silver hydroxide. However, it is reported to be soluble in concentrated hydrochloric acid, sulfuric acid, ammonia, and potassium bromide solution due to complex formation, thus assuming an ionic characteristic [147].

2.5.3. Optical properties

Optical properties describe a material's behaviour when EMR is incident on the material's surface. The measurements of a material's optical properties are required to be accurate and precise, as this is key for the advancement of optical technologies as well as their commercial applications [148]. These measurements include, but not limited to, index of refraction, absorptance, emittance, reflectance, and transmittance. In particular, the index of refraction of semiconductor nanomaterials is directly related to the electric inductive capacity, the magnetic inductive capacity, and specific conductivity [149]. Generally, metallic NPs do not transmit light but are known to be good polarizers of light due to localized surface plasmon resonance [150]. Semiconductor NPs exhibit sizedependant optical properties that are directly related to quantum confinement. As previously mentioned, E_g of semiconductor NPs increases with decreasing size [151]. Therefore, photons with energy that is equal or greater than E_g cause electron excitation from the valence band to the conduction band. Upon returning to the ground state, photons are emitted at a particular wavelength in the visible region, which is characteristic of a material's signature [152].

2.5.3.1. Silver oxide nanoparticles

Ag_2O NPs are known to have extraordinary optical properties and can absorb and scatter light with high efficiency. Their incredibly strong interaction with EMR occurs due to conduction electrons that undergo a collective oscillation when excited by EMR of particular wavelengths [153]. Ag_2O NPs have been extensively applied in ultra-high density optical data storage and photovoltaics [154]. Due to the control of NP size, Ag_2O NPs are reported to absorb EMR of lower wavelengths compared to its' bulk counterpart. This observation is referred to as a hypsochromic shift (blue shift) [155]. The band gap energy (E_g) of Ag_2O NPs have been reported to be in the range of 1.2-3.4 electron volts (eV), which mainly relies on the synthetic method used and reaction parameters [107].

As such, the optical properties of Ag_2O NPs such as spectral width, position, and profile of the luminescence band can be manipulated through direct control of NP size and size distribution to obtain an improved efficiency in specific applications [156]. When the size of bulk semiconductor material is reduced to a nanoscale, the electrons in the semiconductor become quantized. The reduction of the nanometric dimensions of NPs

below the exciton Bohr radius of the bulk exciton causes a collapse of the continuous energy bands, and results in the formation of discrete energy levels, which are similar to those of an atomic character. The E_g of NPs is inversely proportional to size; thus photons of higher energy are required to create excitons as NPs become smaller in size [104].

2.5.3.2. Silver sulfide nanoparticles

Nanoparticles of silver and silver sulfide have received much attention in recent years due to the size-dependant optical properties they exhibit during interaction with EMR of specific wavelengths. These observed properties have prompted exploration of their applications in optoelectronics [157], theranostics [158], and photocatalysis [159]. The excitation of surface plasmon resonances in Ag NPs and Ag₂S NPs demonstrates efficient interaction of light and matter, which surpasses that of most molecular chromophores. The resonances occur mainly due to light scattering (also known as the Tyron effect), so as the energy stored in the oscillation of free surface electrons is effectively radiated into space [160]. The two factors that influence light scattering are Ag₂S NP size, as well as the wavelength of incident light. Therefore, light scattering is enhanced in scenarios when NP size increases from 20-50 nm, and the wavelength of incident light is shorter [161]. The spectral position of surface plasmon resonance of Ag₂S NPs can be customized across the visible and near-infrared segments (280-1300 nm) of EMR. This property makes Ag₂S NPs an excellent candidate material for solar-light harvesting in photovoltaic devices [162]. The type of capping agent, as well as its concentration, has been reported to significantly influence the optical properties of Ag₂S NPs. In certain instances, the increase in hydrodynamic size of Ag₂S NPs is associated with the thickening of the organic capping layer due to polycondensation of the capping agent [163]. This observation can in turn influence the optical properties of Ag₂S NPs, where a red shift in absorption maxima is apparent. Therefore, the anisotropic shape and surface charge of particles play an important role on the manner in which colloids physiochemically interact [164].

2.5.3.3. Silver chloride nanoparticles

Silver chloride nanoparticles are well-known for their high stability and optical photoexcitation by ultraviolet and visible light. These are also known to have high mechanical strength, thermal stability, and electrical conductivity. In addition, AgCl NPs exhibit surface plasmon resonance when photoadsorption occurs due their tuneable band

gap energy [165]. The photoabsorption maxima of AgCl has been reported to be around 350-430 nm, depending on the choice of synthetic route and reaction parameters during synthesis, which have a direct influence on AgCl NPs' size and shape [166]. Biosynthesized AgCl often acquire irregular/no-uniform shapes and a wide particle size distribution [167], while those synthesized using capping molecules and/or surfactants acquire a uniform shape and a narrow particle size distribution [168].

AgCl NPs are photochromic materials used for the preparation of photographic paper/film, as well as light-polarizing optical materials because it interacts with photons to produce latent images through photoreduction [169]. The colour of photochromogenic material changes reversibly from colourless "status" to coloured "status", or vice versa in the presence of light. These kind of materials are classified as P-type, where all colouration and decolouration processes are driven only by light, or T-type, which undergoes photo-induced and thermally-induced colourization or decolourization [170].

2.5.4. Electronic properties

Within nanostructured materials, the state and behaviour of electrons are described by electronic properties. The electrical properties (i.e., electrical conductivity and dielectric response) are strongly associated with electronic properties of nanostructured materials and delineate their response to incident EMR [171]. These responses are distinct to that of bulk materials, which is ascribed to quantum confinement effects acting on electrons in one or more spatial dimensions [172]. Due to size reduction, semiconductor NPs (also known as quantum dots or artificial atoms) experience a pivotal change in the electron density of states (DOS). First-principle density functional theory (DFT) is often used to calculate the electronic density of states of surface atoms that constitute NPs, which reveals size-dependant occupancy and shift of conduction band edge [173]. Considering the electron-in-a-box model, it is observed that the formation of a set of electronic states at discrete energy levels is prevalent [174]. The spacing between these discrete states is directly proportional to effects of quantum confinement, which is dependent on the number of confined spatial directions. Consequently, increases in spacing between electronic states can render metal-to-semiconductor or semiconductor-to-insulator energy transitions [175]. In Fig. 2. 4. lies a schematic diagram of a quantum dot with radius R and associated potential profile along any diameter of the sphere. The grey arrow

in the figure represents the first available excitation state that in first approximation corresponds to the onset of optical absorption [176].

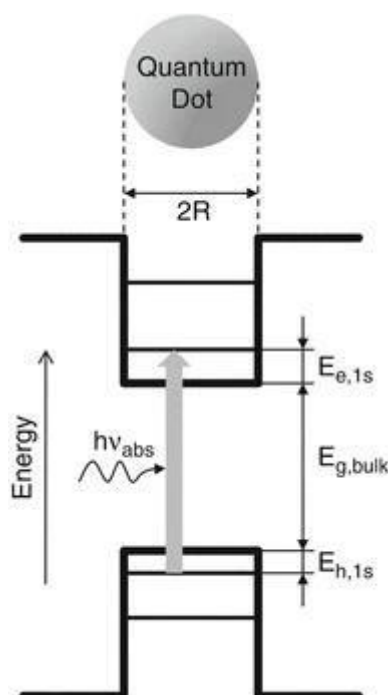


Figure. 2.14. Schematic of a quantum dot with discrete energy states for electrons and holes [177].

2.5.4.1. Silver oxide nanoparticles

Silver oxide NPs have been extensively studied due to their extraordinary electronic properties, which has sparked enthusiasm to explore their efficiency in applications such as bioimaging [178], electrochemical biosensing [179], and electrocatalysis [180]. The electron density of NPs is a highly significant characteristic as far as materials science is concerned, as this property influences catalytic activity. Moreover, the electron density increases with an increase in zeta-potential. This is the electric potential in the interfacial double layer of dispersed Ag_2O NPs versus a point in the continuous phase away from the interface [181]. The Mie-Drude theory explains the resistivity of a conductor in terms of electron scattering by assumably immobile ions in NPs, which are considered as obstructions to the flow of electrons [182]. Therefore, resistivity in Ag_2O NPs is inversely proportional to electrical conductivity. There are three factors that influence the surface plasmon resonance frequency, which are the dielectric constant of NPs, and of the medium, as well as their nanometric size. The surface plasmon resonance frequency is particularly sensitive to the refractive index of the medium, where a change in refractive

index causes a shift in the resonant frequency [183]. Due to this property, Ag_2O has found applications in batteries, where it is used as a cathode and zinc as a cathode [184]. Silver oxide batteries have a flatter discharge curve compared to alkaline batteries. Moreover, Ag_2O batteries have a greater run time, are free from thermal runaway, and do not have issues with flammability, compared to lithium-ion batteries [185].

2.5.4.2. Silver sulfide nanoparticles

Silver sulfide semiconductor NPs are remarkable nanomaterials that have attracted research interest due to their plasmonic character, thermodynamic stability, as well as relatively low cytotoxicity [186]. The size effect in Ag_2S semiconductor NPs (smaller than the exciton size) is strongly manifested in their electronic properties. Transition metal chalcogenides such as cadmium (II) sulfide (CdS), tungsten (VI) sulfide (WS_3), and Ag_2S NPs have demonstrated high-power factor due their less covalent characteristic, good thermal conductivity, and relatively low electronegativity [187]. Moreover, their power factor and electrical conductivity are reported to be directly proportional to temperature [188]. This is due to improved carrier concentration and high charge carrier mobility due to high degree of crystallinity. Because Ag_2S NPs fall under the class of two-dimensional layered material, they are ideal for deployment as channels in field-effect transistors (FETs) [189]. This is because all electrons are confined in atomically narrow channels and are uniformly influenced by the gate voltage [190]. The properties of Ag_2S NPs have demonstrated significant prospects for optical data storage [191], photocatalytic [192], electrocatalytic hydrogen and oxygen evolution reaction [193], as well as thermoelectric [194] and photovoltaic energy conversion and storage applications [195].

Two-dimensional Ag_2S NPs have demonstrated extraordinary optical absorption, thickness-dependent transitions from direct to indirect band gap, sizable exciton-binding energies, and phenomenal photoemission from atomically thin layers. Moreover, the discovery of new properties like low exciton-photon (longitudinal optical photons and acoustic photons) coupling has aroused further exploration in the design of ultrathin thermoelectrics [196]. In addition, investigations into their electronic DOS using scanning tunnelling microscopy (STM) and carrying out optoelectronic measurements of single two-dimensional layered nanomaterials using current-sensing atomic force microscopy (CS-AFM) can give more insights on development and exploitation of such material [197].

2.5.4.3. Silver chloride nanoparticles

Silver chloride nanoparticles, commonly termed as nanocrystals (NCs), are categorized as silver-halide (AgX) nanostructures. Together with AgCl in this category, there lies silver bromide (AgBr), silver iodide (AgI), as well as silver subfluoride (Ag₂F) and silver(n) fluoride (AgF_n). In the Ag₂F compound the oxidation state of silver is fractional. In the case of the AgF_n, 'n' can range from 1-3, and the difference is in the stoichiometric composition of NCs and the arrangement of atoms within the crystal lattices [198]. Nonetheless, the electronic band structure, the photoabsorption and photoemission maxima of AgCl NPs are size-dependent and have a direct influence on their electronic properties. As formerly mentioned, the electrons within small-sized AgCl NPs experience quantum confinement effects. The state of quantization has an impact on electronic properties such as conductivity, resistivity, surface states, surface potential, and oscillation frequency of surface plasmons [199]. Within AgCl NPs, the generation of 'hot' electrons from the decay of localized surface plasmons may occur through intraband excitations within conduction bands or through interband transitions, which results from electronic transitions from occupied band states to unoccupied conduction band states [200]. Moreover, an increase in the size of AgCl NPs (above 30 nm) enhances the relative importance of interband transitions from *d* bands to *sp* bands relative to surface-enabled *sp*-band to *sp*-band transition increases. Reports indicate that the hot-hole generation rate is characterized by a peak at the onset of *d* bands, while the corresponding peak position in the hot-electron distribution may be controlled through the frequency of illumination [201].

2.5.5. Applications in photocatalysis

The presence of natural organic matter NOM and in seawater has showed effects of organic fouling during seawater reverse osmosis (SWRO), which limits operation efficiency [202]. NOM is a term that is used to collectively name organic substances decomposed from plants and animals [203]. NOM is mainly comprised of humic substances, which are said to accumulate in seawater and increase chemical oxygen demand [204]. Several pre-treatment methods such as chlorination, sand filtration, microfiltration (MF) and nanofiltration (NF) have been used to reduce levels of NOM in seawater prior (SWRO) to enhance their lifetime and permeate quality [72]. However, these methods were not able to sufficiently reduce NOM levels below levels which

decrease susceptibility to organic fouling. The semiconducting properties and narrow band gap of nanoparticles permit facile electron transfer followed by radical formation in during photodegradation in aqueous media. The transfer of electrons is assisted by photoluminescence at wavelengths between 520-670 nm (UV), that facilitates the generation of electron-hole pairs [80].

2.5.5.1. Silver oxide nanoparticles

Silver oxide NPs have been identified as good photocatalysts for the degradation of organic pollutants from aqueous solution. This is primarily due to their optical and electronic properties. The ability to tune the energy band gap of Ag₂O NPs through synthesis techniques assists to enhance the photoabsorption in the visible region of the solar spectrum. The wavelength of photons in this region lies in the range of 380-780 nm, thus the energy band gap of Ag₂O NPs is required to be in the range of 1.6-3.25 eV. This will ensure facile formation of excitons, which initiate reduction and oxidation reactions that propagate photocatalytic processes. Laouini et al., reported on the green synthesis of Ag/Ag₂O NPs using aqueous leaves extracts of *Phoenix dactylifera* L. for the degradation of Azo dyes. The obtained NPs were observed be spherical and ellipsoidal, with a crystallite size range of 28-39 nm. The direct and indirect band gap of the NPs were found to be 2.07-2.86 eV and 1.60-1.76 eV, respectively, which permitted harvesting of photons from the visible region. The photocatalysts were observed to have a degradation efficiency of 84 % towards Congo red dye after 50 minutes of irradiation [205]. In another study by Muthukumar et al., reported on the synthesis of Ag₂O NPs using green amaranth leaf extract as a reducing agent. The NPs were determined to have an absorption maximum of 432 nm, an average particle size of 81 nm, and an average surface area of 100.2 m²/g. Caffeine was used as model organic pollutant, where a degradation efficiency of 99 % was achieved with catalyst dosage of 50 mg/L after 15 hours of photocatalytic degradation of 50 mg/L caffeine at pH of 9. The high degradation efficiency of Ag₂O NPs indicated the great potential of Ag₂O NPs to be used as a mediation tool against organic pollutants. Moreover, it was evident that the band gap energy of NPs played an important role on photoabsorption and photocatalytic activity [206].

2.5.5.2. Silver sulfide nanoparticles

Transition metal chalcogenides like Ag₂S NPs have been used for photocatalytic degradation of toxic organic pollutants, with several reports indicating resoundingly high efficiencies. Their semiconducting character and thermodynamic stability position them as good photocatalysts for advanced oxidation processes. In a study performed by Ayodhya and Veerabhadram, Ag₂S NPs were fabricated through a green synthetic route using *Cochlospermum Gossypium*. The obtained NPs were found to have an average particle size of 25 nm and a band gap energy of 1.1 eV. Fluorescein organic dye was used as a model pollutant, and solar-simulated light was used as a source of EMR. Photocatalytic degradation experiments were done with and without the addition of hydrogen peroxide. It was observed that hydrogen peroxide did enhance the efficiency of photocatalysis. Moreover, the effect of temperature indicated that Fluorescein dye degradation efficiency and rate was directly proportional to temperature, which correlated with pseudo-first order kinetics [207].

Another example of Ag₂S NPs being efficient photocatalysts is in the study done by Neelgund et al., where the adsorption efficiency and photocatalytic activity of Ag₂S NPs deposited on carbon nanotubes (CNTs-Ag₂S) were evaluated. It was observed that CNTsAg₂S was able to completely adsorb cadmium ions from aqueous solution in about 80 minutes. Moreover, the photocatalytic degradation of alizarin yellow R dye was done using natural light as a source of EMR. It was observed that when using CNTs and Ag₂S NPs alone, the percentage removal of alizarin yellow R was 77.3 and 41 %, respectively. However, CNTs-Ag₂S achieved a percentage removal of 99 % after 120 minutes of contact. The improved efficiency of alizarin yellow R was ascribed to the combined effect of adsorption by the carbonaceous CNTs and photocatalytic activity of Ag₂S NPs. The kinetic model that was followed by photocatalytic degradation process was determined to be pseudo-first order. The photocatalytic activity of CNTs-Ag₂S nanocomposite under natural sunlight indicated the photoactivity of Ag₂S NPs, in which electro-hole pairs were created and facilitated the formation of free radicals that propelled that photocatalytic degradation of alizarin R yellow dye [159].

2.5.5.3. Silver chloride nanoparticles

Silver chloride NPs are known to be plasmonic materials, with significantly good photoactivity when stimulated by visible light. This characteristic makes AgCl NPs serviceable materials for photocatalysis. The energy band gap of AgCl NPs can be controlled by size and shape engineering of AgCl NPs with the aid of capping agents or surfactants. Wanjari et al., released a report on bactericidal and photocatalytic degradation of methyl orange using silver-silver chloride NPs. *Ehretia laevis* leaf extracts were used as stabilizing agents for Ag/AgCl NPs. The NPs were found to have a bandgap energy in the range of 2.59-2.72, which was a good range for photoabsorption in the visible region. Crystallographic analysis determined the AgCl NPs to have a cubic phase, with peaks at 2θ values of 27.9° , 32.5° , 46.4° , 54.9° and 57.5° , which were assigned to hkl values of 111, 200, 220, 311, and 222, respectively. The Fenton method was used for the photocatalytic degradation of methyl orange dye, which proved to have significantly higher efficiency (99 %) compared to the non-Fenton degradation process (51 %). This was attributed to the rapid formation of hydroxyl and superoxide radicals by the addition of iron (II) and hydrogen peroxide, which facilitated photocatalytic degradation [208].

Choi et al., demonstrated the photocatalytic properties of silver-silver chloride NPs against methylene blue dye, using visible light as a source of EMR. The size and shape of Ag/AgCl NPs was controlled using polyvinyl alcohol in aqueous AgNO_3 solution. The obtained NPs were determined to have a band absorption edge at 465 nm, which translates to a band gap energy of 2.67 eV. In this range Ag/AgCl NPs are capable of photon absorption in the visible region, which constitute approximately 43 % of radiation in the solar spectrum. Spectroscopic analysis of the supernatant solution after 8 hours of photocatalysis demonstrated 99 % efficiency under visible light irradiation. Moreover, total organic carbon (TOC) analysis showed that at least 62 % removal of organic carbon, which indicated significant mineralization of organic pollutants. Dye removal was significantly low when the experiment was done without a source of EMR, which signified the important role of photoabsorption in the formation of free radicals. In addition, the experiment was also performed under visible light without a photocatalyst where dye removal was ineffective, which underpinned the importance of photoabsorption [165].

