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Introduction

1.1 MULTISCALE FABRICATION TECHNIQUES

Recent innovations in micro- and nanofabrication have received significant interest for manufacturing structures and devices that span from the nanometer to millimeter scale. This broad dimensional range, covering six orders of magnitude, allows for the development of structures/devices applicable in various fields, such as sensor technologies and water purification systems. Microfabrication refers to a collection of techniques used to fabricate devices at the micrometer to millimeter scale (Altawell, 2022). While some of these techniques have evolved from established semiconductor industries, others have been specifically tailored for micro-scale manufacturing. The microfabrication process involves carefully arranged steps that build up the desired structures, either within the bulk of the substrate, known as bulk micromachining, or on its surface through surface micromachining.

Microfabricated devices hold several advantages over traditional, larger-scale devices, including their compact size, affordability, rapid operational capabilities, and lower energy and reagent consumption, especially in chemical systems (Franssila, 2010). One key advantage lies in the unique cost structure of microfabrication compared to conventional manufacturing. The minimal material usage allows for a broader range of materials to be utilized, as cost constraints are not a significant limitation when they can be effectively micromachined. The process of creating microdevices involves numerous sequential and often repeated steps. Typically, this includes depositing a thin film, patterning it to incorporate precise micro-scale features, and selectively removing sections of the film to create essential elements for sensing and remediation platforms. Further, the integration of microsystem technology with nanotechnology has enabled the development of miniaturized systems with enhanced functionalities. These advances facilitate the design of functional platforms capable of detection of specific analytes, ensuring environmental and human safety, and efficient remediation of wastewater, including the removal of carcinogenic dyes and oily pollutants.

This chapter will explore the principle of micro- and nanofabrication techniques utilized in the cost-efficient production of sensors and remediation devices. The discussion will center on widely adopted and significant methods, with focus on some specialized approaches. After an initial overview of the specific applications, detailed fabrication strategies will be examined alongside the associated challenges.

1.2 INTRODUCTION TO GAS SENSING

1.2.1 Brief historical background of gas sensing

Since the mid-1950s, when sensor technologies were introduced, metal oxide (MO_x) thin films have been widely used due to their ability to alter resistance when exposed to gases such as carbon monoxide (CO) and Hydrogen (H_2) (Brattain and Bardeen, 1953). Initially, these devices were simple in design and consisted of a MO_x thin layer coated on a ceramic substrate, primarily used for industrial safety purposes. In the 1990s, significant advancements were made in the research of novel MO_x materials, including iron oxide (Fe_2O_3) and titanium dioxide (TiO_2) (Harris, 1980). Additionally, MO_x nanoparticles were introduced, which increased the surface area of the

sensors, resulting in better responsiveness and sensitivity. Researchers also began to synthesized the composite materials using several classes of materials, such as MO_x, polymers, and carbon compounds, which improved performance by boosting selectivity and reducing interference (Neri, 2015; Yeow and Wang, 2009). In the early 2000s, MEMS technologies allowed the fabrication of miniaturized sensors for practical portable applications. This era also saw advancements in sensor designs, including the use of MO_x composite materials with tailored nanostructures, which effectively resolved concerns of selectivity and stability (Wilson and Baietto, 2009). The adoption of digital electronics facilitated advanced signal processing and instantaneous monitoring, expanding the range of applications for the sensors. In the 2010s, the emergence of several 2D materials, such as graphene and transition metal dichalcogenides (TMDs), led to further advancements (Han et al., 2015; Wilson and Baietto, 2009). These materials exhibited exceptional sensitivity and selectivity due to their distinctive electrical characteristics. The emergence of flexible electronics resulted in the development of wearable sensors, revolutionizing environmental and health monitoring.

1.2.2 Chemiresistive sensor and their performance parameters

Chemiresistive sensing devices are a type of economical sensors that detects gases by measuring changes in electrical conductivity resulting from the exchange of electrons between the target gas analyte and the sensing material (Tang et al., 2017). These sensors typically includes a sensing material, heater, and electrodes, and offer advantages such as easy manufacturing and compact size, etc. The increasing use of nanostructured semiconducting materials as the active layer is due to their exceptional properties such as high surface to volume ratio, and enhanced charge transport, etc. When oxidizing and reducing gases react with the sensing materials, a chemical or physical reaction occurs on the surface of these sensing materials, resulting in the transfer of electrons or holes in the materials, changing the resistance of the sensors (see Figure 1.1). When assessing sensors, it is crucial to use specific criteria that are specifically designed for their unique application in environment and health monitoring. There are various evaluating parameters used to assess the performance of sensor. For example, response (R%) can be calculated by taking the ratio of the change in resistance before exposure (R_a) of a target analyte to the change in resistance after exposure (R_g), as expressed in the following equation 1.1.