2.5.6. Application in antibacterial studies

The potential for NPs to be used as bacteriolytic agents has widely been studied, with several positive outcomes published [64]. Bacteria is known as multicellular organisms which replicate in nutrient-rich environments to form a colony [68]. The increase in multi-drug resistant pathogens have necessitated the need to develop alternative agents. It is imperative to mitigate bacterial growth and inhibit potential spread of viruses and disease [69]. Gram-positive and gram-negative bacterial cultures found in seawater have been used in simulation tests for nanoparticle antibacterial activity [202]. Silver NPs and silver-based nano-compounds have been widely studied, where reports demonstrate the remarkable antibacterial and antimicrobial properties of these nanomaterials [66].

2.5.6.1. Silver oxide nanoparticles

Metal oxide NPs have been spotlighted to be suitable material for the mitigation of the spread of harmful bacteria due to their stability in physiological environments. Several reports have shown the effectiveness of silver oxide NPs in the inhibition of bacterial cell proliferation, which has increased the exploration of various synthetic routes using different stabilizing/capping agents [209]. More recently, the biosynthesis of Ag₂O NPs using plant extracts has received ample attention due to the production of biocompatible NPs for biomedical technology and food packing applications [210]. Mani et al., reported on the antibacterial activity of biosynthesized Ag₂O NPs using *Cleome gynandra* leaf extracts. The NPs were observed to exhibit a strong peak at 425 nm, which implied their band gap energy to be 2.92 eV. *E. coli* and *S. aureus* bacterial strains were used to investigate the antibacterial activity of Ag₂O NPs. It was observed that growth inhibition was directly proportional to NP concentration. Moreover, Gram-negative *E. coli* appeared to be more susceptible to cell apoptosis. This was ascribed to the structural characteristics, as it is known that Gram-positive bacterial cells are surrounded by thick layers of peptidoglycan, which is absent in Gram-negative bacterial cells [211]. In another study done by Islam et al., mycogenic Ag/Ag₂O NPs were synthesized using endophytic fungus *Fusarium oxysporum* as stabilizing agents. The NPs were determined to have an average particle size of 6.43 ± 0.05 nm, and a bandgap energy of 2.67 eV. The NPs showed antimicrobial activity against *Aspergillus niger* and *Bacillus subtilis*. This was allotted to the high surface area-to-volume ratio of the NPs. Moreover, higher contact occurred between microbial species and NPs, which helped improve the release rate of Ag⁺ ions

that crossed the cell membrane barrier and induced the generation of reactive oxygen species. In addition, these NPs were applied in electrochemical glucose sensing and showed good, reproducible responses towards glucose detection [212].

2.5.6.2. Silver sulfide nanoparticles

Transition metal chalcogenides have gained ample attention in biochemical applications due to the discovery of their antibacterial and antifungal properties. It has been found that particle size, shape, contact potential difference, and photoactivity play a significant role in their antimicrobial activity. Silver sulfide NPs are known to have good optoelectronic properties and thermodynamic stability, which positions them as useful bioactive material. Delgado-Beleño et al., reported on the synthesis of Ag₂S NPs and their antibacterial activity against *S. aureus*, *S. agalactiae*, and *E. coli* bacterial strains. The NPs were determined to have a bandgap energy of 3.75 eV, an average particle size of 4.2 ± 1.2 nm, and a quasispheroidal morphology. The Ag₂S NPs were observed to have better inhibition activity towards Gram-positive bacteria compared to Gram-negative bacteria, with *S. aureus* showing higher antibacterial susceptibility. The release of Ag⁺ ions was suggested to be responsible for penetration of bacterial cell walls, which perturbs regular DNA functions and debilitates their reproductive abilities [66].

In another study conducted by Bala Subramaniyan et al., Ag₂S NPs were synthesized using N-myristoyethanolamine lipids as stabilizing agents. Ag₂S NPs were evaluated against two Gram-positive bacteria (*B. subtilis* and *S. aureus*) and two Gram-negative bacteria (*E. coli* and *P. aeruginosa*). The minimum inhibitory concentrations for all bacterial strains were determined to be 50 μ M. Moreover, the protein release of the evaluated strains was observed to be ± 80 %, which indicated cell membrane damage after contact with Ag₂S NPs. This was corroborated using scanning electron microscopy, where living cells appeared to have regular shapes and dead cells showed deformation. The percentage of ROS generated by the bacterial strains was determined to be ± 70 %, which are postulated to attack unsaturated fatty acids of cell membranes to form lipid peroxide radicals [213].

2.6.6.3. Silver chloride nanoparticles

Silver chloride NPs are known to be plasmonic materials whose energy states are electron rich, and have good thermodynamic stability, conductivity, antibacterial activity, and relatively low cytotoxicity. These properties make AgCl NPs suitable for biomedical and food safety applications silver [168]. Patil et al. Biogenically synthesized silver-silver chloride (Ag-AgCl) NPs, using *A. Pilosa* extract as a stabilizing/capping agent. The bandgap energy and average particle size were found to be 2.73 eV and 15 nm, respectively. Both Gram positive (*Bacillus cereus* ATCC13061, *Listeria monocytogenes* ATCC7644, *Staphylococcus aureus* ATCC6538p & *Staphylococcus saprophyticus* KCTC3345) and Gram negative (*Escherichia coli* KCTC1682 & *Pseudomonas putida* ATCC49128) were deployed in antibacterial tests. The well diffusion assay and microbroth dilution methods were used to acquire qualitative and quantitative data, respectively. Minimum inhibitory concentration (MIC) was found to be approximately 60 $\mu\text{g/L}$, while minimum bacterial concentration (MBC) was determined to be approximately 75 $\mu\text{g/L}$. The ability of AgCl NPs to inhibit cell growth and induce death demonstrated their efficiency as antimicrobial agents [214].

Another demonstration of antibacterial properties of AgCl NPs was observed in a study performed by Ferreira et al., in which *Chlorella vulgaris* microalgae was used as stabilizing agents. The obtained NPs were observed to be spherical, with an average particle size of 9.8 ± 5.7 nm and band gap energy of 2.95 eV. The antibacterial activity of AgCl NPs were evaluated against *S. aureus* and *K. pneumoniae* bacterial strains, which showed 98 % growth inhibition when 10 $\mu\text{g/mL}$ of AgCl NPs was used. Moreover, at a concentration of 10 $\mu\text{g/mL}$, the bacterial cells were observed to have approximately 90 % viability. At a concentration of 200 $\mu\text{g/mL}$ the viability of *S. aureus* and *K. pneumoniae* were observed to be 40 % and 55%, respectively. The data obtained revealed that Gram-positive *S. aureus* had more resistance to cell apoptosis compared to Gram-negative *K. pneumoniae*. This was due to the former having a peptidoglycan cell wall which itself is surrounded by an outer membrane consisting of lipopolysaccharide. TEM imaging of bacterial cells before and after interaction with AgCl NPs showed shrinking and deformation of the cells, ascribed to cell-wall damage and ROS generation [215].

2.5.7. Applications in RO membranes

Biofouling inhibition in RO membranes has been widely investigated by the desalination industry to increase membrane performance and lower operational costs [65]. Conventional feed pre-treatment methods such as chlorination and sand filtration have been used to limit the number of microbials reaching the water-membrane interface [46]. However, these methods have not been successful in totally removing microbes in seawater. Biofouling occurs in events where microorganisms such as *Bacillus*, *Serratia*, *Pseudomonas*, *Mycobacterium*, *Corynebacterium* and *Flavobacterium* adhere to, grow, and subsequently accumulate on the membrane surface [216]. Membrane technology has been positioned as one of the most effective treatment methods for seawater desalination [217]. However, the need to improve membrane properties still exists as an increase in biofouling inhibition would prolong their practical application by countering bio-film formation on the membrane surface [218] and reduce chemical oxygen demand [219]. Desalination membrane characteristics that determine economic viability include chemical stability, mechanical strength, biofouling inhibition, permeability, and morphology [220]. The use of hydrophilic base polymers has been reported to enhance membrane flux in crossflow systems, which ultimately improves separation [221]. Much progress has been made in membrane technology, recently with the inclusion of nanoparticles via in situ or surface immobilization to mitigate biofouling and increase lifetime [222].

Maharubin et al., conducted a study on the integration of AgNPs in polymeric membranes to inhibit biofilm formation on their surface. Evaluations were done on polysulfone (PSF), 1 w/w% AgNP immobilized PSF and polyaniline nanofibers/PSF blended membranes prepared via the wet phase-inversion method. The average membrane thickness was 200 μm , while average porosity and mean pore size of PSF, Ag-PSF and PANF-PSF were 79, 70 & 56 % and 1.25, 1.13 & 1.02 nm, respectively. The study aimed to address biofilm inhibition and reduce silver leaching by integrating low-intensity direct current (DC) of 14.9 μA and AgNP immobilization. The inclusion of AgNPs was observed to improve biofilm resistance, selectivity, and water permeation. The water flux and flux recovery obtained by silver-loaded membranes were 22.2 L/m²h and 57.4 %, respectively [218].

2.5.7.1. Silver oxide nanoparticles

Silver oxide NPs have been employed in membrane technology to inhibit fouling by microbes or organic contaminants found in water. This is due to their optoelectronic, antibacterial, and photocatalytic properties that were discussed in previous sections. The inclusion of Ag₂O NPs as nanofillers to form thin film nanocomposites has been reported to significantly enhance water permeation, salt rejection, and fouling resistance of membranes [223]. Gul et al., reported on the fabrication of nanocomposite membranes (PES-CA-Ag₂O) with disinfection properties induced by the inclusion of Ag₂O NPs in polyethersulfone (PES) and cellulose acetate (CA) polymers. Nonvalent copper (Cu⁰) NPs were also added for a separate membrane as an endeavour to augment the fouling resistance of the membranes. The membranes that were assessed in this study were labelled as PES, CA, PES-CA, PES-CA-Ag₂O, Cu⁰@PES-CA, and Cu⁰@PES-CA-Ag₂O. It was observed that water permeation increased significantly following the addition of Ag₂O NPs, where PES-CA, PES-CA-Ag₂O, and Cu⁰@PES-CA recorded water fluxes of 63.3, 92.88, and 72.5 L/m².h.bar, respectively. Moreover, a higher flux of (100.2 L/m².h.bar) was achieved in the case of Cu⁰@PES-CA-Ag₂O, together with higher percentage of bovine serum albumin (BSA) rejection (89.5 %). This was allotted to increased hydrophilicity observed when Cu⁰@PES-CA-Ag₂O was assessed for contact angle analysis. Furthermore, the propensity of the as-fabricated membranes to mitigate biofilm formation was also investigated. It was found that Ag₂O NPs played a significant role, as membranes without Ag₂O NPs showed very little to no inhibition of bacterial adhesion and growth [224].

2.5.7.2. Silver sulfide nanoparticles

Silver sulfide nanoparticles have demonstrated significant potential for deployment as antibacterial applications. The antibacterial property of Ag₂S is known to be directly proportional to their concentration. In addition, the cytotoxicity of Ag₂S NPs has been reported to be less than that of most NPs, which positions them as good candidates to be used in water purification. Feng et al., developed a dual-heterojunction photocatalytic membrane reactor based on a photocatalytic film made of Ag₂S-functionalized metal organic framework nanocomposites. Cross-sectional SEM analysis of the membranes revealed the 'finger-like' or 'organ pipe' shaped nanovoids in the active separation layer. Atomic force microscopy showed that addition of Ag₂S NPs smoothened the surface, which provided an advantage of reduced susceptibility to fouling. X-ray photoelectron

spectroscopy (XPS) confirmed the presence of Ag₂S NPs in the nanocomposite, where Ag 3d_{5/2} and 3d_{3/2} peaks were detected. The peaks were deconvoluted to obtain 367.6 eV (Ag⁺, 3d_{5/2}), 367.9 eV (Ag⁰, 3d_{5/2}), 373.6 eV (Ag⁺, 3d_{3/2}) and 373.9 eV (Ag⁰, 3d_{3/2}), which showed that there were two forms of silver chemical states in the Ag₂S/NH₂-MIL88B(Fe)/PEN heterojunction. The transient photocurrent activity of the PEN samples doped with NH₂-MIL-88B(Fe) and Ag₂S was nearly 9.9 times higher than that of the pristine PEN samples. This indicates that doping NH₂-MIL-88B(Fe) and Ag₂S reduced the energy band gap, promoted the generation of photoelectrons, and served as a photoelectron reservoir, overriding the expected electron-hole recombination process. Water contact angle demonstrated that the hydrophilic nature of the nanocomposite increased as Ag₂S was added to the mixture. Nonetheless, the nanocomposite membranes showed high efficacy (99.7 %) in the removal of sulfadiazine (SDZ) pollutant from wastewater through combined adsorption and photocatalytic processes [225].

2.5.7.3. Silver chloride nanoparticles

Silver halide nanostructured material, particularly AgCl, have been reported to exhibit extraordinary photocatalytic and antimicrobial properties against toxic organic pollutants and infectious pathogens, respectively. This property has made AgCl NPs viable for use in fabrication of textiles, food packaging, and medical equipment [226]. More studies on the incorporation AgCl into materials to inhibit formation of bacterial colonies have led to the development of membranes loaded with AgCl NPs. An example of this can be found in a report authored by Lu et al., in which a self-cleaning and photocatalytic cellulose-fibre supported “Ag@AgCl@MOF-cloth” membrane for water remediation was fabricated.

MOFs are known for their effective photocatalytic nature, where the excitation of electrons occurs from highest occupied molecular orbitals of oxygen and/nitrogen to the lowest unoccupied molecular orbitals of the metal cluster [227]. However, low efficiency of excitation and facile recombination of photoexcited charge carriers resulted in low quantum efficiency in photocatalytic reactions. Therefore, Ag@AgCl NPs were earmarked to serve as photocatalyst promoters due to their surface plasmon resonance and high Fermi energy level characteristics.

Transmission electron microscopy (TEM) and elemental mapping were used to verify the presence of AgCl NPs, which were observed to be uniformly distributed on the membrane surface with minimal agglomeration. Control of AgCl nanocrystal growth on the MOF-cloth was achieved by a layer-by-layer method, and Ag NPs were formed in-situ using a photo-induced reduction method. The surface area of as-synthesized Ag@AgCl@MOFcloth material was observed to be 42.39 m²/g. X-ray diffraction analysis detected peaks at 2 θ angles of 27.8° {111}, 32.3° {200}, 46.2° {220}, 54.8° {311}, and 57.5° {331}, which were allotted to AgCl nanocrystals (JCPDS 31-1238). XPS also confirmed the presence of AgCl NPs, where peaks observed at 197.6, 367.2, and 373.5 eV were assigned to Ag⁰, Ag⁺, and Cl⁻, respectively. Moreover, water contact angle (WCA) analysis showed that Ag@AgCl@MOF-cloth membrane had a WCA of 15.1°, which rapidly decreased to 0°, demonstrating the super hydrophilic characteristic of the membrane. Target pollutants where methylene blue dye and oil, which were filtered from the feed with the aid of visible light irradiation. It was determined that removal efficiencies of dye and oil were 97.3 and 99.6 %, respectively. The removal efficiencies showed not significant decrease after five cycles of treatment, indicating fouling resistance and reusability of Ag@AgCl@MOF-cloth membrane under visible light irradiation [228].

In another study by Jin et al., AgCl mineralized thin film composite polyamide membranes were fabricated via interfacial polymerization on a polysulphone support. The aim was to enhance the separation performance and antifouling properties in forward osmosis. WCA analysis indicated that surface hydrophilicity increased as AgCl NP loading increased. Atomic force microscopy showed that average surface roughness was lower for AgCl loaded membranes than those without AgCl NPs. These properties provided an advantage of having reduced susceptibility towards fouling. Moreover, water flux was observed to be higher for AgCl-loaded membranes (24.0 $\pm$ 2.1 L/m²h) compared to those not loaded with AgCl NPs (14.3 $\pm$ 1.2 L/m²h). Furthermore, salt rejection and BSA fouling resistance were also observed to be enhanced by the incorporation of AgCl NPs in the polyamide separation layer [229]. These observations clearly demonstrate the benefit of combining silver-based nanomaterial with filtration membranes to create highly efficient, fouling resistant, and durable materials for effective water purification.

2.6. References

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Chapter 3: Experimental procedures

3.1. Synthesis and characterization of silver-based nanoparticles

3.1.1. Chemicals and reagents

The following were purchased from different suppliers without further processing; silver nitrate (AgNO_3) (99.9%), sulfur powder (S) (99.8%), 1-octadecene (1-ODE) (95.0%), and oleylamine (OLA) (technical grade, 70%) were obtained from Sigma-Aldrich (Germany). Sodium chloride (NaCl) (99%) and sodium hydroxide (NaOH) (99.8%) were purchased from Promark Chemicals (South Africa). The washing solvents hexane (95.0%), methanol (99.9%) and toluene (99%) were bought from Associated Chemical Enterprises (South Africa).

3.1.2. Synthesis of silver oxide nanoparticles

The aqueous synthetic route was employed to synthesize silver oxide (Ag_2O) NPs, where ultra-pure water and 1-ODE were used as solvent and capping agent, respectively. An aqueous stock solution of AgNO_3 (2 M) was prepared in a volumetric flask and covered with tin foil. Aqueous NaOH (1 M) was also prepared in a volumetric flask and stored in the refrigerator. In a three-neck round-bottom flask, 20 mL of the AgNO_3 stock solution and 15 mL were added and heated to 40 °C. 2 mL of 1-ODE was added to the flask, and the temperature was subsequently raised to 60 °C. The reaction continued in open air for 180 min, with 1 mL aliquots extracted after every 60 min. All the samples of Ag_2O NPs were washed and centrifuged (8000 rpm for 5 min) in hexane twice, then air-dried and stored.

3.1.3. Synthesis of silver sulfide nanoparticles

Silver sulfide (Ag_2S) NPs were synthesized using the solvothermal method, where OLA was used as a solvent and capping agent. In summary, 10 mL OLA was transferred into a three-neck round-bottomed flask and pre-heated to 80 °C using a heating mantle with magnetic stirrer under gaseous nitrogen flow prior the addition of AgNO_3 and S at a molar ratio of 2:1. The reaction temperature was raised to 180 °C and allowed to continue for 240 minutes. Aliquots of 1 mL were drawn between 90-240 min, washed and centrifuged (8000 rpm for 10 minutes) in hexane/toluene (60:40) three times, then air-dried and stored for further use.

3.1.4. Synthesis of silver chloride nanoparticles

Silver chloride (AgCl) NPs were synthesized by the co-precipitation method. 1-ODE was used as a solvent and capping agent, where 10 mL was transferred into a three-neck round-bottom flask and pre-heated to 80 °C. The precursors AgNO₃ and NaCl were added to the flask in a 1:1 molar ratio. The temperature was subsequently raised to 160 °C under gaseous nitrogen flow, and the reaction continued for 240 minutes. Aliquots of 1 mL were taken every 60 min, washed and centrifuged (10000 rpm for 10 min) in hexane/methanol (40:60) four times, then dried in a desiccator and stored for future use.

3.1.5. Characterization

3.1.5.1. Optical properties

The optical absorption spectra of silver-based NPs were obtained using a SPECORD 210 PLUS UV-vis spectrometer supplied by Analytik Jena (Thuringia, Germany). Fluorescence spectroscopy was done using a Perkin Elmer LS 45 photoluminescence (PL) spectrometer equipped with a xenon lamp (Waltham, USA). Quartz cuvettes used for optical measurements had a standard 12,50 mm square outer dimensions and 10,00 mm transmitted path length through the sample (excitation wavelength of 250 nm).

3.1.5.2. Crystallographic measurements

Powdered X-ray diffraction (XRD) patterns of the as-synthesized NPs were acquired using a Meas Srv D2-205530 diffractometer supplied by Bruker (Billerica, USA) with CuK α radiation ($\lambda = 1,54056 \text{ \AA}$) at 30 KV and 10 mA. Measurements were taken at a glancing angle of incidence detector at an angle of 2°, for 2 θ values over 10–90° in steps of 0.026° (step time of 37 s) at ambient temperature. A silicon crystal low background holder with sample cavity was used to secure powdered NP samples for analysis.

3.1.5.3. Transmission electron microscopy (TEM) analysis

Particle morphology and size was observed using FEI Technai T12 TEM microscope (Hillsboro, OR, USA), with a LaB₆ gun and accelerating voltage 20-120 kV. The samples were prepared by dispersing the materials in ethanol and drop casting into a lacy carbon coated Cu grid.

3.1.5.4. Fourier transform infrared spectroscopy

The chemical composition and functional groups on the prepared TFC and TFN reverse osmosis membranes were studied using an attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrophotometer (PerkinElmer Spectrum UATR Two).

3.2. Photocatalytic degradation of humic acid by silver-based nanoparticles

The potential of the as-synthesized NPs to photocatalytically degrade humic acid (HA) in aqueous media was investigated. HA (product number: 53680) was supplied by Sigma Aldrich, Germany. Seawater contains approximately 100 to 500 micromoles of dissolved organic carbon per kilogram of seawater; hence HA was selected as a model analyte. An Oriel Sol2A class ABA solar simulator equipped with an ozone-free xenon short arc lamp (450 watts) and proprietary filter was used as a source of electromagnetic radiation. A stock solution of 50 mg/L HA was prepared using ultra-pure water, from which working solutions (2.5-10 mg/L) were made. For preparation of working solutions, predetermined volumes of the stock were drawn using a syringe fitted with a Whatman Spartan syringe filter (cellulose membrane with pore size of 0.45 μm). This was followed by dilution of the filtered stock solution with ultra-pure water to prepare desired concentrations of the working solutions. For the separate photocatalytic degradation experiments, 20 mg of each NP (Ag_2O , Ag_2S , and AgCl NPs) was weighed and dispersed in 30 mL of working solution in a beaker. The beaker was placed on a magnetic stirrer positioned beneath the lamp housing to have a working distance of ≈ 15 cm. The beaker and its contents were initially stirred in the dark for 30 minutes. This was subsequently followed by exposure of the beaker and contents to solar simulated light with constant stirring at 250 rpm. Aliquots (1 mL) were drawn periodically to monitor the rate/kinetics of degradation by UV-vis spectroscopy. Due to the complex composition of HA, aliquots assessed by UV-Vis exhibited several absorption bands between 190-260 nm and a broad absorption band around the region of 340-640 nm. Therefore, the ratio of absorption maxima at 254 and 436 nm was used as a yardstick to determine degradation efficiency.

3.3. Antibacterial susceptibility of silver-based nanoparticles

3.3.1. Chemicals and reagents

Luria Bertani Broth (LB), Tryptic Soy Agar (TSA) were obtained from Sigma-Aldrich (Germany). *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were supplied by the American Type Culture Collection (ATCC). Apparatus was washed in aqua regia, and the ultra-pure water required for experiments was sourced from a Milli-Q system.

3.3.2. Well-diffusion method

Silver-based NPs were applied in antibacterial studies against Gram-negative *E. coli* and Gram-positive *S. aureus* bacterial strains. The pathogens were inoculated in sterile solutions of LB broth and cultured overnight at 37° C with agitation speed of 250 rpm. TSA plates were prepared and allowed to set at ambient temperature. Bacterial suspensions were standardized to 1×10^6 CFU/mL according to the McFarland turbidity scale. Bacterial strains were individually inoculated on agar surfaces, and wells of 8 mm diameter were forged in the agar gels. Serial dilutions of dispersed NPs were made (0.015625-2.0 mg/mL), where 100 μ L of known concentration was added to each well. Standard streptomycin antibiotic and sterile ultrapure water were used as the positive control and negative control, respectively. This was followed by incubation of the agar plates in an oven at 37° C for 18 - 24 hours. Treatments were done in triplicates and mean values were given after statistical analysis. The presence of translucent areas surrounding the wells are termed 'zone of inhibition (ZON)', which is used as a yardstick for the evaluation of antibacterial activity.

3.3.3. Broth micro-dilution assay

Equal volumes (2 mL) of LB Broth were added to sterile test tubes, in which 2-fold serial dilutions of NP suspensions were made (2.5-0.07813 mg/mL). Bacterial inocula of *E. coli* and *S. aureus* were adjusted to 0.5 McFarland turbidity standard with optical density of 0.1 au. at 600 nm (OD₆₀₀). To every test tube, 100 μ L of each inoculum was transferred. The tubes were incubated in a rotary oven for 24 hours at 37 °C. The positive control and negative control for this experiment was streptomycin antibiotic and sterile ultra-pure water, respectively. The concentration in the test tube with the least visual bacterial growth was considered as the minimum inhibitor concentration (MIC). The test tube for which MIC was determined, and those containing higher NP concentration, were

aseptically swabbed on TSA plates. This was followed by incubation in an oven at 37 °C overnight, and colony-forming units (CFU) were determined. The lowest NP concentration at which no CFU were observed was regarded as the minimal bactericidal concentration (MBC).

3.4. Cytotoxicity studies

3.4.1. Chemicals and reagents

Dulbecco's Modified Eagle's Medium (DMEM), Fetal Bovine Serum (FBS), streptomycin, penicillin-streptomycin (Pen-Strep), and trypsin-EDTA, were obtained from Sigma Aldrich (Germany). The cell proliferation assay kit I (3-[4,5-dimethylthiazole-2-yl]-2,5diphenyltetrazolium bromide (MTT) dye) was purchased by Promega Corporation (USA). Human Embryonic Kidney 293T cell (HEK 293T) strains were supplied by the American Type Culture Collection (ATCC).

3.4.2. MTT assay for cell viability and proliferation

Nanomaterials used in biomedicine, consumer goods, and packaging materials should be non-toxic, water-dispersible, biocompatible, non-immunogenic, and not susceptible to physicochemical change in physiological environments. NP cytotoxicity is dependent on size, shape, surface charge, surrounding moieties on their surfaces, NP concentration, and release rate of metal ions [1]. Cytotoxic effects of Ag₂S, Ag₂O and AgCl NPs towards human cell lines were conducted in vivo. HEK 293T cells were used as specimen and MTT dye was used as a colorimetric agent. In summary, HEK 293T cells were seeded in DMEM containing 10% FBS (10% DMEM) and 1% Pen-Strep was incubated for 24 hours at 37 °C in an atmosphere of 5% CO₂. Once a confluence of 99% was achieved on the cell culture flask, the supernatant solution was discarded and replaced with 0,5% trypsin solution to enzymatically detach the cells. Viable cells were collected via centrifuge and resuspended in 10% DMEM. 300 µL was transferred into 96 well flat bottom tissue culture plates and incubated over 24 hours for cell attachment. Silver-based NP suspensions (2,00,015625 mg/mL) were prepared in fresh media and 500 µL of each were separately added to the wells. The control group was cultured without addition of NPs. This was followed by incubation for 48 hours at 37° C under 5% CO₂. MTT dye was added to each well and the plate was further incubated for 4 h, under similar conditions. Metabolically active cells converted MTT to insoluble 2-(4,5-Dimethyl-1,3-thiazol-2-yl)-3,5-diphenyl2H-tetrazol-3-

ium bromide (formazan), which exhibits a distinctive purple colour. A plate reader was used to measure absorbance at 490 nm. All experiments were repeated at least three times and conducted in a cleanroom.

3.5. Fabrication of thin film composite and thin film nanocomposite membranes

3.5.1. Chemicals and reagents

Silver sulfide NP precursors silver nitrate (AgNO_3) salt (99.9%), sulphur powder (99.8%), as well as oleylamine (OLA) solvent (technical grade, 70%) were purchased from SigmaAldrich (Germany). The washing solvents, methanol (99.9%) and toluene (99%) were both procured from Associated Chemical Enterprises (South Africa). The flat-sheet of polysulfone (PSF) ultrafiltration membrane (MICRODYN-NADIR, US 100, molecular weight cut-off 100 kDa) was purchased from Memcon (South Africa). mPhenylenediamine (MPD) monomer, sodium dodecyl sulfate (SDS), trimethylamine (TEA, 99.5% purity), and camphor sulfonic acid (CSA, 99% purity) were bought from SigmaAldrich (Germany). High-performance liquid chromatography (HPLC) grade anhydrous hexane (n-hexane, 97% purity) and trimesoyl chloride (TMC), which were supplied by Merk Corporation (South Africa). Sodium hypochlorite (NaOCl), sodium chloride (NaCl) and bovine serum albumin (BSA) protein were obtained from Sigma-Aldrich (Germany). The deionized (DI) water used during experiments was sourced from a Milli-Q system.

3.5.2. Synthesis of silver sulfide nanoparticles

Details on the synthesis of silver sulfide nanoparticles can be found under section 3.1.3.

3.5.3. Interfacial polymerization of composite and nanocomposite RO membranes

An aqueous phase and an organic phase were separately prepared to form the active TFC layer via interfacial polymerization on the surface of PSF support membrane. The aqueous phase of DI water contained 2.0 wt% MPD, 1.0 wt% CSA to maintain a pH of ≤ 9.5 , 2.0 wt% TEA as an acid acceptor, and 0.1 wt% SDS surfactant. This mixture was stirred, then sonicated for 5 min at 25 °C. The organic phase of 0.1 wt% of TMC dissolved in n-hexane was subsequently prepared and sonicated for 5 min at 25 °C. The PSF membrane was pre-soaked overnight in DI water and air dried, then soaked in aqueous phase for 120 seconds. A soft rubber roller was used to rid the MPD populated surface of bubbles. The membrane

surface was then immersed in organic phase for 45 seconds, followed by rinsing with n-hexane to remove excess TMC. Hereafter, the membrane was baked in an oven for 10 minutes at 80 °C, followed by cooling and storage in DI water at 4 °C. Similar procedures were followed during the synthesis of thin film nanocomposites (TFN) with varied Ag₂S NP loadings. Moreover, Ag₂S NPs (20, 30, and 50 mg) were added to the aqueous phase and collectively sonicated prior polymerization [2].

3.5.4. Characterization of RO membranes

3.5.4.1. Fourier transform infrared spectroscopy

Details on Fourier transform infrared spectroscopy analysis can be found in section 3.1.5.4.

3.5.4.2. Field-emission scanning electron microscopy

The surface topography and cross-sectional analysis of RO membranes were performed on a ZEISS Sigma 300 VP (ZEISS, Germany) field-emission scanning electron microscope (FE-SEM). Samples were coated with gold/palladium as a conductive layer to inhibit charging, reduce thermal damage, and improve the secondary electron signal.

3.5.4.3. Atomic force microscopy

Atomic force microscopy (AFM) is an important surface technique for membrane characterization, as it gives insights on the morphology of membranes and helps predict their performance characteristics. Average surface roughness (R_a) and the root mean square (R_q) average of height deviations were recorded by atomic force microscope (AFM) nanoscope IV (Veeco, USA).

3.5.4.4. Water contact angle analysis

Water contact angle (WCA) analysis is a key measurement in RO membrane fabrication and application. It provides information on the degree to which membranes are hydrophilic. Contact angle (θ) is the angle formed by a liquid at the three-phase boundary where liquid, gas and solid intersect. The contact angle measurements were done using the drop shape analyzer-DSA 100 (Krüss, USA) which has high precision measurement of statistical contact angle.

3.5.5. Evaluation of water flux and salt separation performance of membranes

The Ag₂S-loaded RO membranes were required to demonstrate good trans-membrane flow and high (> 95%) salt rejection. A crossflow RO system was utilized for the tests, which is equipped with three-unit cells. Membrane sheets were cut to sizes of and fitted into the cells with membrane area of 0.0042 m², which were subsequently screwed watertight. Deionized (DI) water was used to compact the membranes at 350 pounds per square inch (psi), purposed to dilate the nano-channels within networks of TFC and deduce a stable water flux. Water flux was monitored at 250 psi over a period of 30 minutes. This was followed by the preparation of a 2000 ppm saline solution of NaCl, which was also passed through the membranes at similar conditions. The water flux (J_w) and apparent salt rejection (R_{NaCl}) were calculated using equations (3.1) and (3.2), respectively.

$$J_w = \frac{V}{A_e \times t} \quad (3.1)$$

Where J_w is water flux (L/m²h), V is the volume (L) of permeate obtained within a framed duration of time, A_e is the surface area (m²) of the membrane under observation, and t is the time frame in which the membranes were tested.

$$R_{NaCl} = \left(1 - \frac{C_p}{C_f}\right) \quad (3.2)$$

Where C_p and C_f represent the salt concentration in the permeate solution and feed solution, respectively. Salt content was measured using a conductivity meter.

3.5.6. Antifouling performance characteristics of membranes

3.5.6.1. Biofouling test

The biofouling resistance test of TFC and TFN reverse osmosis membranes was conducted using 50 mL centrifuge tubes as vials. RO membrane coupons sized at 4 cm² were attached by double sided tape onto centrifuge tube caps, with the active TFC layer poised perpendicular to the cap. *E. coli* was cultured in nutrient-rich LB Broth, followed by incubation in an oven at 37 °C. Dilute bacterial suspensions of concentration 10⁶ CFU were prepared, where a sterile isotonic solution of 0.9% NaCl was used as a solvent. Membrane coupons were tested in triplicate, where 10 mL of dilute bacterial suspension was added to each vial. The coupons were contacted with the bacterial suspension by inverting the centrifuge tubes and agitation at 250 rpm, at 37 °C for 3 h. The suspension was decanted,

followed by addition of 10 mL isotonic saline solution, inversion of centrifuge tubes, and sonication for 10 min to detach the pathogenic bacteria from the surfaces of membrane coupons. The effectiveness of biofouling method was done via the plate counting assay method, where each sample was swabbed on agar plates and incubated at 37 °C for 24 h. The same approach and conditions were applied for nonnano-enhanced membrane coupons. The CFU counted from agar plates emanating from TFC (N_b) and those from TFN (N_m) were instrumental to determine antibacterial efficiency (A_e). Equation (3.3) was used to calculate A_e .

$$A_e = \left(\frac{N_b - N_m}{N_b} \right) \times 100\% \quad (3.3)$$

3.2.6.2. Bovine serum albumin fouling test

The anti-fouling characteristics of TFC and TFN reverse osmosis membranes against organic macromolecules were determined using BSA as a model protein foulant. In brief, 350 ppm of BSA was prepared in DI water and used as the feed. The membranes were initially compacted by passing the feed water through them at 350 psi for 30 min. This was followed by evaluation of water flux at a reduced pressure of 250 psi, over a duration of 30 min. Similar parameters were applied to TFC membranes without NPs. Water flux (J_f) during RO filtration of BSA was periodically measured over 24 h. The membranes were subsequently washed with DI water and tested for pure water flux to measure flux recovery (J_r). The flux recovery ratio (FRR) and total fouling ratio (R_t) were determined using equations (3.4) and (3.5), respectively.

$$FRR = \frac{J_r}{J_w} \times 100\% \quad (3.4)$$

$$R_t = \left(1 - \frac{J_f}{J_w} \right) \times 100\% \quad (3.5)$$

Where J_w , J_r , and J_f denote initial water flux, flux recovery, and flux during BSA RO filtration, respectively.

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Chapter 4: Characterization of silver oxide, silver sulfide, and silver chloride nanoparticles

4.1. Introduction

The synthesis of nanomaterials composed of noble metals (i.e., silver, gold and platinum) has gained traction in recent years due to their plasmonic character induced by incident EMR [1]. Surface plasmons are referred to as collective oscillations of conduction band electrons that couple with incident photons at specific wavelengths. These create significantly high electromagnetic fields on the surface of metallic NPs [2]. The composition, size, shape, and orientation of NPs with respect to incident EMR have been reported to influence the spectral position and intensity of plasmons, which could either be surface plasmon resonance (SPR) or localized surface plasmon resonance (LSPR). The decay period in SPR is relatively longer than in LSPR, however, sensitivity to interference is more in scenarios of SPR compared to LSPR [3]. Moreover, surface plasmons are more intense on spherical NPs than on anisotropic NPs due to more proportionate distribution of density of states (DOS). The frequency of resonance is influenced by the dielectric constant of both NPs and dispersing medium, as well as photoexcitation wavelength [4]. This property has made noble metal NPs desirable for applications such as gas sensing [5], electrocatalysis [6], photocatalysis [7], and photonics [8].

Another emerging application of plasmonic NPs is fluorescence imaging due to surface plasmon-coupled emission (SPCE), which is useful in clinical diagnostics [9] and optical biosensors [10]. This is due to interactions between surface plasmons and excited fluorophores (plasmaphores) near the metallic film surface [11]. An example of related work was done by Jiang et al., who reported on the development of a novel surface plasmon-coupled chemiluminescent immunosensor for the detection of multiplex mycotoxins with ultrahigh sensitivity. The immunosensor was made by immobilizing carboxyl-functionalized silver NPs and bovine serum albumin (BSA)-combined antigens sequentially on a glass chip functionalized with amino groups. The SPR of silver NPs were observed to amplify the chemiluminescence induced on the microchip. The model analytes used were citrinin, aflatoxin B₁ and ochratoxins A. Optimum parameters showed that the surface-plasmon-coupled chemiluminescent immunosensor had a wide linear

range of up to 4 orders of magnitude. Moreover, the fabricated immunosensors demonstrated unprecedented limits of detection for mycotoxin monitoring [12].

4.2. Results and discussions

4.2.1. Optoelectronic properties of silver-based nanoparticles

Ultraviolet and visible (UV-vis) spectroscopy was used to determine the optical and electronic properties of the synthesized NPs. UV-vis spectra were recorded at room temperature over a range of 300-600 nm. Fig. 4.1(a) depicts the spectra of Ag₂O NPs synthesized between [60-240 min]. The 60 min sample exhibited a band at 408 nm and E_g was determined to be 3.04 eV, using the Tauc relation ($\epsilon h\nu = C(h\nu - E_g)^n$). A bathochromic shift towards 419 nm was observed in the [120 min] sample, and the same value was attained by [180-240 min] samples. The E_g of the samples was estimated to have decreased to a value of 2.97 eV. This eventuality meant that lower energy was required to excite an electron from ground state, which facilitates facile electron-hole pair generation when exposed to visible light. The spectra of Ag₂S NPs synthesized for [90, 120, and 240 min] are illustrated in Fig. 4.1(b). Absorption peaks were observed to be 381 nm [90 min], 390 nm [120 min], and 408 nm [240 min].

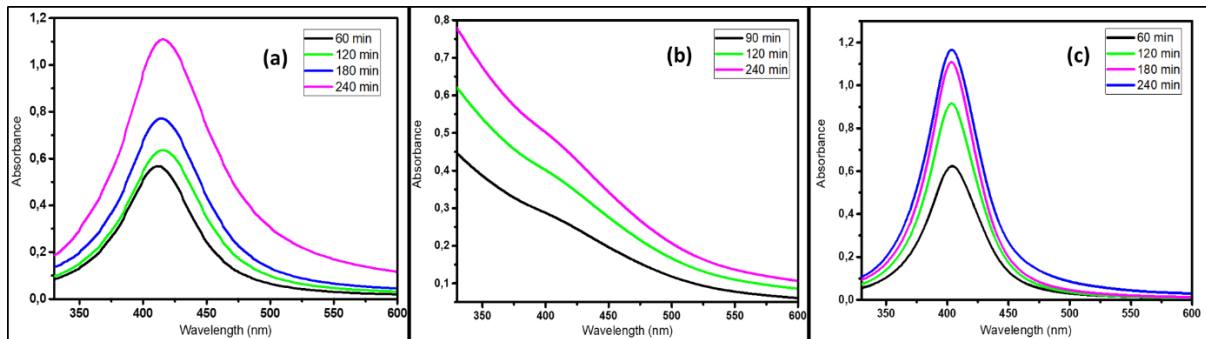


Figure 4.1. UV-Vis of (a) Ag₂O, (b) Ag₂S, and (c) AgCl NPs synthesized at different time intervals.