$$R(\%) = \left|\frac{R_g - R_a}{R_a}\right| \times 100\% \tag{1.1}$$

$$LOD = 3 \times \left(\frac{rms}{slope}\right) \tag{1.2}$$

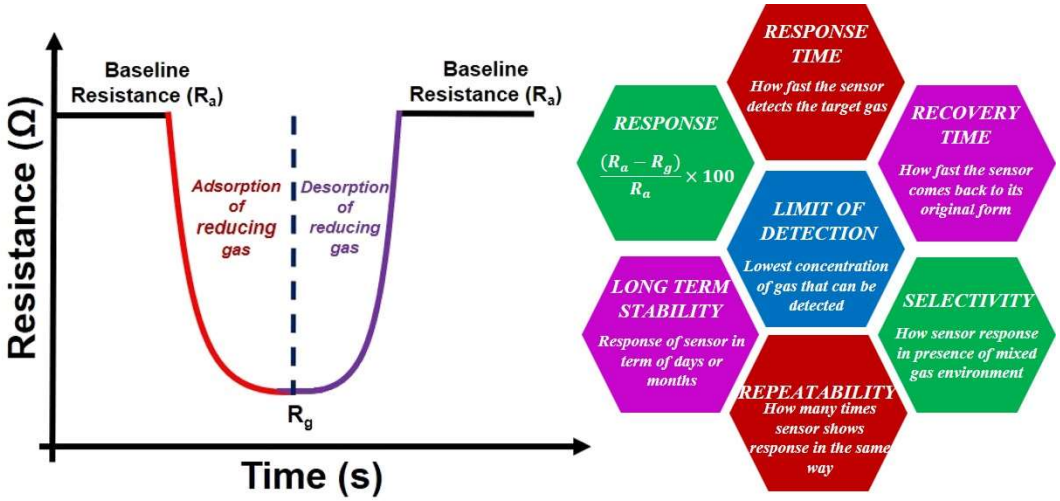

Figure 1.1: Principle of chemiresistive sensor with their performance factor

The sensitivity is determined by the change in response for every 1 ppm variation in the target analyte concentration, which is represented by the slope of the linear regression line in the calibration curve (Duong et al., 2021). Using this slope, the limit of detection (LOD) can be measured using the equation 1.2 (Le et al., 2019; Shahzad et al., 2022). Additionally, the response and recovery time, which are the time taken by the sensor to achieve a 90% change in resistance after exposure and removal of the target analyte, respectively, must be considered (Sun et al., 2020). Another important parameter is selectivity, which refers to the sensor's ability to accurately detect the target analyte in the presence of a mixed gas environment. Lastly, the long-term stability, which is the maximum duration during which the sensor maintains its initial sensing performance (Deng, 2023). These are some of the important sensing parameters required to efficiently determine the performance of sensors.

1.2.3 Need of flexible sensor

Flexible gas sensors have become increasingly vital across multiple fields and hold the potential to revolutionize gas sensing technology, enabling the identification and tracking of various gases and chemicals through their ability to detect electrical changes when exposed to target gases. With rapid industrialization globally, electronics waste has emerged as a significant threat to the environment. Researchers are turning their attention to flexible substrates due to their desirable properties such as lightweight, portability, and flexibility, ideal for sensing applications (Ou et al., 2022). The primary function of a flexible sensor is to provide users with convenient access to their environment and health information. Another application of a flexible sensor is in the area of wearable sensor, that enables user to get a real time health monitoring, however these sensor must have the ability to withstand the fluctuating deformations caused by body movements. Furthermore, for sensing applications, it is crucial to use mechanically compliant substrates that conform to soft and irregular surfaces. Desirable properties of these substrates include low surface roughness, chemical stability, and compatibility with large areas (E. Liu et al., 2023). The utilization of these materials can facilitate the development of flexible and wearable devices that can adapt to body movements. Furthermore, the selection of lightweight and low cost materials is essential for developing flexible sensors that are both practical to fabricate and comfortable for wearer (Hassan et al., 2022).

(a) Selection of Substrate

Recent advancements in flexible and wearable sensors have led to a shift in the focus on selecting different materials such as plastic, paper, and textile substrate options.

Polymers based substrate

Polymeric materials that can be used for fabricating flexible sensors should possess properties that are comparable to those of conventionally used rigid substrates (Wong et al., 2009). Polymers exhibits a low coefficient of thermal expansion with improved thermal stability, and excellent resistance to chemicals, along with their effective barrier to humidity (Wang et al., 2021). Furthermore, polymers possess a variety of physical, chemical, mechanical, and optical properties, which must be considered in addition to their fundamental characteristics (Kim et al., 2020). Polymer-based flexible sensors use a diverse array of polymeric materials, each possessing unique qualities suitable for different applications, particularly in the realm of wearable sensing. Polyimide (PI) is widely preferred owing to its exceptional flexibility, robust thermal and chemical stability, and broad glass transition temperature (360–410 °C). Additionally, along with the use of PI for wearable applications, properties such as stability, electrical insulation, and temperature tolerance from 190 °C to 540 °C make it an alternative choice for high-temperature environments, particularly in conventional microelectronics (Lin et al., 2019; Wang et al., 2021). Polyethylene terephthalate (PET) is another commonly used substrate, favoring cost-effectiveness, good chemical and humidity resistance, and adequate temperature tolerance (Riheen et al., 2019). PET is particularly popular in gas sensing applications where moderate temperature resistance and chemical stability are sufficient. Similarly, polyethylene naphthalate

(PEN) provides an exceptional balance of thermal, mechanical, and chemical stability, making it a suitable option between PI and PET in terms of cost and performance (Hornak et al., 2022). Furthermore, other polymers, such as polydimethylsiloxane (PDMS) (Tavares et al., 2022), Ecoflex, and polyurethane (PU) (F. Wang et al., 2023), are frequently utilized in diverse applications as substrates or as polymer matrices in nanocomposites. PDMS is gaining significant traction in the fabrication of flexible sensors owing to its remarkable properties, including its capacity to stretch up to 100-1100% without compromising its elasticity and compatibility with biological systems (Sheshkar et al., 2021b).