The peaks exhibited a hypsochromic shift compared to that of bulk Ag₂S, which has a value of 620 nm. A shift in absorption edge towards higher wavelengths (lower energies) was observed in samples synthesized for longer time, which could be attributed to Ostwald ripening. As seen in Fig. 4.1(c), UV-vis spectra of AgCl NPs exhibited an excitation peak at 403 nm for the 60 min sample. This was due to surface plasmon resonance (SPR) induced by interaction between electrons on nanoparticle surface and radiation in the visible region. Slight hypsochromic shifts were observed in samples [120-240 min] to 400, 398,

and 397 nm. The photoabsorption of visible light at lower wavelengths as synthesis time increased indicated enhanced confinement of electrons.

Photoluminescence (PL) spectroscopy was used to determine the electronic structure and emission properties of silver-based NPs. The luminescence occurs because of radiative and recombination of photogenerated electron-hole pairs between ground state vibrational energy levels and excited state vibrational energy levels that compete with non-radiative processes. As shown in Fig. 4.2., both fluorescence and phosphorescence were observed for the NPs, which implies that intersystem crossing of electrons took place from the singlet states to triplet states. Ag₂O [120 min] NPs exhibited fluorescence and phosphorescence at 500 and 504 nm, respectively. Considering that the absorption peak was at 419 nm, Ag₂O NPs underwent a Stokes shift of 81 nm. Ag₂S [120 min] and AgCl [180 min] were observed to exhibit emission spectra that were analogous to one another. Their fluorescence and phosphorescence peaks were seen at 498 and 504 nm, respectively. The absorption peaks of these samples were recorded at 390 and 398 nm, which implies that a Stokes shift of 108 and 100 nm occurred in Ag₂S [120 min] and AgCl [120 min], respectively. Therefore, it was determined through Warburg's equation that the quantum yields of Ag₂O, Ag₂S, and AgCl were determined to be 83.8%, 78.3%, and 79.9%, respectively.

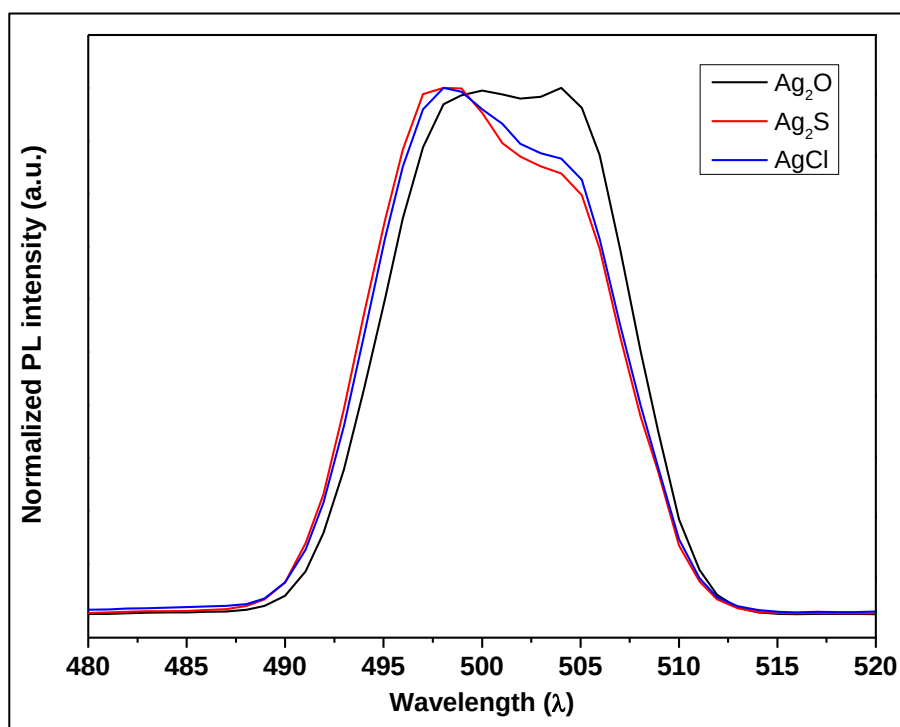


Figure 4.2. Photoluminescence of Ag₂O [120 min], Ag₂S [120 min], and AgCl [180 min] NPs.

4.2.2. X-ray diffraction analysis

XRD analysis of nanoparticles under study was done in a temperature-controlled environment (22 ± 2 °C), steps of 0.0262° with a step time of 5 seconds were applied. Recordings were taken from a glancing angle (2°) of incidence over a 2-theta (2θ) angle range of 10° - 80° . XRD diffractograms of Ag₂O, Ag₂S and AgCl NPs are presented in Fig. 4.3(a), 4.3(b), and 4.3(c), respectively. The XRD analysis of Ag₂O NPs is depicted in Fig. 4.3(a), from which a cubic crystal structure (JCPDS 00-001-1041) of space group Pm-3m (221) was observed. Peaks of interest were found at 2θ values of 26.6° {110}, 32.9° {111}, 38.1° {200}, 54.9° {220}, 65.7° {311}, and 69° {222}. The average crystallite size was determined to be 17.9 nm. As shown in Fig. 4.3(b), X-ray Diffraction patterns obtained matched monoclinic Ag₂S acanthite (JCPDS 00-014-0072) nanocrystals. The NPs were determined to have an average crystallite size of 22.3 nm and space group of P21/n (14).

Ag₂S NPs have been reported to have three temperature-dependent polymorphic structures, namely monoclinic α -Ag₂S (space group 14-P21/n), body-centered cubic β -Ag₂S (space group 229- $I m\bar{3}m$) and face-centered cubic γ -Ag₂S (space group 225- $Fm\bar{3}m$) [11]. Significant peaks were observed at $2\theta = 22.3^\circ, 26.4^\circ, 29.7^\circ, 37.2^\circ, 43.1^\circ$, and 54.1° , which were assigned hkl values of {-101}, {021}, {111}, {112}, {200}, and {041}, respectively. The intensity of the peaks increased with prolonged duration of synthesis, which can be related to a higher degree of crystallinity. The X-ray diffractograms of AgCl NPs are shown in Fig. 4.3(c). The NPs were observed to have a cubic crystal system (JCPDS 00-002-0848), with space group Fm-3m (225). The peaks of interest were observed at 2θ values of 27.9° {111}, 32.5° {200}, 46° {220}, 54.9° {311}, 57.2° {222}, 66.8° {400}, 74.7° {331}, and 76.1° {420}.

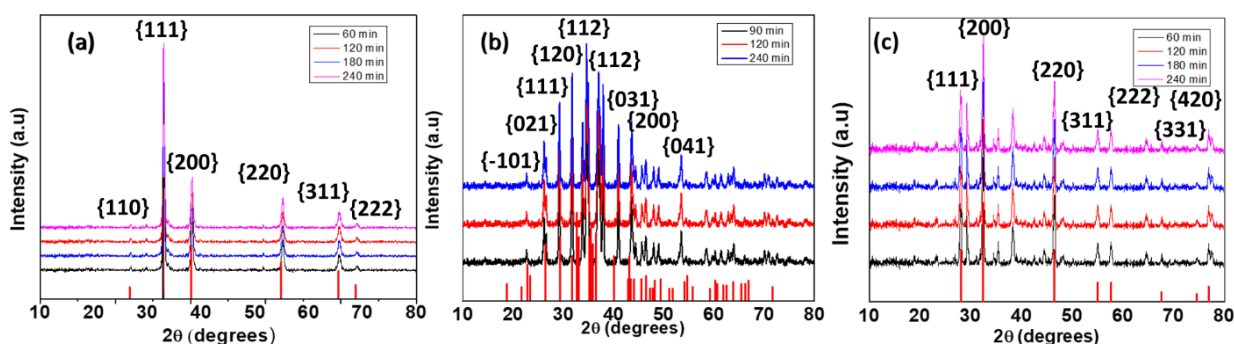


Figure 4.3. Powdered X-ray diffraction graphs of (a) Ag₂O, (b) Ag₂S and (c) AgCl NPs synthesized at different reaction times.

4.2.3. Microscopic analysis of silver-based nanoparticles

TEM analysis was used to examine 2-dimensional properties of the synthesized NPs, which include shape, diameter, size distribution, and possible agglomeration. As shown in Fig. 4.4 (a, b, & c), NPs with well-defined shapes (ellipsoidal (a & c) and hexagonal (b)) were produced with good size distribution. The use of capping agents during synthesis enabled controlled nucleation and growth of Ag₂O (a), Ag₂S (b), and AgCl (c) NPs, which were determined to have average sizes of 23.0 ± 5.7 nm, 30.6 ± 7.4 nm, and 10.6 ± 7.2 nm, respectively. Moreover, the capping agents attached organic moieties around NPs that induced electrostatic repulsions to prevent agglomeration. The spherical shape of Ag₂O and AgCl NPs provide advantages of high surface-to-volume ratio, and their strength and/or rigidity is symmetrically distributed along their total surface area. Ag₂S NPs were observed to have hexagonal-shaped NPs which have a high degree of monodispersity and form a honeycomb structure when dispersed next to each other.

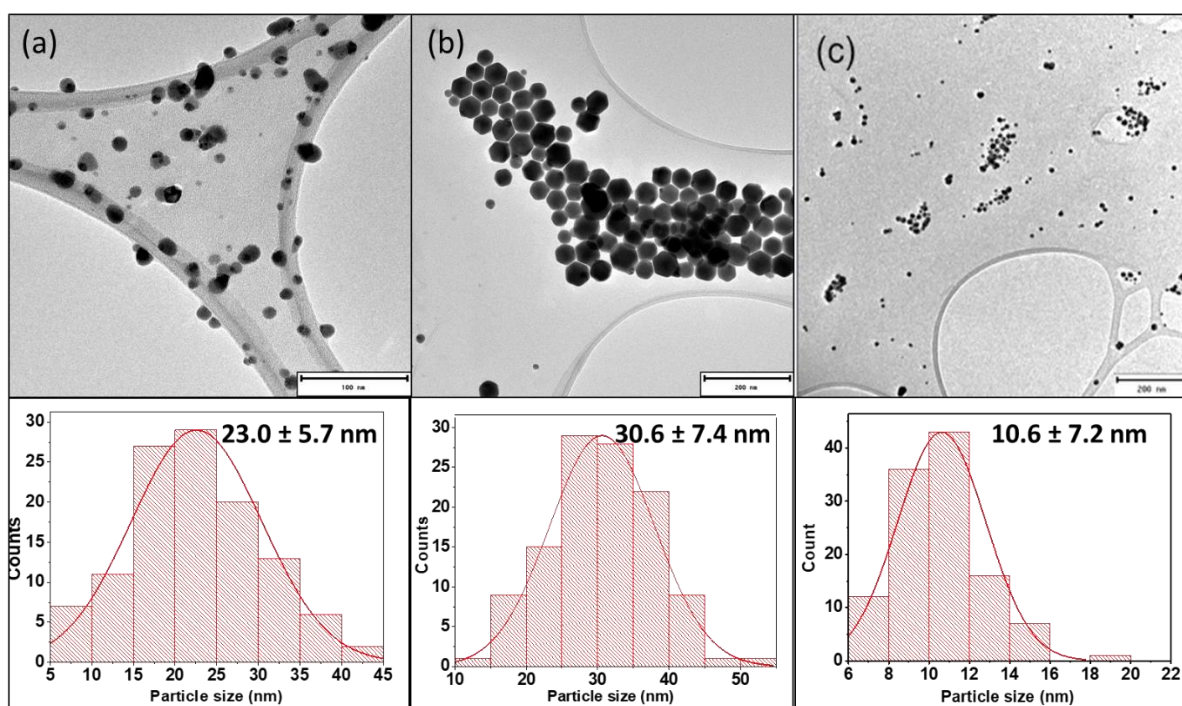


Figure 4.4. Transmission electron microscopic imaging of (a) Ag₂O [120 min], (b) Ag₂S [120 min], and (c) AgCl NPs [180 min] and their respective size distribution curves.

4.2.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to probe the presence of organic moieties surrounding NPs emanating from capping molecules. Fig. 4.5. Shows the FTIR spectra of 4.5 (a) Ag₂O NPs capped with 1-ODE, 4.5 (b) Ag₂S NPs capped with oleylamine, and (c) AgCl NPs capped with 1-ODE. The molecular formulae of 1-ODE and oleylamine are $(\text{CH}_3-(\text{CH}_2)_{15}\text{CH}=\text{CH}_2)$ and $(\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_8-\text{NH}_2)$, respectively. It was observed in Fig. 5(a) Ag₂O NPs had stretching and bending O-H functional groups at 3321 and 984 cm⁻¹, brought about by water. Symmetric and asymmetric C-H stretching, and bending were seen at 2974 and 700 cm⁻¹. An alkene (C=C) vibrational peak was observed at 1482 cm⁻¹ which is usually observed between 1640-1680 cm⁻¹. This was ascribed to its interaction with Ag₂O NPs. The peak detected at 514 cm⁻¹ was assigned to metal-oxygen (Ag-O) stretching vibration. Fig. 5(b) illustrates that Ag₂S NPs had a C-N-H₂ stretch and N-H bending vibrations at 3345 and 1487 cm⁻¹. Sp² and sp³ hybridized C-H stretching was observed at 2988 and 2971 cm⁻¹, respectively. Out of plane C-N bending and C-H bending vibrations were noted at 1244 and 850 cm⁻¹. The peak observed at 530 cm⁻¹ was allotted to Ag-S bonding vibration. As shown in fig. 4.5 (c), AgCl NPs had a strong O-H stretch and a sharp O-H bend peak at 3381 and 997 cm⁻¹, respectively. Sp² and sp³ C-H symmetric and asymmetric vibrations were found at 2981 and 2897cm⁻¹. Functional groups of C=C and C-C were seen at 1613 and 1500 cm⁻¹. Moreover, C-H wagging and bending vibrations were observed at 1472 and 751 cm⁻¹, respectively. Vibrational peaks observed confirmed the presence of organic moieties on NPs surfaces due to capping molecules used during the size-controlled synthesis of silver-based NPs. Considering the fabrication of nanocomposite polymers, these moieties are instrumental for covalent bonding.

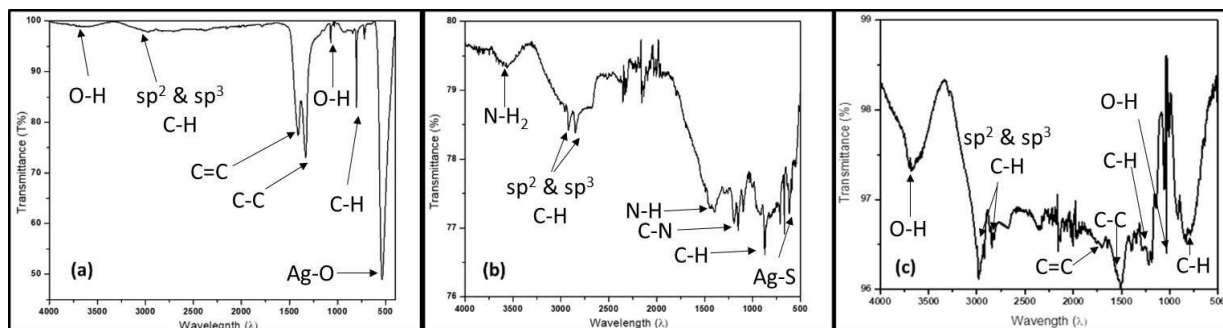


Figure 4.5. IR spectra of (a) Ag₂O [120 min], (b) Ag₂S [120 min], and (c) AgCl [180 min] NPs.

4.3. Conclusion

TEM analysis determined the average sizes of Ag₂O, Ag₂S, and AgCl NPs to be 23.0±5.7, 30.6±7.4, and 10.6±7.2 nm, respectively. XRD showed that Ag₂O, Ag₂S, and AgCl NPs had cubic, monoclinic, and cubic crystal lattices, respectively. UV-vis spectroscopy determined Ag₂O, Ag₂S, and AgCl NPs to have band gap energies of 2.97, 3.11, and 3.05 eV, respectively. PL spectroscopy indicated that Ag₂O, Ag₂S, and AgCl NPs exhibited stokes shifts of 81, 108, and 100 nm, respectively. The relatively small stokes shifts implied that the changes in dipole moment in ground and excited states was negligible. These observations inferred that crystalline NPs that exhibit surface plasmon resonance (SPR) in the visible region were successfully synthesized. Moreover, applications in SPCE imaging may be explored using Ag₂O, Ag₂S, and AgCl NPs.

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Chapter 5: Photocatalytic degradation of humic acid in aqueous solution using silver-based nanoparticles

5.1. Introduction

Riverine and oceanic systems often contain a gradient of solutes (i.e., DOM), which are longitudinally transported by water flow. Sources of DOM have been identified to be natural (i.e., plant decomposition), as well as anthropogenic (i.e., agriculture). DOM represents classes of organic matter such as HA, fulvic acid, and humus [1]. HA macromolecules contain an assembly of conjugated olefinic, aromatic, and phenolicsemiquinone structures. Organic matter is omnipresent in nature and is prone to physicochemical interactions with co-constituents such as heavy metals within their environment [2]. The concern with the presence of DOM in aquatic systems is their ability to become precursors for the generation of carcinogenic disinfection by-products. Moreover, DOM introduces turbidity and foul odor to water, increases chemical oxygen demand (COD) and facilitates bacterial re-growth in water distribution systems [3]. In addition, DOM is a major source of organic fouling on membranes during seawater reverse osmosis and groundwater ultrafiltration systems [4]. Membrane fouling is defined as the adsorption and accumulation of organic pollutants on the water-membrane interface. This creates a resistance towards transmembrane permeance of water molecules, and in turn deteriorate the quality of the collected permeate [5].

It is therefore necessary to eradicate DOM in natural waters to minimize their adverse effects. Conventional methods of dealing with DOM include coagulation/flocculation [6], adsorption [7], and photocatalysis using metallic NPs [8]. Nanoscience has paved way towards the exploitation of electronic and optical properties of materials. The size, shape and crystallographic structure of nanomaterials have been proved to highly influence their optical properties, as well as the quantum confinement of their electronic states [9]. Metallic nanoparticles and chalcogenides have received substantial attention in medical, biochemical, as well as water remediation industries [10]. This is due to their tunable band gap energy (E_g), semiconducting ability, and thermodynamic stability at elevated temperatures [11]. The control NP E_g is essential to obtain serviceable nano crystals [12].

Variables such as precursor concentration, reaction time and temperature, solvent used (or a combination), as well as stirring speed during the reaction, influence geometric and electronic properties of NPs [13], [14]. Semiconducting NPs, also known as quantum dots (QDs), are typically fluorescent when in the path of electromagnetic radiation (EMR) [15]. Relatively small-sized QDs have larger E_g and thus emit high-energy photons (blue), compared to large-sized QDs which have smaller E_g and emit relatively low-energy photons (red) [16]. Electronic energy states become increasingly discrete as NP size decreases, where NPs with large E_g require higher energy to form excitons [17]. Thus, it is important to design photocatalysts whose E_g is suitable to absorb photons of EMR chosen to induce exciton formation. Excitons are defined as quasi-particles that form as a result of electrons and holes in semiconductors that are bound into pair states due to Coulombic interactions [18]. Excitons partake in oxidation of water molecules to form hydroxyl radicals, which interact with NOM and propagate photocatalytic reactions [19].

In a study performed by Mohtar et al., synthesized hematite (α -Fe₂O₃) NPs, nickel sulfide (NiS₂) NPs, and α -Fe₂O₃/NiS₂ nanocomposites for applications in the photocatalytic degradation of HA. The band gap energies of α -Fe₂O₃, NiS₂, and α -Fe₂O₃/NiS₂ were found to be 2.00 eV, 1.11 eV, and 2.49 eV, respectively. This showed that fabrication of the nanocomposite formed a photocatalyst which is capable of photoabsorption in the visible region. Moreover, the photoluminescence profile of the nanocomposite indicated a lower rate of recombination of the photo-induced electron-hole pairs. The degradation efficiency (%) of HA at 30 ppm by α -Fe₂O₃, NiS₂, and α -Fe₂O₃/NiS₂ was determined to be 88.7%, 86.0%, and 93.7%, respectively. This demonstrated the significance of E_g [20].

5.2. Results and discussion

5.2.1. Photocatalytic degradation of humic acid

HA is a common organic compound used to assess photocatalytic degradation dissolved organic matter in aqueous media. The solar-simulated photocatalytic degradation of HA in the presence of Ag₂O, Ag₂S, and AgCl NPs at neutral pH was observed to be an effective technique. As demonstrated in Fig. 5.1. (a-c), it was observed that initial stirring that occurred for 30 min in the absence of solar radiation had minimal effect in the removal of HA from solution. During this time frame, each type of NP demonstrated about 10-13 % removal of HA concentrations of 2.5-10 mg/L, which was ascribed to physisorption via

Van der Waals interactions on the surfaces of NPs. Moreover, physisorption was observed to be more prevalent for AgCl NPs. This was ascribed to their relatively smaller particle size, which translated to higher surface-area-to-volume ratio. Solar irradiation was observed to propagate the catalytic processes by the formation of excitons between the valence band and the conduction band of NPs, which facilitated reduction-oxidation reactions to produce scavenging radicals for HA degradation.

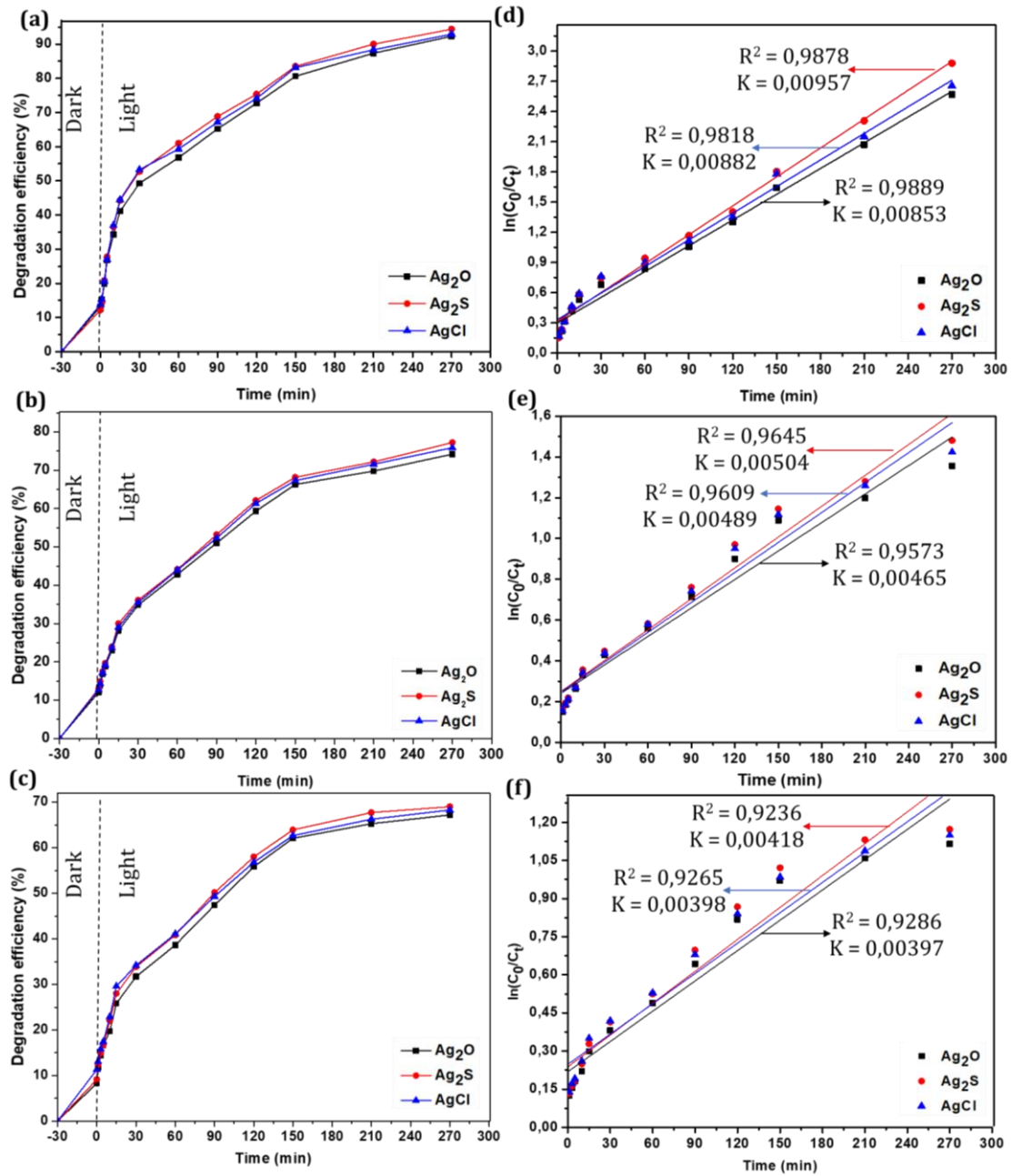


Figure. 5.1. Photocatalytic degradation efficiency by Ag₂O [120 min], Ag₂S [120 min], and AgCl [180 min] of HA at (a) 2.5, (b) 5, and (c) 10 mg/L with their corresponding rates of photocatalysis on (d), (e), and (f), respectively.

All photocatalysts seemed to substantially degrade HA after 270 min of photocatalysis, however, the Ag₂S NPs were seen to have higher efficacy across all concentrations. The photocatalytic degradation efficiency of HA showed to be inversely proportional to its concentration. This was ascribed to increased turbidity of the supernatant solution as HA concentration increased. The increase in turbidity had a direct influence on photon mobility through the supernatant, and concurrently reduced photoexcitation of electrons and free radical generation. The obtained degradation efficiencies by Ag₂O, Ag₂S, and AgCl NPs at 2.5 mg/L HA (Fig. 5.1.(a)) were 85.3, 87.4 and 88.1 %, respectively. A concentration increase of HA to 5 mg/L (Fig. 5.1.(b)) decreased the degradation efficiencies of Ag₂O, Ag₂S, and AgCl NPs to 74.2, 77.2, and 75.9 %, respectively. In the case when 10 mg/L HA (Fig. 5.1. (c)) was used, the obtained degradation efficiencies by Ag₂O, Ag₂S, and AgCl NPs were 66.1, 68.3, and 68.0 %, respectively. The rates of photocatalytic degradation of HA at concentrations of 2.5, 5, and 10 mg/L are shown in Fig 6. (d), (e), and (d), respectively. In general, Ag₂S NPs were determined to have relatively higher rates of photocatalytic degradation of HA across all concentrations, followed by AgCl NPs, then Ag₂O NPs. In addition, pseudo first order kinetics was followed by all the tested photocatalysts. Below is a set of equations that postulate the photocatalytic degradation mechanism of HA.



5.3. Conclusion

TEM analysis showed that the as synthesized Ag₂O, Ag₂S, and AgCl NPs were observed to have controlled sizes and shapes, attributed to surface capping ligands which were detected from FTIR spectra. Crystallographic data showed that silver-based NPs had sharp peaks with good signal-to-noise ratios, whose Miller indices matched those from the reference library. This implied that no significant impurities and/or defects were detected in the samples. The optoelectronic characterization of Ag₂O, Ag₂S, and AgCl NPs demonstrated good photoabsorption in the visible region and photoemission properties, which were instrumental for photocatalytic degradation of HA under solar simulated light. The degradation efficiency of 2.5 ppm HA obtained by Ag₂O [120 min], Ag₂S [120 min], and AgCl [180 min] was found to be 85.3%, 87.4%, and 88.1%, respectively. The degradation efficiency of the applied photocatalysts was observed to decrease with an increase in HA pollutant, which was due to saturation of the active sites. In addition, the interaction of solar-simulated EMR with NPs induced surface plasmon resonance on crystal facets. This concurrently emitted electrons that cleaved organic pollutants in aqueous solution, which created a chain reaction that produced radicals and perpetuated the photocatalytic degradation process.

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Supporting information for chapter 5

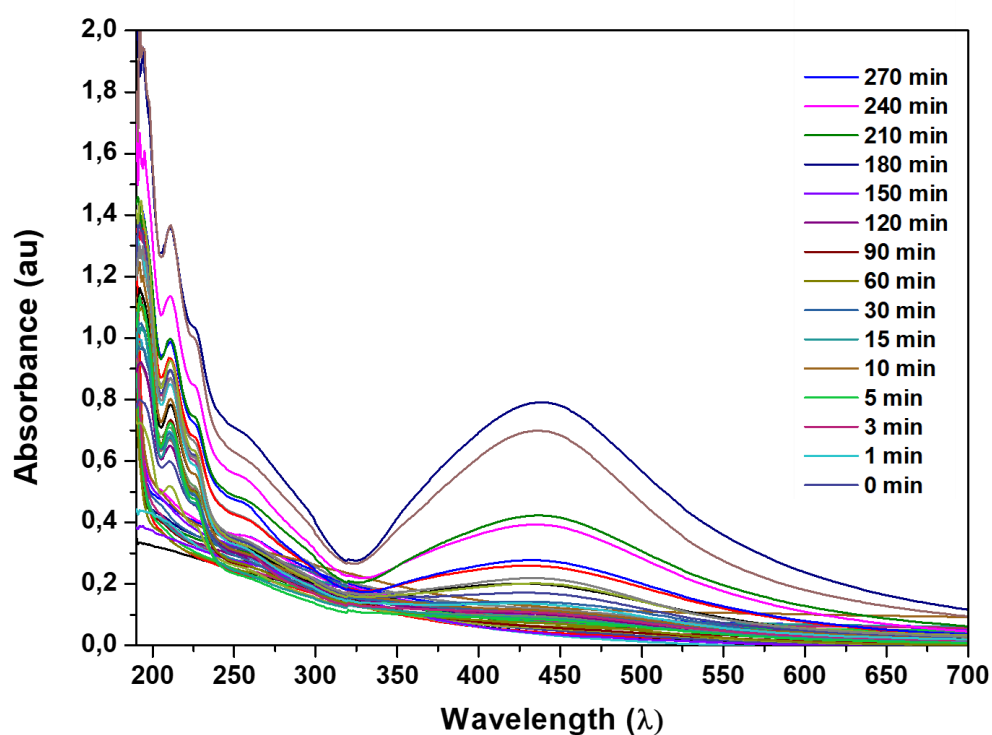


Figure S1: UV-vis of photocatalytic degradation of 10 mg/L humic acid by Ag_2O [120 min].

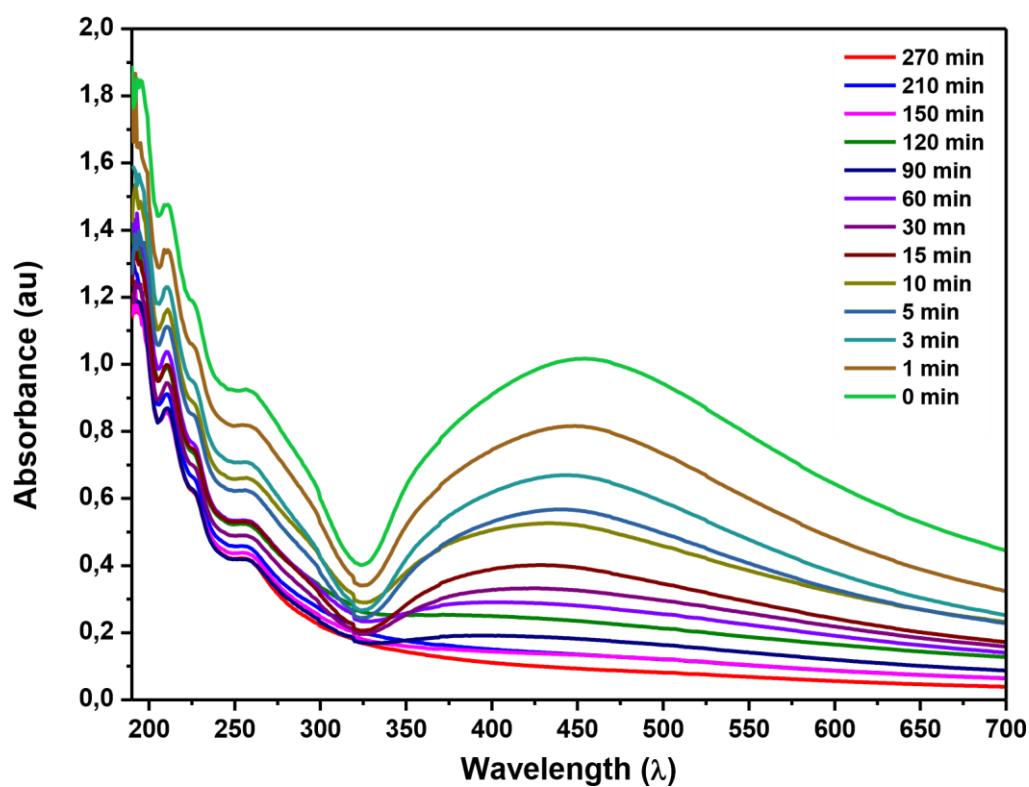


Figure S2: UV-vis of photocatalytic degradation of 10 mg/L humic acid by Ag_2S [120 min].

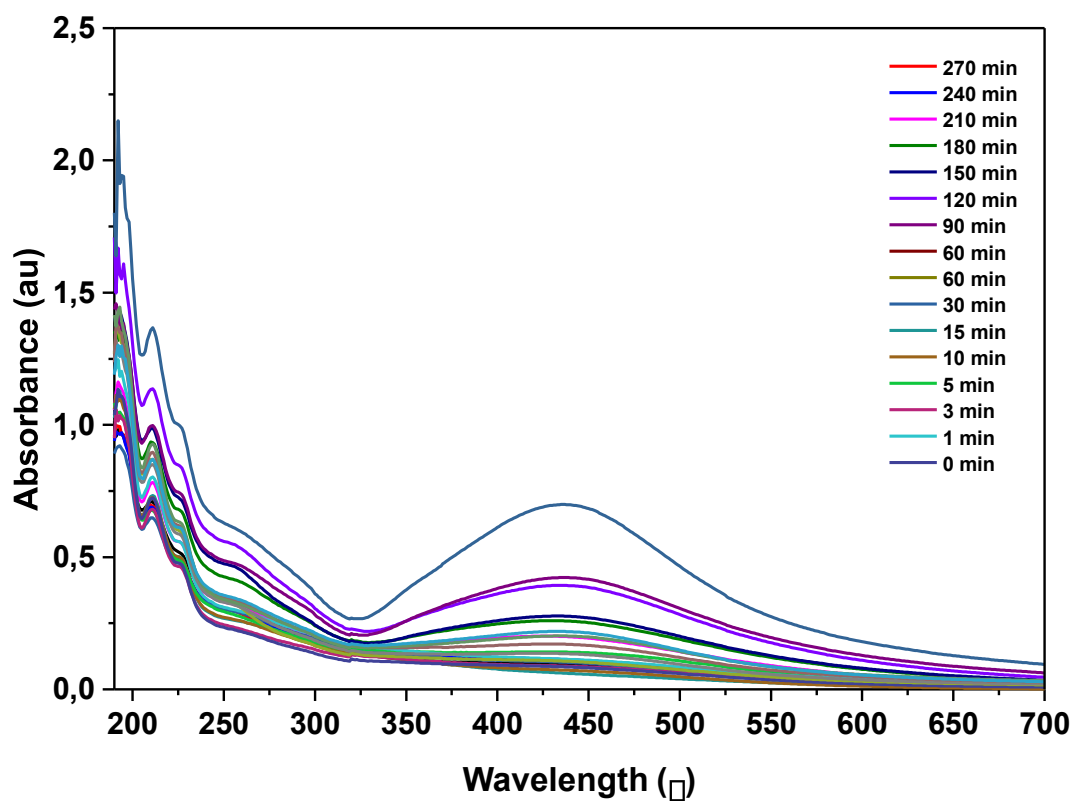


Figure S3: UV-vis of photocatalytic degradation of 10 mg/L humic acid by Ag_2Cl [180 min].

Chapter 6: Antibacterial and cytotoxicity activities of silver oxide, silver sulfide, and silver chloride nanoparticles

6.1. Introduction

Antibiotic and multi-drug resistant pathogens have become common in recent years, due to genetic mutations that occur in their plasmids [1]. Two examples of such pathogens are methicillin-resistant *Staphylococcus aureus* (MRSA) and penicillin-resistant *Enterococcus* (PRE), which acquire resistance to penicillin-related drugs because they release an enzyme called penicillinase [2]. These nosocomial pathogens are infectious, capable of causing urinary tract infections (UTI) and meningitis. Endeavours to mitigate the proliferation of such pathogens include the use of semiconductor nanoparticles, mainly silver and silver-based NPs due to their extensively reported antibacterial activity [3]. Nanobiotechnology has enabled novel therapeutic abilities in biomedicine, where NPs improve drug delivery, magnetic resonance imaging (MRI) wound dressing, and bacteriolysis [4]. Various pathways and mechanisms have been postulated for the pharmacokinetics of NPs in microorganisms. These include, but not limited to; (i) adhesion to and partial destruction of the bacterial cell wall, (ii) gradual liberation of Ag⁺ oxidant ions from the nanoparticles leading to oxidative stress, and (iii) Formation of reactive oxygen species which disorientate regular DNA functions [5]. The processes effectively mitigate cell proliferation and inhibits bacterial colony formation.