Paper based substrate

Recently, the exploration of paper for flexible sensors has increased owing to their unique characteristics (Quan et al., 2023). Cellulose, which is the primary component of paper and a naturally occurring biopolymer, is often regarded as highly biocompatible due to its natural occurrence. Additionally, these materials are highly flexible, foldable, and bendable making them suitable for breath sensing applications (Zhu et al., 2022). The advantage of utilizing paper-based materials lies in their affordability and accessibility, which is primarily attributed to the inexpensive raw materials and the absence of highly specialized manufacturing processes. In addition to being lightweight and biocompatible, one of the key features of these paper-based substrates is their ability to degrade on their own, which not only helps reduce electronic waste but also supports the development of environmentally friendly electronics. A plethora of techniques can be used to fabricate sensors on paper-based substrates. These include the development of electrodes via methods such as printing, sputtering, and even simple pencil drawing (Zhu et al., 2018). In addition, various techniques are used to form sensing materials, including drop-casting, spin-coating, soaking treatment, vacuum filtration, printing, and handwriting (Tai et al., 2020; Yang et al., 2024; Yao et al., 2022). Paper substrates pose certain challenges owing to their high absorption capacity and inherent surface roughness. These factors can affect the consistency and functionality of the sensors (Park et al., 2022). To overcome these challenges, paper are usually decorated with polymers, which help to create a smoother surface and enhance their functional properties for adaptation to different breath parameters such as pressure and humidity. For instance, Thiyagarajan et al. developed an inexpensive screen-printing ink by incorporating MWCNTs in PDMS matrix for wearable sensing applications on a paper substrate (Thiyagarajan et al., 2021). The dielectric constant of the paper, which is hygroscopic, changes during breathing and expiration, resulting in variations in the capacitance of the sensor. These substrates are a promising option for flexible and wearable sensors due to their versatility in fabrication methods and the inherent advantages of paper.

Researchers worldwide have introduced a variety of techniques for fabricating electrodes on paper substrates. These methods include thermal evaporation, electrodeposition, screen printing, and inkjet printing, among others. Qin et al. demonstrated the use of sulfur defect tungsten disulfide (WS_2) decorated paper for NH_3 detection (Qin et al., 2022). This sensor demonstrated a significantly enhanced response to 10 to 500 ppm NH_3, achieving a sensitivity three times greater than WS_2 grown by chemical vapor deposition (CVD) at RT. The sensor demonstrated rapid response times and high stability during breathing detection and bending tests, as illustrated in the study. To assess its practical use, the sensor was attached to the skin of a volunteer to monitor breathing patterns under both mild and deep breathing conditions. It was also tested in the presence of 500 ppm NH_3 and subjected to multiple bending cycles, confirming its flexibility and potential for real-world applications. Fujita et al. reported a miniaturized wearable NH_3 sensor using a composite of PEDOT: PSS and iron as the sensing material, notable for its strong resistance to humidity (Fujita et al., 2022). Initially, the carbon electrodes are produced on the cellulose paper using a stencil technique. Subsequently, a layer of PEDOT: PSS is printed onto these electrodes. Finally, the device is immersed in a $FeCl_3$ solution and heated to release the final product. Further the sensor is attached to the facial mask and nasal filter for breath monitoring applications. Upon closer examinations, the sensor exhibited a fast response of ~10% to NH_3. However, the desorption rate of NH_3 was slower than in a controlled environment, likely due to the reduced gas convection within the mask. Interestingly, the sensor

embedded in nasal filters showed faster response/recovery in comparison to facial masks, possibly because of a smoother airflow through the filter, which enhances ventilation. In contrast, some NH_3 molecules may remain trapped under the facial mask, leading to ongoing adsorption by the sensor.