E. coli is a rod-shaped bacterium with adhesive fimbriae on the outer surface. These allow them bind to receptor structures and colonize the surface area. The cell wall consists of an inner cytoplasmic semipermeable membrane that regulates metabolic processes. It is enveloped by a peptidoglycan membrane which maintains morphology, supported by an outer lipopolysaccharide membrane that protects the cell from stress. These features are characteristic of Gram-negative bacteria and protects them from biochemical attack [6]. *S. aureus* is a quasi-spherical shaped bacterium which has a relatively thick cell wall consisting of peptidoglycan, polysaccharides, teichoic acids, and proteins. Foreign material can easily be absorbed, due to it lacking an outer lipid membrane. *S. aureus* is classified as microbiota of the body, mostly found in the upper respiratory tract and on the skin, and have mobility due to microscopic appendages called flagella [7]. Considering

the structural and biochemical defense mechanisms of bacteria against apoptosis, it is empirical to develop antibacterial agents to overcome these obstacles. The use of metallic NPs as bacteriolytic agents has gained notable popularity, attributed to their effective mitigation of cell proliferation and ability to disrupt metabolic activity [8]. Silver (Ag), silver oxide (Ag₂O), silver chloride (AgCl), and silver sulfide (Ag₂S) NPs have demonstrated significant potential to be developed and commercialized as antibacterial agents [9], [10]. Nevarro Gallón, et al. [4] prepared Ag NPs using microalgal exopolysaccharides as capping agents. The antibacterial activity of NPs was tested against Gram-positive *S. aureus* and Gram-negative *E. coli*. Bacteriolytic activity was observed to be dose-dependent (2.5-30 µg/mL) and directly proportional to NP concentration. Moreover, cytotoxicity studies were done on fibroblast cells. It was observed that cell viability (%) was inversely proportional to NP concentration and had no significant change when exposed to NPs (0.5-10 µg/mL) over a period of 5 days.

Kharaghani, et al. 2019 [11] reported on the development of antibacterial contact lenses containing metallic NPs. Polyvinyl alcohol (PVA) hydrogels were coalesced with AgNPs, copper NPs (CuNPs), and a combination (1:1) of AgNPs and CuNPs. The bacterial strains used for this study were *S. aureus* and *Pseudomonas aeruginosa* (*P. Aeruginosa*). It was determined that PVA/AgNPs hydrogels exhibited a higher zone of inhibition compared to PVA/CuNPs and PVA/AgNPs/CuNPs. This observation demonstrates the effectiveness of metallic NPs to mitigate formation of microbial keratitis. This work aims to evaluate antibacterial activity of Ag₂O, Ag₂S, and AgCl NPs against *S. aureus* and *E. coli*, as well as determine their cytotoxicity towards human embryonic kidney 293 T cells (HEK 293 T).

In this study, Ag₂O, Ag₂S, and AgCl NPs were synthesized and comparatively applied in antibacterial tests. Both Gram positive and Gram-negative bacteria were used as specimen. The cytotoxicity of these NPs towards HEK 293T cells was also determined to evaluate concentrations at which each NP induces loss of human cellular functions [12]. The potential for the use of silver-based NPs as alternatives to commercially available drugs will address the issue of drug-resistant bacteria, as well as create more pathways towards mitigation of proliferation of bacterial cells.

6.2. Results and discussion

6.2. Nanoparticle antibacterial susceptibility and MIC determination

6.2.1. Well-diffusion method

The antibacterial activity of the synthesized nanomaterials was evaluated by the well diffusion qualitative technique, using *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) as specimen. Standardized quantities of bacterial strains were exposed to NPs of varied concentrations, followed by incubation of the agar plates for 24 hours at 37⁰ C. Wells in which an active concentration of NPs was added were found encircled by a clear zone, formally referred to as 'zone of inhibition' (ZOI). A standard streptomycin antibiotic and sterile ultrapure water were used as positive and negative control, respectively. Each treatment was replicated three times, and diameters of the zones were measured using a caliper gauge. Plots of ZOI (mm) around agar wells for *E. coli* and *S. aureus* exposed to different NP concentrations are exhibited in Fig. 6.1 (a) and 6.1 (b), respectively. It was observed that ZOI of Ag₂O NPs were categorically larger than those of Ag₂S and AgCl NPs.

It was observed that Ag₂S and AgCl NPs did not show any ZOI bigger than 8 mm, while Ag₂O NPs showed growth inhibition for both strains at a concentration of 0.0625 mg/mL. The diameters of the ZOIs were directly proportional to NP concentration, with the highest ZOI achieved at NP concentration of 2 mg/mL by Ag₂O NPs for *E. coli* and *S. aureus* being 14.83 and 15.27 mm, respectively. The susceptibility of *E. coli* and *S. aureus* towards Ag₂O NPs was attributed to the rapid release of Ag⁺ ions, and concurrent generation of ROS in the microorganisms. Moreover, *E. coli* proved to be categorically more resistant to growth inhibition compared to *S. aureus*. *E. coli* is a Gram-negative bacterium surrounded by a thin peptidoglycan cell wall, which is encapsulated by an outer membrane containing lipopolysaccharide. This outer layer was allotted to the improved protection of *E. coli* against cell apoptosis.

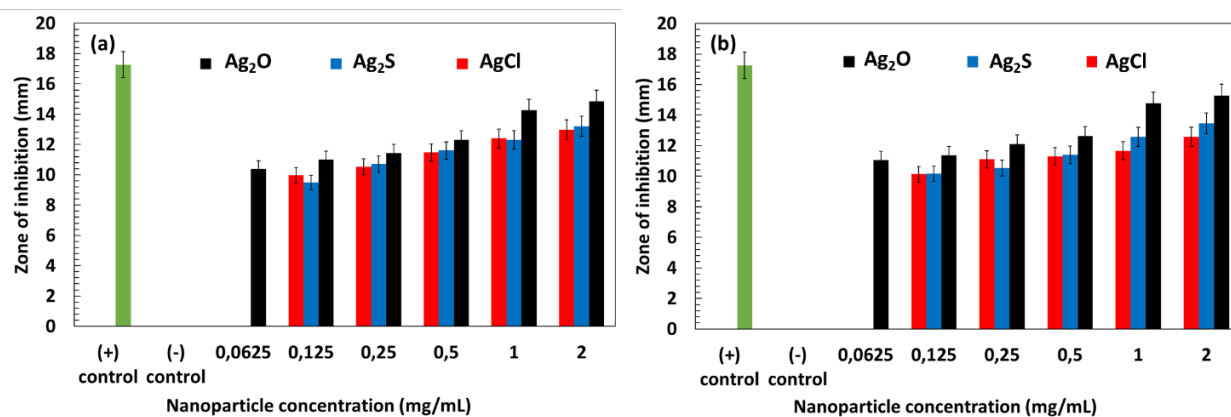


Fig. 6.1. Concentration-dependant antibacterial activity of Ag₂O, Ag₂S, and AgCl NPs against (a) *E. coli* and (b) *S. aureus*.

6.2.2. Broth micro-dilution method

Following confirmation of antibacterial susceptibility of NPs towards *E. coli* and *S. aureus*, the broth micro-dilution method was used to determine the minimum inhibitory concentration (MIC). Suspensions of bacteria were adjusted to have OD₆₀₀ of 0.1 a.u., using sterile LB nutrient medium. Two-fold serial dilution of NPs (2-0.015625 mg/mL) were prepared in LB broth, and 100 μ L of bacterial inocula were transferred into the separate vials then incubated overnight. It was found that both *E. coli* and *S. aureus* exhibited a concentration-dependent response towards NPs. MIC of Ag₂O, Ag₂S, and AgCl NPs against *E. coli* were observed to be 0.03125, 0.125, and 0.125 mg/mL, respectively. In the case of *S. aureus*, the MICs of Ag₂O, Ag₂S and AgCl NPs were 0.03125, 0.0625, and 0.125 mg/mL. The MIC values of Ag₂O and AgCl NPs were unchanged when applied to *E. coli* and *S. aureus*, while that of Ag₂S NPs decreased by two folds when applied to *S. aureus*. Observing that less concentration of Ag₂S NPs required to inhibit bacterial growth of *S. aureus* compared to *E. coli* signified that the former was more vulnerable to cellular apoptosis. Moreover, Ag₂O NPs categorically demonstrated superior antibacterial activity compared to its counterparts. The suspended NPs were effective in bacterial growth inhibition due to rapid release of Ag⁺ ions and higher surface area-to-volume interaction with the strains of bacteria.

Colony-forming unit (CFU) of *E. coli* and *S. aureus* bacteria on agar plates was persistent over the selected concentration range and was observed to increase as NP concentration decreased. This implied that even though no visible bacterial growth was observed at

concentrations above 0.5 mg/mL, a considerable fraction of the cells survived exposure to NPs. Therefore, no MBC was established for *E. coli* within the selected concentration range as bacterial cells were not completely killed. A similar trend was seen in the case of *S. aureus* bacteria, which was treated under similar conditions. This observation indicated that Ag₂O, Ag₂S, and AgCl NP were predominantly bacteriostatic. However, it was evident that the number of *S. aureus* CFU were significantly less than those of *E. coli*. This observation confirmed that the Gram-positive bacterium was more resilient to apoptosis, which may be attributed to the presence of an outer lipid layer found outside *E. coli* microorganisms.

6.2.3. Colorimetric assay of nanoparticle cytotoxicity

Approximately two to three decades ago, nanostructured materials became an important asset to modern society and the global economy. Strategic sectors that are custodians of nanoscience include pharma, biomedicine, agriculture, food technology, energy, and water purification [21]. The use of nanomaterials and discard of waste emanating from these sectors may result in leaching or erosion of nanomaterials into the environment. An area of concern is their potential to become secondary pollutants and lead to bioaccumulation within ecosystems. It is therefore essential to determine NP type and concentration levels at which cytotoxic effects are eminent towards biotic species. Herein, the MTT assay was performed to determine the cytotoxic effects of Ag₂S, Ag₂O, and AgCl NPs on HEK 293 cells. This is a facile and cost-effective technique to evaluate nanoparticle concentration-dependant cell viability by colorimetric measurements. The process relies on enzymatic reduction of 3-[4,5-dimethylthiozole-2-yl]-2,5diphenyltetrazolium bromide (MTT) to water-insoluble MTT-formazan, which is catalysed by mitochondrial succinate dehydrogenase. This enzyme is responsible for the citric acid cycle and electron transport within metabolically active cells [22].

The effect of NPs concentration (0.015625-2 mg/mL) on cell viability (%) is displayed in Fig. 6.2. The trend observed was that cell viability is inversely proportional to NP concentration. The highest concentration (2 mg/mL) is on row number 'A' and the lowest concentration (0.015625 mg/mL) is on row number 'H'. For Ag₂S and AgCl NPs, cell viability of HEK 293 cells remained above 90% at a concentration of 0.125 mg/mL. An exponential decrease was observed between 0.25-2 mg/mL, which implied severe

disruption of DNA processes and cellular oxidative stress. Considering Ag₂O NPs, cell viability averaged 69% and 41% at concentrations 0.015625 and 0.125 mg/mL, respectively. The faint-pink colour and maroon colour represent non-viable cells and viable cells, respectively. The maroon colour arises from the reduction of tetrazolium by viable cells to generate formazan. This indicated that Ag₂O NPs were most cytotoxic, ascribed to rapid release of oxidative Ag⁺ ions in physiological solution.

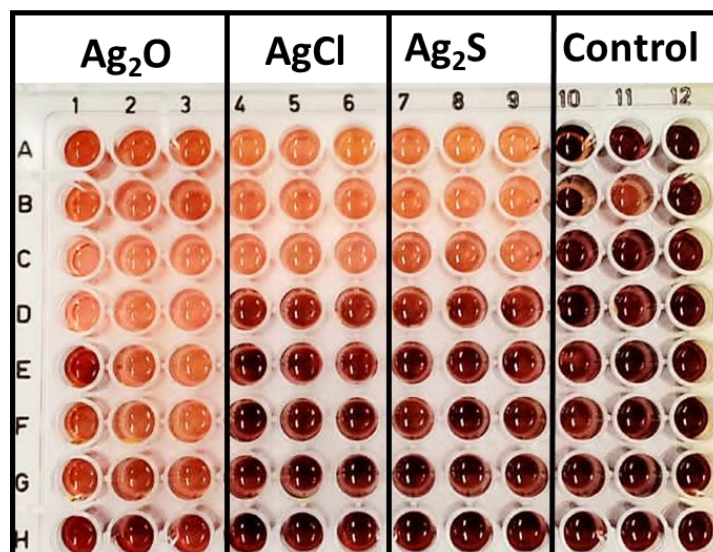


Figure. 6.2. Colorimetric cytotoxicity assay of silver-based NPs on HEK 293 cells.

Furthermore, the cytotoxic concentration at which HEK 293 cells had 50% viability (CC₅₀) was estimated to be 0.3606, 0.0302, and 0.3412 mg/mL for Ag₂S, Ag₂O, and AgCl NPs, respectively. This implied that Ag₂O NPs were more cytotoxic than Ag₂S and AgCl NPs by approximately ten-fold. The relatively low cytotoxicity of Ag₂S NPs indicates their feasible applicability in biomedical, food and beverage, as well as water treatment industries. The graphical demonstration of the concentration-dependant cytotoxicity assay, together with cytotoxic concentration values at 50 % viability are shown in Fig. 6.3.

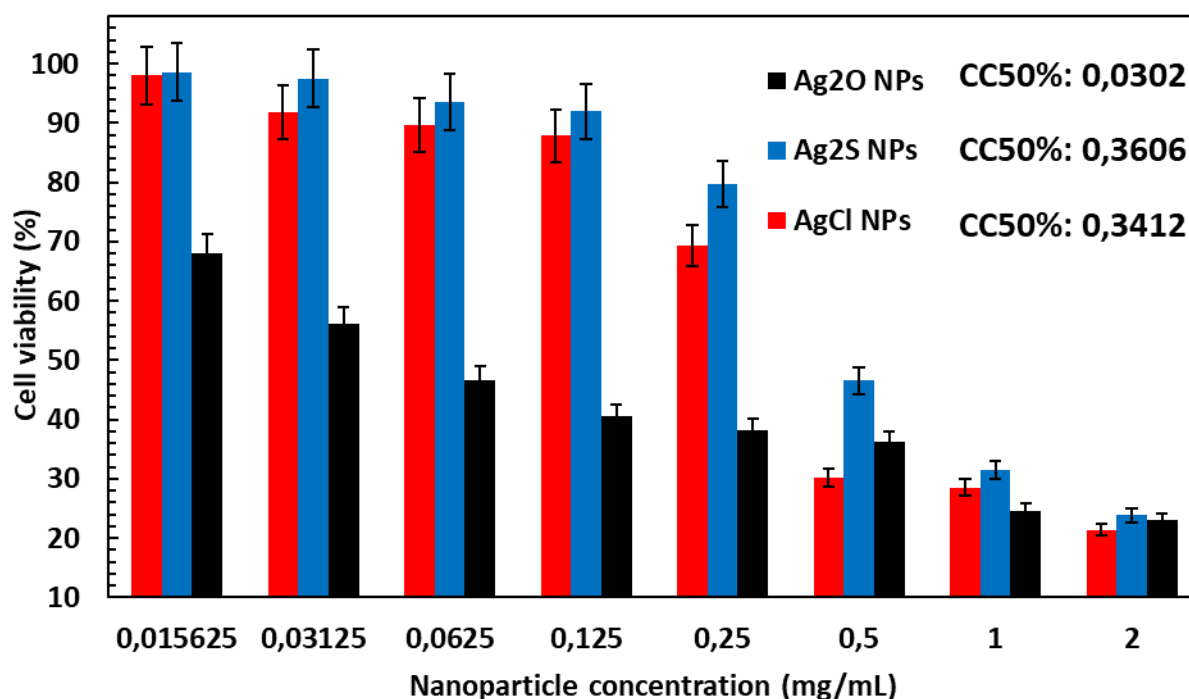


Figure 6.3. Effect of concentration of Ag₂O, Ag₂S, and AgCl NPs on HEK 293T cell viability.

6.3. Conclusion

In the study at hand, it was demonstrated that silver-based NPs have significant antibacterial activity against *E. coli* and *S. aureus*. The use of capping agents during synthesis enabled facile nucleation and crystallization of NPs. The interruption of cellular metabolic functions was attributed to ROS generation upon exposure to NPs, followed by gradual apoptosis. Cytotoxicity assessments indicated a concentration-dependent relationship, which was directly proportional to nanoparticle concentration. Moreover, Ag₂S and AgCl NPs proved to be less toxic towards HEK 293T cells. Ag₂O NPs were observed to exhibit high toxicity, even at low concentrations, which can be ascribed to rapid release of Ag⁺ ions and inducing apoptosis. The obtained results demonstrate that Ag₂O, Ag₂S, and AgCl NPs have great potential to induce antibacterial characteristics when applied on surfaces. More applications to explore include coating of medical apparatus, surface disinfectants, as well as coalescence with dental implants.

6.4. References

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Chapter 7: Fabrication of Ag₂S-incorporated Polyamide thin film nanocomposite reverse osmosis membranes with antifouling properties

7.1. Introduction

The desire for safe and consistent water supply has increased due to rapid population growth and proportional rise in competition for this commodity [1]. A decline in sources of fresh water has been observed in various parts of the world due to geoclimatic events and anthropogenic activity [2]. Water scarcity can be defined as inadequate volumes of fresh water available to meet demands, which can be caused by inappropriate allocation of potable water, infrastructure mismanagement and contamination of freshwater bodies [3]. Climate change has been observed to contribute largely towards fluctuating precipitation patterns, and circumstantially leads to drought or flooding. Global warming has also contributed to quantitative loss of glaciers, causing rises in sea levels and saltwater intrusion in coastal aquifers [4]. Access to potable water enables domestic, economic, and industrial activities of importance to take place, for which treatment methods such as desalination have been developed due to abundance of seawater on earth [5]. One of the leading technologies for desalination is membrane technology, which is used for separation of salts and natural organic matter from brackish and/or seawater [6]. An alternative desalination method is thermal distillation. However, this process energy-intensive and mostly has a high carbon footprint. Reverse osmosis (RO) has become a leading tool for desalination due to simplicity, high throughput (flux), and excellent separation properties [7]. Advancements in RO membrane development (i.e., chemical composition and fabrication parameters) have enhanced membrane robustness against components found in seawater, as well as reduced plant operational costs [8].

A challenge associated with seawater reverse osmosis (SWRO) is fouling, which deteriorates membrane integrity and efficiency, as well as the quality of permeate obtained. Membrane fouling is often caused by adsorption, accumulation, and crystallization of microbial, organic, and inorganic constituents on the feed water-membrane interface [9]. Membrane fouling reduces water flux and arises the necessity to

operate at higher than usual pressure, thus increasing the overall energy requirements of the desalination plant [10]. Microorganisms are known to secrete extracellular polymer substances (EPSs), which have been identified as contributors towards membrane fouling [11]. EPSs are high-molecular-weight natural polymers such as polysaccharides, lipids, nucleic acids and humic substances, which form part of natural organic matter (NOM) found in seawater [12]. Ultimately, the membrane life span is shortened, which increases operational costs due to frequent membrane replacement [13]. Endeavours to mitigate membrane fouling include pre-treatment of the feed, surface modification and the development of nano-enhanced membranes (NEMs) [14].

NEMs have been developed by the coalescence of nanoparticles (NPs) such as graphene oxide (GO), carbon nanotubes (CNTs) and metallic NPs with membrane thin film composites (TFC) [15]. Therefore, high levels of plant efficiency can be achieved by the integration of NEMs, which introduce robustness, high water throughput, and bestow antifouling properties to RO membranes [16]. Furthermore, research interest has grown around incorporation of metallic nanomaterials (i.e. silver) in SWRO membranes and has led to breakthroughs in desalination processes [17]. Related work was done by Li et al., where they fabricated TFN RO membranes modified by two dimensional laminar MoS₂ with improved desalination performance and fouling-resistant characteristics. The modified membranes demonstrated superior salt rejection, normalized flux, and fouling resistance compared to unmodified RO membranes [18]. Ahmed Al Mayyahi provided insights on thin film composite fabrication for enhanced performance. It was emphasized that the choice of monomers, surface modification of the PA layer, and the coalescence of NPs with the active TFC layer exhibited potential to significantly influence RO membrane performance [19]. A direct benefit observed from immobilization of NPs were the retardation of biofilm formation and deposition of dissolved organic matter on the membrane-water interface. [20].

Ideally, nanomaterials used in enhancing fouling resistance should be photoactive, bioactive and have low levels of cytotoxicity. In this study, TFC will be coalesced with Ag₂S NPs to form TFN to improve water flux, salt rejection, fouling resistance and stability. Ag₂S NPs are semiconductors with good optoelectronic properties, are plasmonic, are stable, and have low cytotoxicity [21]. These properties make them useful in digital technology,

photocatalysis, and bionanotechnology. Interfacial polymerization method was used to fabricate the Ag₂S NPs embedded PA active layer on a polysulphone (PSF) ultra-filtration membrane support. This innovative technology holds the potential to contribute towards cost effective provision global water security.

7.2. Results and discussion

7.3. Characterization of NPs and nano-enhanced RO membranes

7.3.1. Crystallographic properties of silver sulfide NPs

As illustrated in Fig. 7.1, the XRD patterns obtained matched monoclinic Ag₂S nanocrystals with an average crystallite size of 22.3 nm. Significant peaks were observed at $2\theta = 22^\circ, 33^\circ, 35^\circ, 38^\circ, 44^\circ$, and 54° ; which had *hkl* values of $\{-101\}$, $\{012\}$, $\{111\}$, $\{120\}$, $\{112\}$, $\{031\}$, $\{200\}$ and $\{041\}$, respectively. The peaks were referenced to acanthite (JCPDS: 00014-0072) with monoclinic lattice, and space group of P21/n. The sharp, narrow peaks signified a high degree of NP crystallinity and small crystallite sizes. Munaro et al. investigated synthetic pathways of Ag₂S NPs using different sources of the sulfur ion. It was found that sodium sulfide, thiourea, and thioacetic acid produced monoclinic acanthite with average crystallite size of 14, 28, and 29 nm, respectively [23].

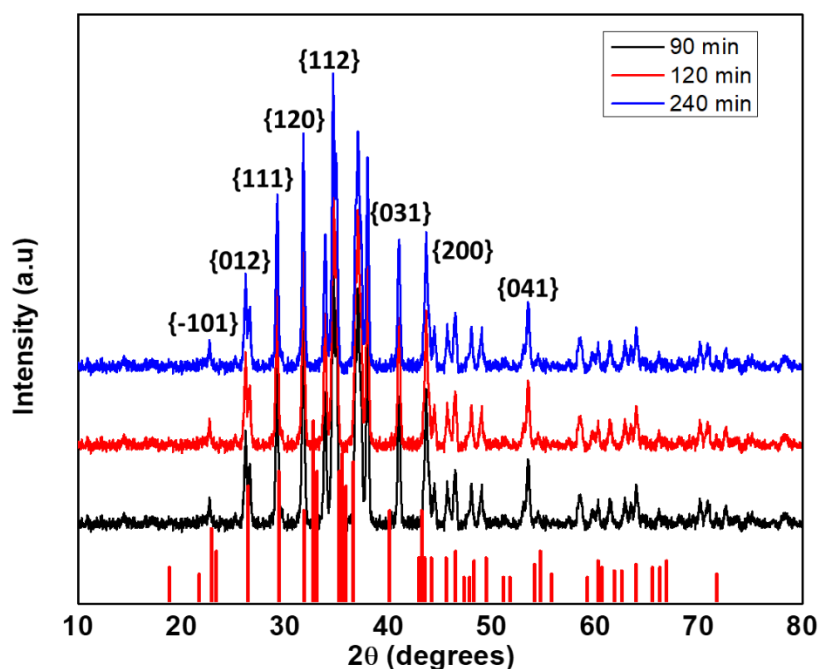


Figure. 7.1. X-ray diffraction patterns of Ag₂S NPs synthesized at different time intervals.

7.3.2. Morphology and size distribution of silver sulfide NPs

Nanoparticle morphology and dispersity were determined by TEM analysis. The images illustrated in Fig. 7.2 represent Ag₂S NPs synthesized for (a) 90, (b) 120, and (c) 240 min, as well as corresponding size distributions, respectively. It was observed that Ag₂S NPs were hexagonal in shape. Ag₂S NPs showed little to no agglomeration due to capping with OLA. The average particle size obtained was (a) 27.5, (b) 30.9, and (c) 37.2 nm. The increase in particle size as the time was prolonged is due to Ostwald ripening.

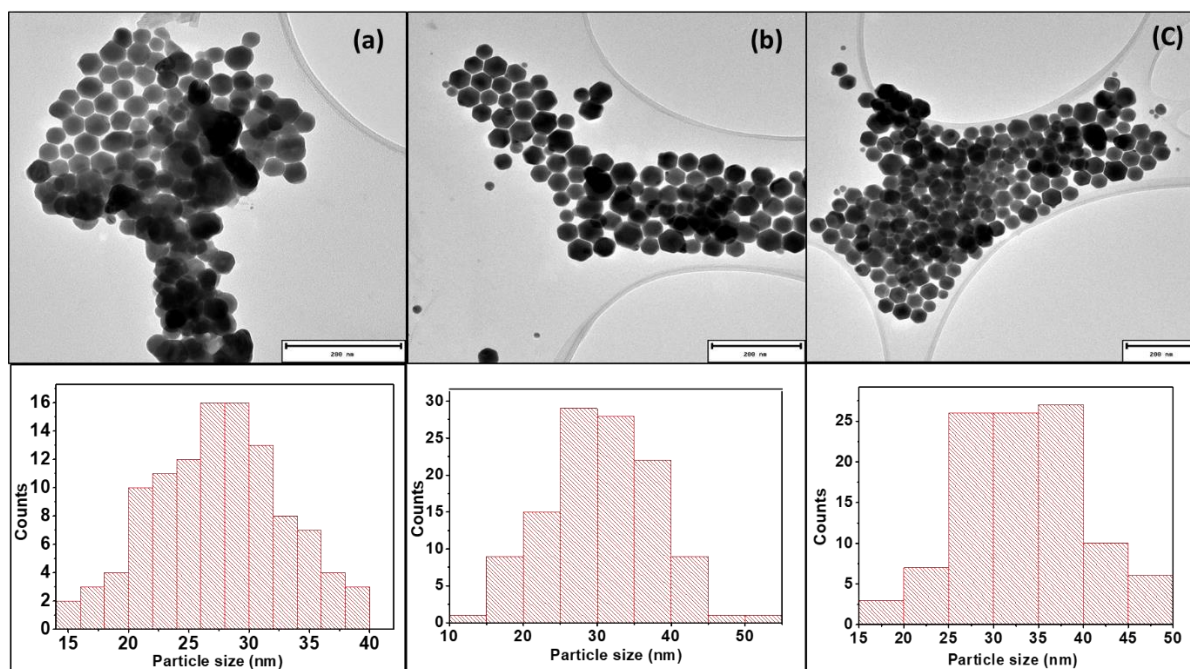


Figure. 7.2. TEM of Ag₂S NPs synthesized for (a) 90 min, (b) 120 min, and (c) 240 min.

7.3.3. Structural properties of TFC and TFN membranes

The recorded infrared spectra of membranes shown in Fig. 7.3 illustrated several changes in chemical composition of the membranes. The PSF support was observed to contain hydroxyl groups at 3341 cm⁻¹ mainly from water molecules. Other characteristic groups of PSF polymeric chain (C₂₇H₂₆O₆S) were identified at 1659 cm⁻¹ (amide C=O stretch), 1585 cm⁻¹ (amide N-H bend), 1151 cm⁻¹ (C-O stretch), as well as 1106 cm⁻¹ (symmetric S=O) and 1041 cm⁻¹ (asymmetric S=O). Interfacial polymerization of the PA TFC and TFN layers lead to a disappearance of the hydroxyl group due anhydrous hexane used in the organic phase. The absence of Sp₂ and Sp₃ hybridized carbons and diminishing of sulfonic groups confirmed the presence of a newly formed PA layer on the PSF surface. Vibrational peaks ascribed to PA were found at 1659 cm⁻¹ (amide I C=O stretch), 1542 cm⁻¹ (amide II C-N stretch) 1481 cm⁻¹ (C-H bend), 1385 cm⁻¹ (C-O stretch), 1242 cm⁻¹ (C-N stretch), and 779 cm⁻¹ (aromatic C-H and C=C wagging).

The presence of aromatic and amide functional groups corroborated the formation of the TFC active layer, which is responsible for RO filtration of dissolved ions in water. In a study conducted by Ng, et al., graphene oxide was incorporated into the active polyamide RO membranes for desalination. FTIR spectra were used to verify formation of the active layer. Peaks observed at 1665 cm^{-1} , 1610 cm^{-1} , and 1545 cm^{-1} were assigned to C=O stretching vibrations from amide I, aromatic ring breathing and in-plane N-H bending, and C-N stretching vibrations of amide II, respectively [24]. Similar IR bands were seen for TFC and TFN in the current study, which signified the presence of the PA layer.

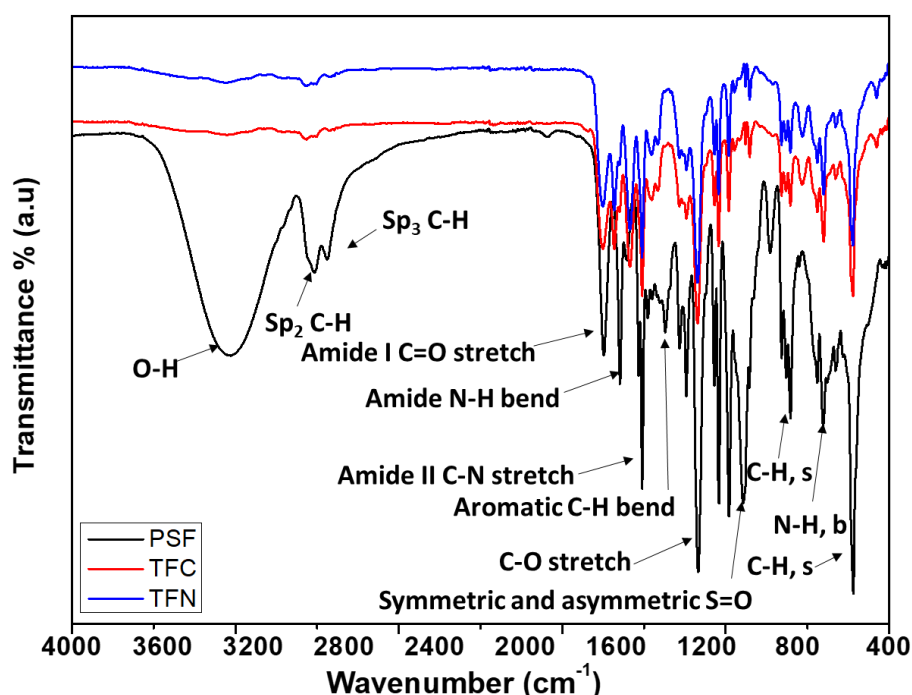


Figure. 7.3. FTIR spectra of PSF support, TFC, and 30 mg Ag_2S NP loaded TFN membranes.

Topographical and morphological characteristics of the fabricated RO membranes were surveyed using SEM (Fig. 7.4.) and AFM (Fig. 7.5.). The commonly observed trend was that TFC active layers consisted of ridges and valleys created by the polymer scaffold, as shown in Fig. 7.4. SEM images of the pristine (a) TFC membrane and TFN membranes containing (b) 20, (c) 30, and (d) 50 mg are depicted. It was evident that incremental loading of Ag_2S NPs resulted in the formation of less pronounced ridges on the PA layer. This may be attributed to nano filling of the valleys, as well as a dielectric effect introduced by Ag_2S NP addition. The smoothening of the loaded PA layer can potentially reduce the surface area on which foulants may attach, leading towards fouling resistant membranes [9]. However, the smoothening of the membrane surface may possibly have undesirable effects on water

flux and salt rejection. Therefore, a synergistic balance should be obtained in order to optimize membrane performance while maintaining resistance to fouling. This trend was corroborated by atomic force microscopy (AFM) analysis, the results of which are shown in Fig. 7.5. and summarized in Table 7.1. It was observed that average roughness (R_a) and the root mean square average of height deviations (R_q) decreased with higher dosage of Ag_2S NPs. The ratio (R_q/R_a) for 30 mg and 50 mg loaded TFN membranes was determined to be 1.34 and 1.35, respectively.

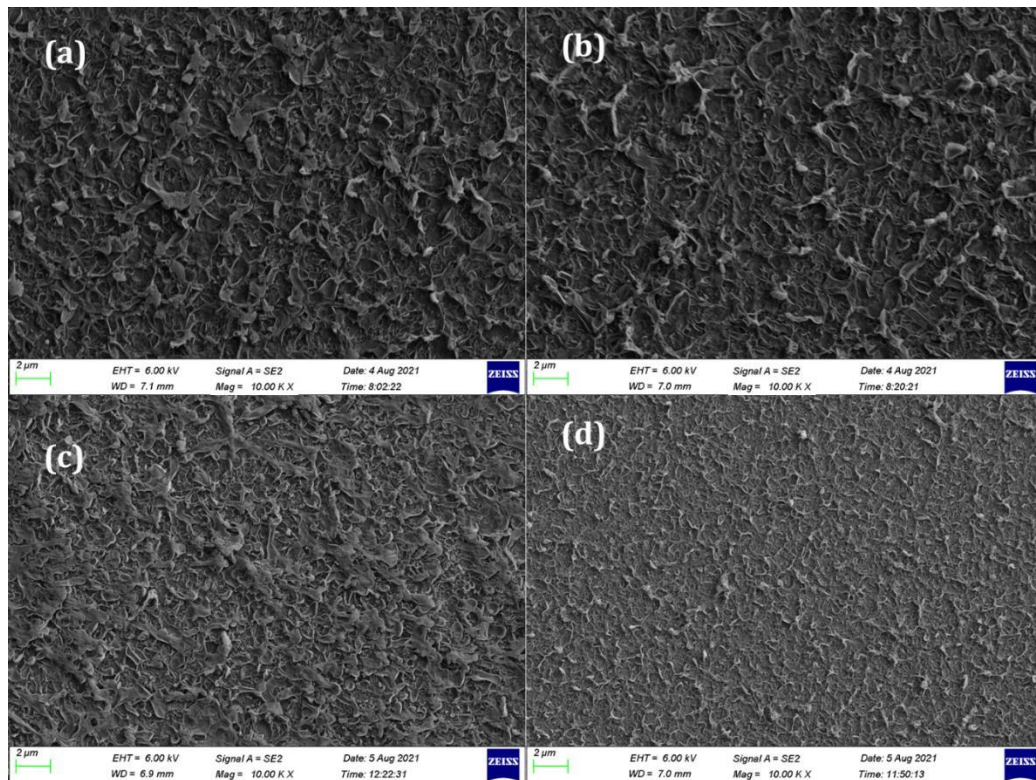


Figure 7. 4. SEM analysis of (a) TFC, (b) 20 mg, (c) 30 mg, and (d) 50 mg TFN.

This demonstrated a Gaussian distribution of asperity (harsh) heights approximated. For TFC and 20 mg loaded TFN membranes the obtained values were 1.51 and 1.51, respectively. The observed trend indicates a Wald distribution [25]. The maximum vertical distance (R_{max}) between the highest and lowest data point was directly increased with NP loading. This may be attributed to NP immobilization on the surface, the partial filling of nano-voids, as well as valleys observed on the PA layer.

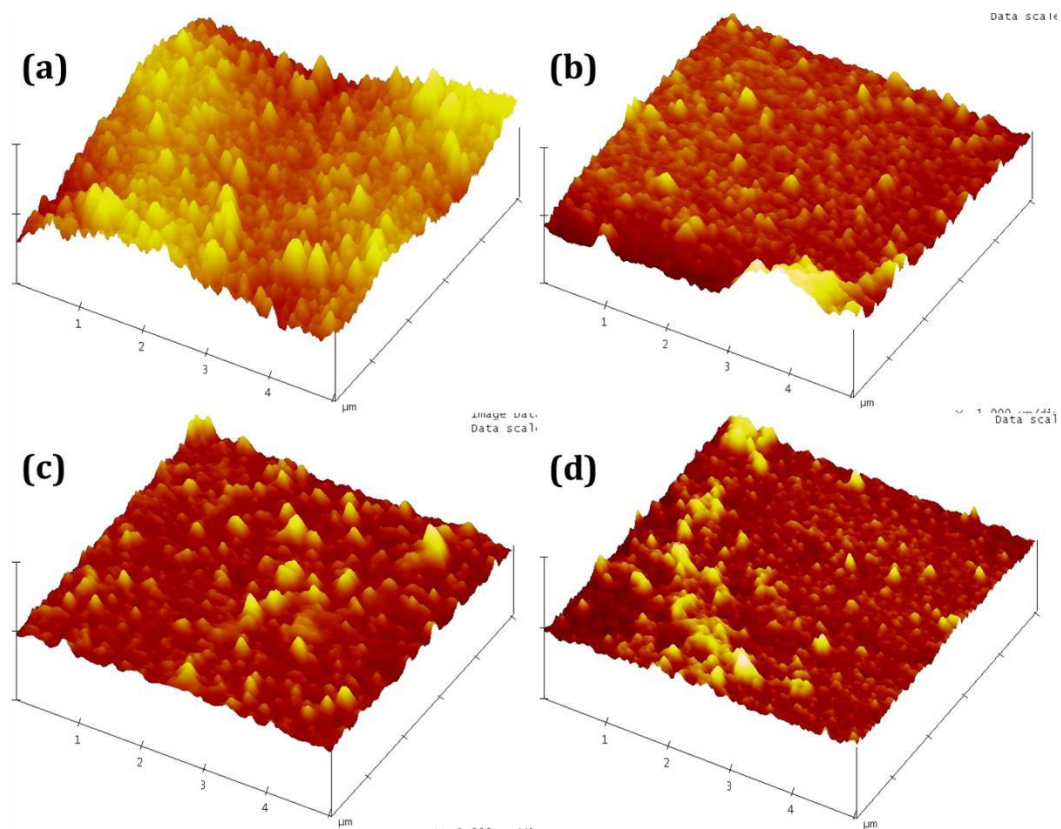


Figure. 7.5. AFM analysis of (a) TFC, (b) 20, (c) 30, and (d) 50 mg TFN.

Research done by Bian et al. employed SEM to assess the effect of zwitterionic colloid nanoparticle loading in PA layer on membrane morphology [26]. The ridge-and-valley structure was observed to become less prominent with increased NP loading. This was ascribed to the miscibility of zwitterionic colloid nanoparticles (ZCPs) with the polyamide matrix, where hydroxyl on ZCPs could react and bind with acyl chloride groups.

Table 7.1: AFM analysis of TFC and Ag₂S NP loaded TFN membranes.

Membrane	R _a (nm)	R _q (nm)	R _q /R _a	R _{max} (nm)
TFC	89,51	135,04	1,51	284,96
20 mg	87,03	131,77	1,51	377,04
30 mg	74,16	99,33	1,34	404,78
50 mg	46,56	63,04	1,35	682,54

7.3.4. Surface hydrophilicity of TFC and TFN RO membranes

Static water contact angle (WCA) was used to estimate the surface hydrophilicity of the as prepared membranes. This parameter is often used to determine the propensity of obtaining high transmembrane water permeability. It was observed in Fig. 7. 6. that WCA of TFC was recorded to be 73.5°. Following the addition of Ag₂S NPs during synthesis to form TFN, the WCA was seen to decrease. The TFN membranes loaded with 20, 30, and 50 mg Ag₂S NPs recorded contact angles of 54.1, 45.4, and 43.3°, respectively. This demonstrated improved hydrophilicity, which was attributed to hydrophilic aliphatic side chains of OLA on Ag₂S NPs used as capping agent. Acyl chloride groups often undergo hydrolyzation, which forms carboxylic groups and enhance hydrophilicity [26].