Textile based substrate

The growing potential of textiles as a substrate for wearable breath sensors is attributed to their inherent qualities, such as durability, breathability, flexibility, and washability (Dulal et al., 2022). Textiles are sourced from a different materials, such as natural (like wood, cotton) and synthetic (like nylon) fibers, each contributing unique chemical and physical properties. These textile fibers not only have the ability to provide comfort during extended wear, but they also offer a dependable platform for incorporating sensor technology (Chen et al., 2023). The fabric can either be directly fabricated with wearable breath sensors, allowing it to serve as the sensing medium, or integrated into the textiles as separate components (Smith et al., 2024). The dual functionality of these fibers makes textiles an ideal choice for creating innovative, comfortable, and effective wearable sensors that can effortlessly blend in with everyday clothing(Khan et al., 2023). For example, research suggests that wearable sensor tags and antennas can be secretly and comfortably monitored by sewing them into textile substrates (El Gharbi et al., 2022; Elgeziry et al., 2022). Furthermore, Kim et al. demonstrated the use of excellent flexibility and resilience nonwoven textiles with screen-printed silver (Ag) electrodes for continuously monitoring breathing using capacitive sensors (Kim et al., 2023). Wearable sensing has also been made simpler with the use of fabric-based electrodes and metamaterial textiles, making them suitable for cardio-respiratory monitoring (Kang et al., 2006; Shen et al., 2017; Tian et al., 2019).

Yang et al. developed an innovative approach to creating a breathable and flexible NO_2 sensor by incorporation of silver (Ag) NPs into laser-induced graphene (LIG) foam (Yang et al., 2022). The sensor exhibited a response of 12% with a rapid response/recovery of 40/291 sec, respectively for successful detection of low concentration of 1 ppm NO_2 at room temperature (RT). In similar research, Yun et al. reported the potential of commercially available cotton and polyester yarns as flexible and washable gas sensors by decorating them with reduced graphene oxide (rGO) (Yun et al., 2015). These fabric-based sensors exhibited impressive chemical durability, enduring multiple detergent washes, and maintained mechanical stability under extreme bending conditions, resulting in a high sensitivity to NO_2 gas at RT. Furthermore, the researchers demonstrated that the rGO-decorated yarns, which can be as long as one meter, could be wound onto a bobbin, embroidered into fabric, and integrated with a wearable circuit and alarm system for real-time NO_2 monitoring. These fabric-based sensors could effectively detect 250 ppb of NO_2 at RT, with a three-fold higher response than rGO sensors fabricated on flat counterpart. In another study, researchers developed fiber-based sensors by assembling chemically functionalized graphene oxide (FGO) on yarn fabrics (Kang et al., 2018). The FGO provided strong mechanical adhesion to the yarn, significantly improving their performance to detect target gases. These sensors, with dimensions of ~540 µm in length and 470 µm in width, exhibited notable response to NH_3 and NO_2 at RT. Specifically, the sensor exhibited a 70% change in resistance for NH_3 at a LOD of 0.5 ppm and a response to NO_2 at 1.5 ppm. In similar research, a ultrafast responsive humidity sensor was developed by decorating fabric with GO for continuous monitoring of nasal and oral respiration (Yamei Wang et al., 2020). Bovine Serum Albumin (BSA) was used to improve the adhesion of GO onto the fabric, and the impact of their concentration on the sensing performance was examine. The study found that an optimal 2 wt% (w/v) BSA resulted in a response/recovery of ~9/12 sec, respectively, leading to high sensitivity.

(b) Selection criteria for sensing material

Advanced sensing materials are crucial for gas sensors used in detecting toxic, flammable, and harmful gases in environmental monitoring and healthcare applications. These materials can be tailored through nanoengineering techniques that modify properties such as surface area, surface functionality, morphology, and composition. This customization allows for tailored

properties that are crucial for effective environmental and medical applications. To achieve real-time monitoring, the following criteria's must be met: (1) the ability of fast detection of target analyte, and (2) the use of non-toxic, easily fabricated, and durable materials that are resistant to significant mechanical deformations. Conventional gas sensor were developed on rigid semiconductors, but these materials are limited in their use owing to their higher sensing temperatures and their intrinsic brittleness and stiffness, which limit their use in wearable sensing applications. Furthermore, optimized wearable sensors require careful necessities of structural and chemical designing of the functional materials. For example, high-surface-area materials are critical in sensing applications because of their ability to produce more active sites for gas adsorption, thereby enhancing sensor sensitivity. The significant surface area-to-volume (S/V) ratio of these materials ensures the effective interaction of the sensor surface with the trace target gas molecules, resulting in measurable changes in physical or chemical characteristics. This characteristic is particularly advantageous for trace detection of target gas, making it ideal for applications requiring high sensitivity. Furthermore, the interconnected porous structure facilitates efficient gas diffusion throughout the material, allowing rapid and uniform gas interactions with the sensor's surface, resulting in a faster response/recovery of the sensor desirable for continuous monitoring of transient changes in gas concentrations. Furthermore, the pore size and distribution can be finely tuned during fabrication to selectively allow certain gas molecules to access the sensor surface while excluding other molecules, thereby improving the selectivity of the sensor. This capability is particularly valuable in complex environments, where the presence of multiple gases can interfere with accurate detection. Additionally, nanomaterials can be functionalized with specific chemical groups to improve the selectivity, enabling the discrimination of target gases in complex mixtures. The durability and stability of these materials under various environmental conditions further enhance their suitability for long-term use in diverse settings, including environmental monitoring and healthcare diagnostics.