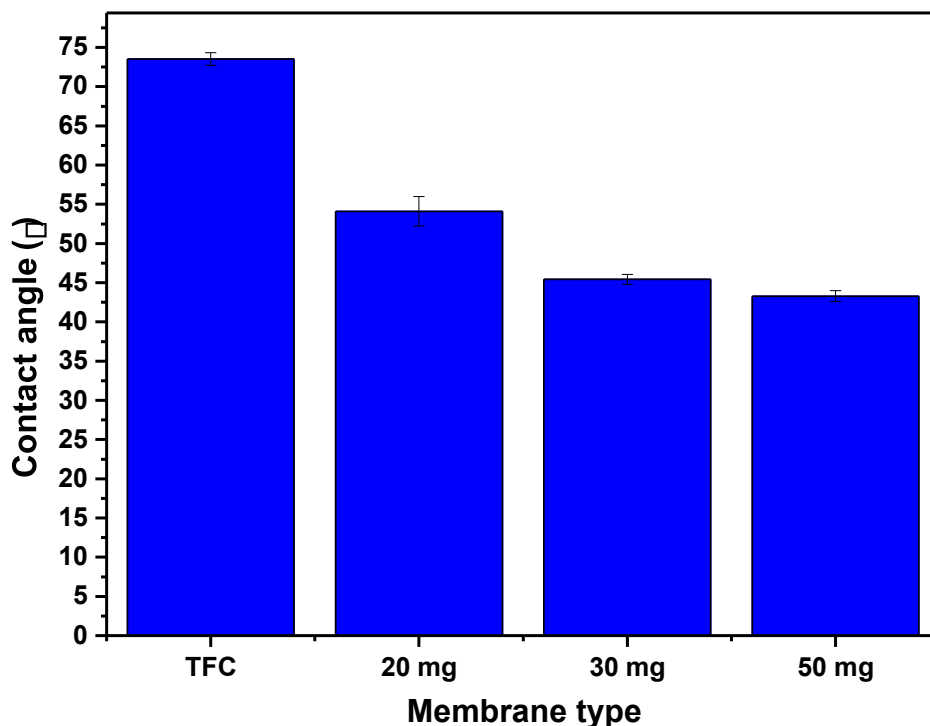


Figure. 7.6. Static water contact angle analysis of TFC and TFN membranes (0-50 mg Ag₂S NPs in aqueous phase).

7.4. Water flux and salt rejection tests of RO membranes

The separation characteristics of TFC and TFN membranes were evaluated, and the data obtained is displayed in Fig. 7. 7. Initial conductivity of NaCl ions was 4.42 μ S. TFC membranes obtained water flux and salt rejection of 24.76 ± 0.97 L/m²h and 97%, respectively. The 20 mg and 50 mg loaded membranes performed approximately similar. However, it was the 30 mg loaded membranes that demonstrated optimum water flux and

salt rejection of 32.68 ± 0.62 L/m²h and 98%, respectively. Surface morphology and hydrophilicity of the PA layer, as well as the availability of nano-voids had an important contribution towards water flux and salt rejection of Ag₂S NP loaded RO membranes. In a study conducted by Li et al, 2019, molybdenum disulfide nanosheets were incorporated into the PA layer to form MoS₂/TFN. The concentration of MoS₂ was varied between 0.005-0.05 wt%. Following performance tests, it was found that higher wt% lead to loss of water flux and salt rejection [18].

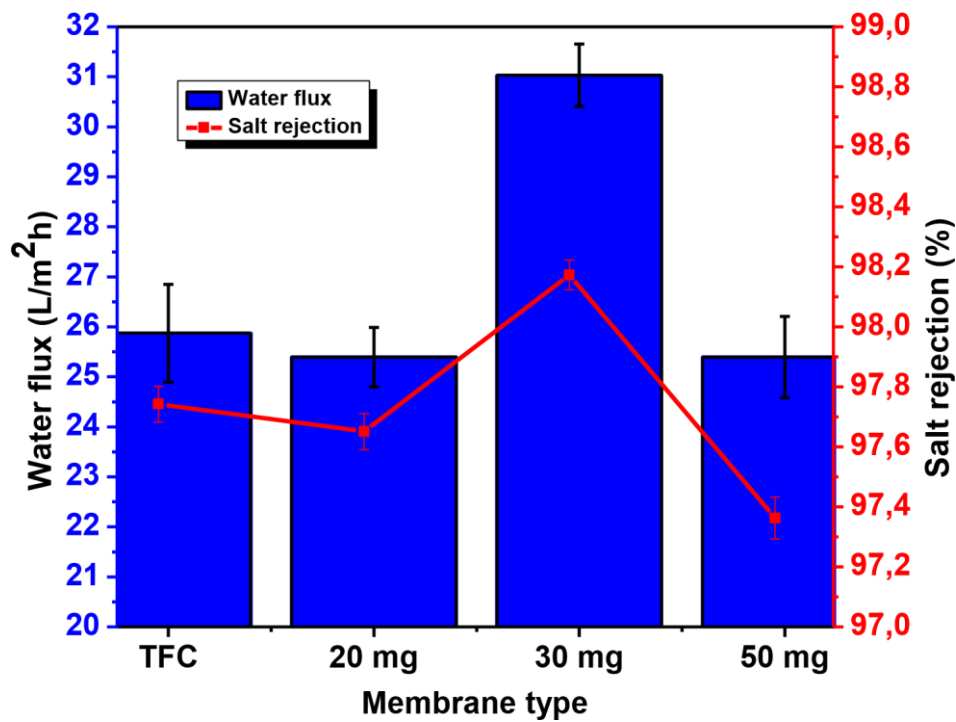


Figure. 7.7. Separation performance of TFC and Ag₂S NP loaded TFN RO membranes.

7.5. Anti-biofouling properties of RO membranes

Biofouling occurs via adhesion of pathogens and subsequent colony formation on the water-surface interface. The propensity for this process to occur is dependent on bacterial concentration versus membrane morphology and NP dosage. Gram-negative *E. coli* bacteria was used as a model bio-foulant, as it is considered to be a foodborne and waterborne pathogen. Following incubation, supernatant solutions were sampled onto agar plates using a micropipette and incubated overnight. It is widely known that CFU ≥ 300 on an agar plate, are regarded as too numerous to count (TNTC), while CFU ≤ 30 are referred to as too few to count (TFTC) [20]. The trend observed was that CFU were dependent on the bacterial concentration (OD), versus the concentration of Ag₂S NPs.

It is depicted in Fig. 7. 8. that TFC membranes acquired higher colony forming units (CFU), while TFN membranes acquired less. The bacterial growth inhibition was observed to increase with increased Ag₂S NP dose. This was ascribed to the advantage of immobilized Ag₂S NPs on the membrane surface. TFN membranes demonstrated enhanced growth inhibition properties and had a positive effect on the ability to mitigate biofouling. The released Ag⁺ ions from Ag₂S NPs have a propensity to bind with thiol functional groups of proteins, which may disrupt cellular functions [27]. A similar observation was made by Yang et al., who fabricated RO membranes modified with silver NPs. It was reported that bacterial cell proliferation was mitigated by silver NP immobilization, which significantly enhanced antifouling characteristics of the membrane [28]. In another study carried out by Nguyen et al., the antifouling effects of silver NPs regenerated by TiO₂ (Ag/TiO₂) on forward osmosis membrane was evaluated. It was found that NP immobilization reduced propensity of bacterial growth by up to 11 times, compared to pristine membranes. Moreover, the presence of NPs on the membrane surface decreased the fouling propensity of membranes [29].

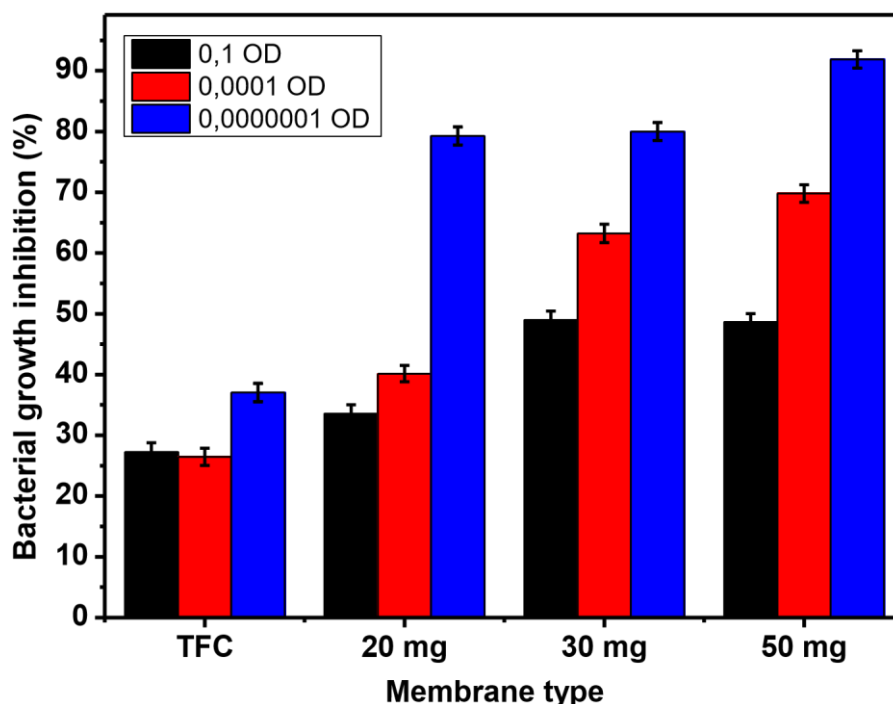


Figure. 7.8. Antibacterial activity of membranes against varied concentrations of *E. coli*.

7.6. Benchmarking

Previous contributions made towards the development of RO membranes have provided key insights about this technology. To benchmark the current study, several research publications and their outputs were scrutinized. It was observed in Table 7.2. that Ag₂S TFN exhibited performance characteristics that were equal, at times better than recently produced RO membranes. This demonstrates a significant competence of Ag₂S TFN and provides an opportunity for further improvement and more rigorous testing prior commercialization. The developed membranes should also be tested on real seawater.

Table 7.2: Comparison of separation and antifouling properties of TFN membranes

Membrane type	Water flux (L/mh)	Salt rejection (%)	Operating pressure (psi)	BSA antifouling (%)	Bacterial growth inhibition (%)	Reference
Ag-NP 15s PA	16.56	2000 ppm, 99.3	225	-	Pseudomonas fluorescenes: 28.3	[31]
pSM-AgNP	45	2000 ppm, 97.5	218	-	Shingomonas paucimobilis: 87	[28]
β-CD-f-GO PA	36.02	2000 ppm, 95.8	225	FRR: 85.4 R _t : 23	Bacillus subtilis: 90 <i>E. coli</i> : 45.9	[32]
PVA-NC-γ(0.5)	5.1	25000 ppm, 99.5	263	-	-	[33]
TFN-GOQD/AP	39.6	2000 ppm, 98.4	232	FRR: 83.2 R _t : 36.4	<i>E. coli</i> : 99.9	[34]
ZnOPMAA-g-PA(TFC)	21.17	2000 ppm, 96.9	218	-	<i>E. coli</i> : 40.1	[35]
TFN-Ag/HPS-6	64.0	2000 ppm, 97.8	261	FRR: 91.4 R _t : 9.9	<i>E. coli</i> : 96.7	[26]
Ag ₂ S-TFN	32.68	2000 ppm, 98.2	250	FRR: 80.3 R _t : 18	<i>E. coli</i> : 49	This work

7.7. Conclusion

RO membranes with an active PA layer coalesced with Ag₂S NPs were prepared and tested. The evaluated characteristics were chemical composition, surface topography, resistance to organic fouling and biofouling, hydrophilicity, water flux, and salt rejection. Infrared spectra detected functional groups which provided evidence of interfacial polymerization of the TFC layer. Surface roughness decreased with increased Ag₂S NP dose, which proved to significantly improve performance characteristics. With reference to TFC membranes, the 30 mg loaded TFN membranes exhibited improved water flux and salt rejection by 27% and 1%, respectively. It was clear that intrinsic properties of the membrane mainly enhanced transmembrane permeation of high-quality RO water. The propensity of bacterial colonies to form on TFN decreased with increased NP concentration. Ag₂S NPs had dose-dependent cytotoxic effects on HEK 293 cells, where concentrations above 0.25 mg/mL yielded cell viability of less than 80%. The BSA fouling test revealed that 30 mg loaded TFN membranes had superior antifouling characteristics compared to TFC membranes, where a 34% improvement in biofouling resistance was observed at bacterial concentration of 0.1 OD. The performance characteristics of PA-based membranes were enhanced by Ag₂S NPs loading, which rendered TFN an excellent candidate for seawater desalination in the presence of organic foulants and biofoulants.

7.8. References

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Chapter 8: General conclusions and recommendations

8.1 conclusions

Nanoscience and nanotechnology have become one of the frontiers in scientific research over the past few decades. The physicochemical properties exhibited by nanostructured materials has attracted the exploration and mastery of their synthesis, with several reproducible methods having been developed over the years. Previous work done has shown evidence that nanomaterials acquire varied structural, mechanical, optical, electronic, and thermodynamic properties; depending on the selected route of synthesis, as well as reaction conditions applied. The properties of nanomaterials have ushered them into a vast number of applications, which include biomedicine, water reticulation, optics, electronics, as well as energy generation and storage.

In the current study, silver-based NPs (i.e., Ag₂O, Ag₂S, and AgCl) were each synthesized using different synthetic routes. Ag₂O NPs were formed using the aqueous synthetic method under mild conditions, where aqueous silver nitrate and sodium hydroxide were used as precursors. Water was used as a solvent, with the addition of oleylamine capping agent to control the nucleation and growth kinetics of Ag₂O NPs. Ag₂S NPs were synthesized using the solvothermal method, where solid silver nitrate and sulphur powder were used as precursors. In this case oleylamine performed a dual purpose of being both the solvent and capping agent that controlled the size and shape of NPs. The co-precipitation method was used to obtain AgCl NPs, whereby solid silver nitrate and sodium chloride salts were used as precursors. The organic solvent chosen as the supernatant solution was 1-octadecene, which also performed the role of capping NPs.

Ideally, the desired NPs were those with band gap energies that are suited for photoabsorption and photoemission in the visible region of the solar electromagnetic spectrum. NPs with this property were indeed obtained under the reaction conditions previously mentioned, where the band gap energies of Ag₂O, Ag₂S, and AgCl NPs were observed to be 2.97, 3.11 and 3.05 eV, respectively. The as-mentioned NPs acquired sizes of 23.0±5.7, 30.6±7.4, and 10.6±7.2 nm, respectively. These properties enhanced efficiency in the photocatalytic degradation of organics using solar-simulated radiation. Ag₂O, Ag₂S, and AgCl NPs obtained degradation efficiencies above 65%.

Another application of the silver-based nanoparticles was antibacterial studies against the proliferation of *Escherichia coli* and *Staphylococcus aureus* bacterial cells. The as-synthesized NPs were found to assume unique intrinsic physicochemical characteristics and had shared optoelectronic properties due to the presence of the silver noble metal. Size and shape control of the NPs was done using organic capping agents, which had an influence on their interaction with bacterial cells. Moreover, the release rate and mechanism of Ag^+ ions from NPs which diffuse through cell membranes and perturb cellular metabolic functions also varied based on type and quantity of capping agents. Nonetheless, Ag_2O NPs were formed using 3.1 v/v % of OLA capping agent, unlike Ag_2S and AgCl NPs which were formed in 70 v/v % and 95 v/v %, respectively. Therefore, the significantly higher antibacterial activity of Ag_2O NPs was ascribed to facile release of Ag^+ ions due to low concentration of capping agent used during synthesis.

Furthermore, cytotoxicity studies on HEK 293 cells showed significantly higher toxicity levels of Ag_2O NPs compared to Ag_2S and AgCl NPs. The cytotoxic concentration at which HEK 293 cells had 50% viability was estimated to be 0.0302, 0.3606, and 0.3412 mg/mL for Ag_2O , Ag_2S , and AgCl NPs, respectively. This indicated that Ag_2O NPs were most cytotoxic (at least tenfold), ascribed to rapid release of oxidative Ag^+ ions in physiological solution. Considering the data obtained from antibacterial, cytotoxicity, and photocatalysis studies, it was observed that Ag_2O NPs had remarkable bacterial inhibitory capacity, was the most toxic to mammalian cells, and showed good photocatalytic activity. Ag_2S and AgCl NPs both showed exceptional antibacterial and photocatalytic activity, while Ag_2S NPs exhibited less cytotoxic effects on HEK 293 cells compared to AgCl NPs. Therefore, Ag_2S NPs were selected to fabricate TFN reverse osmosis membranes due to their high potential to mitigate biofouling and organic fouling, while posing less potential toxicity risk to biotic species and the environment.

TFN membranes loaded with Ag_2S NPs, compared to TFC membranes, demonstrated superior water permeation and salt rejection properties. Moreover, the BSA fouling resistance and biofilm growth inhibition were enhanced by the presence of Ag_2S NPs. This was ascribed to improved surface hydrophilicity, reduced surface roughness. These characteristics were observed to increase with higher amounts of Ag_2S NP loading. The retention of antibacterial and plasmonic properties by immobilized NPs showed their

long-term stability, which is a substantial benefit for production of durable membranes. The qualities of TFN demonstrate that high-end performance can be maintained over long periods of time, which takes away the need for frequent membrane replacement due to rapid fouling. This reduces the over-all cost of desalination in terms of input energy versus transmembrane pressure due to lower fouling rates.

8.2. Recommendations

The nanoparticles obtained through different synthetic routes demonstrated remarkable optical, electronic, and structural properties. However, an attempt to improve their energy band gap, size distribution and shape uniformity, or gain more control over the nucleation and growth phases of NPs can be made. This can be achieved through employing different types of capping ligands and surface surfactants, or their combination in reaction systems, and investigate their impact on the abovementioned properties. In addition, other reaction parameters such as temperature, pressure, pH, and precursor concentration may be explored and evaluated against characteristics of NPs.

Silver-based NPs like Ag₂O, Ag₂S, and AgCl have been reported to be useful in applications such electrochemical catalysis, biosensing, as well as energy generation and storage. The efficiency of these NPs should be explored within those areas of research. Biogenic means of NP production or using plant extracts with medicinal and therapeutic properties may be explored. This could decrease cytotoxicity of NPs and improve their antibacterial activity. Moreover, biocompatibility may be found for a wide range of biomedical applications such as theranostics, dentistry, optometry, and bio implants.

The good water flux and separation performance of membranes demonstrated high prospects to produce stable TFN membranes with antifouling properties. Hydrophilicity of TFN may be enhanced by capping NPs with ligands that have more aliphatic groups along their backbone. Alternatively, NP surfaces can be functionalized to improve their hydrophilicity. Resistance to fouling may be further improved by exploring the loading of different nanomaterials in the nanocomposite layer (i.e., Ag₂S plus carbon nanotubes). In addition, membrane testing on a real seawater which has been screened through high performance liquid chromatography and genetic sequencing/profiling should be done. Computational modelling could be used to further understand fouling mechanisms.