1.2.4 Microfabrication strategies

Fabricating a gas sensor on a flexible substrate is challenging because the sensor must have equivalent sensing performance as compared to rigid substrates, which are capable of operating at lower temperatures (Claramunt et al., 2013; Li et al., 2018). The performance of a gas sensor is largely determined by the size of the IDE's and the morphology of the sensing material. IDEs are formed by arranging and combining a certain number of micro/nanoelectrodes. Previously, researchers investigated various techniques for the preparation of IDEs, such as photolithography, focused ion beam (FIB), nanoimprint lift-off, laser-induced forward transfer (LIFT), screen printing, inkjet printing, and micro plotter printing (Chang et al., 2009; Filippidou et al., 2019; Liu et al., 2020; Mokrushin et al., 2021; Soga et al., 2013). The fact that printing processes such as LIFT, microplotter printing, inkjet printing, and screen printing are conducted without using a vacuum and in the absence of a cleanroom environment is a significant factor that greatly contributes to the ease with which IDEs can be printed on a wide variety of materials and substrates (Kumar et al., 2014).

(a) Photolithography

Photolithography technique plays a crucial role in the fabrication of gas sensors as it allows for the precise patterning of materials on both rigid and flexible substrates. This technique involves a series of steps that begin with the creation of a patterned mask which is used for transferring the desired pattern onto the substrate. The mask is typically made of a photoresist material that is selectively exposed to ultraviolet light, causing it to harden in the desired pattern. The unexposed photoresist is then removed (negative resist), leaving behind a patterned mask. This pattern is then transferred onto the substrate (Hartwig et al., 2018). Another advantage of photolithography in the fabrication of gas sensors is that it allows for the creation of multiple sensors on a single substrate. This is important because it reduces the size and weight of sensors, making them more practical to use in portable devices. Additionally, developing multiple sensors on a single substrate reduces the cost of production, making sensors more accessible to a wider

range of industries. Acuautla et al. used a patterning technique to develop a flexible ozone gas sensor with Ti/Pt IDEs (Acuautla et al., 2014). The sensor showed a good response (2-16%) and a rapid response/recovery time when exposed to 5-300 ppb of ozone at a temperature of 200˚C. Similarly, Sanskar et al. demonstrated the use of photolithography to fabricate a multi-sensor array with IDEs on an Au and Cr-coated Si/SiO_2 substrate (Thakur, 2020). In another study, a multi-sensor array was developed using PM_{10} and $PM_{2.5}$ sensors on a flexible substrate with a traditional lithography technique. The sensor was exposed to different concentrations of CO_2, NH_3, and NO_2 gases and demonstrated an inability to detect CO_2, low response to NH_3 (5%), and selectivity to NO_2 gas (Oluwasanya et al., 2019). In another research, a periodical TiO_2 NWs based ethanol gas sensor was fabricated using electron beam lithography (Tian et al., 2013). At 300˚C, the ethanol sensor displayed a fast response/recovery time of 3.2/17.5 sec and a response of 21.7%. Using the same technique, Rasch et al. presented the fabrication of graphene oxide (GO)-ZnO microwires for the detection of H_2 gas (Rasch et al., 2020). This sensor demonstrated an excellent response to H_2 gas sensing with a response/recovery time of 114/30 sec.

(b) Focused ion beam (FIB)

The FIB technique uses heavier ions that strike the substrate with more energy at shorter wavelengths, allowing patterns to be directly transferred onto rigid substrates. FIB technology also has a very low lateral exposure, enabling the direct fabrication of nanostructures by writing narrow lines and exposing specific areas on the substrate (Tseng, 2005). One main advantage of the FIB technique is its high flexibility in producing shapes that can achieve high resolution (<100 nm for deposition). However, the size of structures that can be produced is constrained by the processing time available. The main disadvantage of FIB is its slow processing speed, limiting the size of structures that can be realized in a reasonable time (Sloyan et al., 2021). Lupan et al. used the FIB technique to fabricate H_2 gas sensors using ZnO nanorods film on a Si substrate. At ambient temperature, the sensor has a sensitivity of 4% for 200 ppm of H_2 gas (Lupan et al., 2008a). Previous research reported the use of a dual-beam FIB instrument for the fabrication of metallic nanocontacts to access various nanomaterials (Hernández-Ramírez et al., 2006; Kannegulla and Cheng, 2016). For example, a graphene-based sensor with platinum nanoelectrodes patterning was fabricated using the FIB technique (Polichetti et al., 2010). To demonstrate the viability of using FIB instead of electron-beam lithography in gas sensor fabrication, Vila et al. presented the development of a WO_3 NPs based gas sensor on a SiO_2/Si substrate and evaluated its electrical response (Vilà et al., 2006).

(c) Nano-imprint lithography (NIL)

The NIL technique is a subset of soft lithography, and its simple process enables the fabrication of nanostructures with high throughput at resolutions below 10 nm without the use of optical diffraction, which is a limiting factor in traditional lithography techniques. NIL mechanism uses a patterning technique based on the mechanical deformation of polymer resists, which are pressed into a mold (Byeon and Leea, 2012). NIL is appropriate for inexpensive manufacturing techniques because it eliminates the need for a wet development process, which is associated with the formation of adhesion errors. NIL does not have this adhesion problem because the resist is directly deformed and released (Hirai et al., 2003). The applied force has a significant impact on pattern transfer on the substrate; if the force is too small, the patterns may not transfer correctly, whereas a large force may even damage the stamp (Simonenko et al., 2022). In another research, Mackenzie et al. used the NIL technique to make a nanopattern in a large wafer-scale graphene for NO_2 gas sensing (Mackenzie et al., 2017). This was done using the NIL technique. The graphene patterns that were created after nanopatterning served as adsorption sites, which increased the average time for the reagents to stay in contact with the gas sensor. The result demonstrated a favorable response to 50 ppb of NO_2 concentration. Similarly, Jang et al. used the NIL technique to fabricate an H_2 gas sensor using Pd thin film on a patterned PDMS substrate (Jang et al., 2015). The result demonstrated a quick response of 0.8/ppm with a response time of 1 sec to H_2 gas.

(d) Inkjet printing

The inkjet printing technique involves five step processes such as ejection, flight, impact, spreading, and solidification of droplet (Cummins and Desmulliez, 2012). The quality of the printed line width of the features is better understood after completing these steps. The minimum size of the pattern also depends on drop volume, and interactions between the substrate and the ink. The majority of deposition techniques require the use of a high vacuum (more than 10^{-6} Torr). These processes involve the use of deposition, lithography, and etching for achieving desired pattern sizes that generally require a Class 100 clean room and a long deposition time (X. Wang et al., 2022). Crowley et al. produced an inkjet-printed NH_3 gas sensor using PANi NPs based ink on a flexible substrate (Crowley et al., 2008). The developed gas sensor responded to NH_3 gas in ~15 sec at an ambient temperature. The author suggested that operating the sensor at 80°C significantly enhanced the sensor's selectivity, sensitivity, and response/recovery time. Fang et al. proposed the development of an rGO-based vapor sensor using the inkjet printing technique on a flexible Kapton substrate (Fang et al., 2016). This study demonstrated the trace level detection of various gases by varying the phase of surface-confined acoustic wave propagation and electronic gain. Similarly, Rieu et al. reported the development of inkjet-printed SnO_2 sensors which are integrated with a microheater on a polyimide (PI) substrate operating at 300 °C (Rieu et al., 2016). Ando et al. fabricated an inexpensive flexible carbon dioxide sensor (Andò et al., 2015). The sensor is prepared by depositing graphene and PEDOT/PSS composite on inkjet-printed Ag IDEs. The presence of graphene improves the sensor's electrical conductivity, resulting in a sensitivity of 45Ω/ppm at 100 ppm of CO_2 gas. Similarly, Huang et al. presented the development of an inexpensive paper based NH_3 gas sensor (Huang et al., 2014). The Ag IDEs were inkjet printed on the photo paper first, followed by the poly (m-aminobenzene sulfonic acid) (PABS) and SWCNT composites. The sensor demonstrated an excellent response with a quick response/recovery time to various ppm levels of NH_3. In another study, a ZnO-rGO nanocomposite was used to develop an inkjet printed multiplex sensor. The fabricated sensor array has an ultra-high sensitivity of 1500% for detecting 10 ppm NH_3, as well as a quick response/recovery time of 28/43 sec, with excellent cross-device and cross-cycle consistency (Wu et al., 2019).

(e) Screen printing

Screen printing is another simple and highly explored technique used to develop a flexible gas sensor. The screen printer consists of a mesh screen and a squeegee. A mesh screen is used to transfer ink or other materials onto a substrate, resulting in a patterned layer. There are several steps involved in the screen printing technique. To begin, a mesh screen is coated with a photosensitive emulsion. The screen is then covered with a mask and exposed to UV light. The areas containing the emulsion which are not exposed to UV light are washed away, leaving a patterned emulsion area on the screen. The screen is then placed over the substrate, and the ink or material is pushed through it with a squeegee. The ink is deposited onto the substrate in the emulsion-defined pattern. The ink or the material used for screen printing on flexible gas sensors is typically a conductive material, such as metal or carbon ink. This technique offers various advantages such as the ability to precisely control the chemical composition and thickness of the printed layer, is completely compatible with MEMS technology, and is relatively inexpensive for mass production (Viricelle et al., 2005),(Chapelle et al., 2015). Mbarek et al. reported the preparation of a screen printed Sn-doped In_2O_3 sensor for the detection of NH_3. The resistance of the synthesized material is strongly dependent on the working temperature and the concentration of NH_3 (Mbarek et al., 2006). Tupe et al. proposed the fabrication of a screen printed H_2S gas sensor with SnO_2 as the sensing material. The prepared sensor demonstrated an excellent sensitivity of 63.8% to H_2S gas with a response/recovery time of 9/19 sec, respectively (Tupe et al., 2021). In another research work, Dubourg et al. studied the development of a humidity sensor on a PET substrate using a screen printing technique (Dubourg et al., 2017). The results indicate a rapid response/recovery time and a high degree of repeatability for 5-70 RH% (humidity) at an ambient temperature.

(f) Micro-plotter technique

The Microplotter printing technique is a type of additive technology that enables a user to produce 3D shapes and solid continuous lines without compromising on the geometric features of the resulting layer, which is hard to accomplish with inkjet printing techniques (Simonenko et al., 2021). The discharge process of microplotter printing is based on the ultrasonic pumping action which is at the core of the plotter. This mechanism can deposit ink droplets as small as 5 μm with a highly viscous solution close to 450 mPas (Kwon et al., 2020). Furthermore, unlike ink-jet printing, micro-plotter printing is distinguished by the dispersion of high accuracy of functional ink, the ability of the technique to quickly replace the functional ink without changing the ink cartridge, and the lack of strict rheological properties of the ink. Microplotter printing can be used in optical, bio, and gas sensors, for the production of surface metallization, composite electrodes, and flexible electronics. Mokrushin et al. produced Pt-decorated ZnO functional ink and used a micro-plotter technique to detect benzene gas on an Al_2O_3 substrate (Mokrushin et al., 2021). When exposed to 100 ppm of benzene, the sensor demonstrated a remarkable response of 17.4% in less than 171 sec.

(g) Laser-induced forward transfer (LIFT)

The LIFT technique is a contactless direct write approach that allows high-resolution patterns to be deposited in a user-defined area with a very small volume (pL) of functional material. LIFT is functionally similar to inkjet printing, but it avoids common issues associated with nozzle printing techniques such as clogging of the nozzle and ink material compatibility. These features enable the LIFT technique to print solids, liquids, and complex fluids with varying viscosities (Morales et al., 2018). In this technique, a pulse laser is used to transfer functional materials from a source film to a substrate. This enables the laser to write patterns directly on the substrate's surface, regardless of the material or the type of surface (Serra and Piqué, 2019). The use of this method to design chemical sensors has been reported. LIFT technology has recently been used to fabricate SnO_2 and Pd-SnO_2 based gas sensors. The Sn metal-based composite precursor is spin-coated on a thin layer and then laser-transferred to the sensor structure at high resolution. The fabricated gas sensor has low ppm sensitivity to ethanol and methane (Palla Papavlu et al., 2016). Bonciu et al. proposed the first development of a SWCNT@SnO_2 nanocomposite-based resistive sensor using the LIFT technique, which shows a low 0.59 ppb level detection of NH_3 gas (Bonciu et al., 2021). Thus, with the help of the LIFT method, miniaturized planar nanostructures having high-resolution functional characteristics can be developed. Table 1.1 shows the comparison of above mentioned fabrication techniques.

Table 1.1: A comprehensive comparison of above mentioned fabrication techniques

Techniques	Advantages	Disadvantages
Photolithography	• Useful for creating patterns with nanometer level details • Repeatable and scalable patterns • Suitable for batch fabrication	• Expensive mask fabrication and mask contamination issues • Technique suitable for flat substrates • Require cleanroom environment
Nanoimprint lithography	• The direct contact nature of the imprinting process minimizes feature size variation • Large scale production • Used for three-dimensional patterning	• High cost of template fabrication • Template wear and deformation • Imprint defects
Inkjet Printing	• Low-cost technique with high efficiency • High spatial resolution (20–50 μm) • Suitable for batch fabrication	• Limited to low viscous inks • Issues with Nozzle and print head clogging • Specific rheology requirement

		• Low printing speed
Screen printing	• Suitable for batch fabrication • Resolution (>2 µm) • Low-cost and scalable fabrication technique • Can control the chemical composition and thickness of the printed layer	• Not suitable for complex multilayered gas sensor • Issues with uniformity and reproducibility • Required highly viscous ink and resolution limitations to nm.
Microplotter printing	• This technique can handle a wide range of materials, including conductive inks, polymers, and functional materials. • The non-contact nature of this technique makes it suitable for the use of temperature sensitive substrates.	• Slow printing speed • Clogging of nozzles • Limited layer thickness • High equipment and maintenance cost
Laser-induced forward transfer	• High precision with a small feature size • Minimal thermal effects • Non-contact process	• Initial equipment and maintenance cost • Equipment complexity

1.2.5 Challenges

The selection of material significantly influences the detection of the specific target analyte. Many reported gas sensors exhibit poor sensitivity characteristics, including delayed response and inadequate recovery at RT, mostly due to the absence of surface imperfections, limited adsorption of oxygen, and challenges in controlling the band gap (Z. Wang et al., 2023). However, by using techniques such as doping, the sensing characteristics of the resulting sensor can be improved, leading to higher sensitivity. Therefore, an effective method of synthesis of these functional materials is needed. Most chemical methods usually result in the formation of nano-cluster, and agglomeration, leading to non-uniform and uncontrolled size of resulting material that adversely affects sensing performance. These irregularly sized materials, when coated onto a substrate, result in uneven distribution and spreading, causing a rise in resistance at the interface of electrodes and functional materials. This ultimately impacts the stability and reproducibility of the sensor. Hence, it is imperative to advance the development of efficient ways to enhance the interaction between materials and substrate.

Chemiresistive sensors often exhibit a drift in response, which poses an additional challenge to the long-term stability of signals. The occurrence of drift signal is a result of sensor response noise, which leads to a gradual change in the output over time, finally causing the sensor to reach a saturation point where it cannot return to its original resistance. This can significantly decrease the sensor's lifespan and necessitate frequent recalibration (Ellis and Star, 2016). Additionally, the development of breath sensors is particularly challenging due to the influence of high humidity levels present in human breath. The presence of higher concentrations of humidity can reduce the quantities of target analytes that are easily soluble in water (Mochalski et al., 2013). One approach could be to involve the creation of sensing material with hydrophobic properties, as demonstrated by many researchers to synthesized these functional materials with different hierarchical nanostructures. Additionally, the process of nano-structuring further improves the sensing capability by taking use of the quantum confinement qualities, thus boosting the characteristics of charge transportation (Srinivasan et al., 2019). In addition, the nanostructured morphology increases the ratio of surface area to volume, providing additional sites for oxygen adsorption. This ultimately boosts the selectivity of the target analyte. Another problem with a flexible sensor is its operating temperature, which has a significant influence on its sensing capabilities. However, the many documented work on metal oxide has shown that these materials are operated at high temperatures, resulting in a significant loss in selectivity and

sensitivity sensing data. These issues, however, can be addressed through the development of improved functional materials and composites.

Furthermore, there is a substantial demand for the development of miniaturized flexible detection systems that can be combined with wireless technologies to provide immediate monitoring data to users. However, there are significant challenges in integrating these technologies into wearable sensors, including the requirement to reduce the size of electronic components, design and integrate the integrated circuit (IC) with the sensor, and provide dependable data transmission. Further, the assistance of a smart algorithm, such as advanced deep learning, is a promising option in accurately detecting and discriminating coexisting analytes in environment. The detection of low amounts of target analytes is a significant difficulty in flexible sensors. This makes it very difficult to accurately separate and measure a specific target analyte from other interfering analyte present in the background signal. Thus, the need for advanced algorithms integrated with flexible sensor technology is necessary to solve these issues.

1.3 INTRODUCTION TO WATER REMEDIATION

The escalating challenges posed by a rapidly growing global population, rapid urbanization, and expanding industrial activities have significantly exacerbated the contamination of water bodies (Chauhan et al., 2017). For example, a large quantity of refractory oily and textile wastewater has been produced as a consequence of the extraction and transportation of crude oil, offshore crude oil spills, and large-scale textile production, etc., leading to a number of issues with human health, the environment, and the economy (Gupta et al., 2015b; Zhang et al., 2013). Attempts to efficiently separate water/oil from oily wastewater sources have sparked considerable public and government concern, and hence have become a pressing issue (Kintisch, 2010). With the course of industrialization, the discharge of oil-contaminated wastewater is continually rising yearly (L. Zhang et al., 2012). Accidental oil spills and the discharge of oily wastewater not only result in significant financial losses but also substantial water contamination and other ecological and environmental issues (Zhao et al., 2021). Traditional techniques have been utilized to control oily wastewater by thoroughly integrating physical, chemical, and biological approaches, including centrifugal separation, air flotation, gravity separation, ultrasonic separation, biological treatment, and coagulation (Hodges et al., 2018; Kota et al., 2012; Yue et al., 2019). For example, mechanical skimmers are often used to recover oil/water mixture after spills, but this mixture is still challenging to handle. Contrarily, physical adsorption materials for oil-water separation like activated carbon, linoleum, sponge, cloth, porous materials, and metal wire mesh present the drawbacks of small absorption capacity, low absorption rate, and constrained recyclability because water absorption exerts a lot of pressure on recovery and recycling (Ma et al., 2016). However, these systems have historically been challenging to utilize because of their poor separation efficiency, production of secondary pollutants, and large size, which has prompted researchers to come up with more efficient approaches. In addition, wastewater that is released from industrial processes, agricultural runoff, and improper disposal comprises of various substances (Jangid and Inbaraj, 2021; Kyzas and Mitropoulos, 2021). These pollutants include oily wastewater, heavy metals, organic compounds, pharmaceutical residues, and microplastics, among others. The consequences of such pollution are dire, encompassing environmental degradation, compromised public health, and diminished water resources. As a result, there is an urgent need for innovative and efficient wastewater treatment technologies that can effectively combat the increasing levels of pollutants in our water systems (Umar et al., 2022). Conventional treatment approaches, however, struggle to provide the level of purification required to address the diverse and persistent nature of these pollutants (Gupta et al., 2018).

In this context, advanced micro and nanomanufacturing techniques have emerged as a beacon of hope. These cutting-edge manufacturing methods empower researchers and engineers to design and produce materials, structures, and devices at the micro and nanoscale with

unprecedented precision and tailored functionalities (Gupta et al., 2015b). By leveraging these techniques, it becomes possible to create novel materials and systems that exhibit enhanced capabilities for the removal and remediation of pollutants from wastewater (Bhattacharya et al., 2018a). Micro and nanomanufacturing techniques encompass a plethora of strategies such as additive manufacturing, soft lithography, membrane technologies, and microfluidics (Rai et al., 2022; Sharma et al., 2021). These methods allow for the manipulation of matter at scales that were once unimaginable, paving the way for the creation of structures with finely tuned properties that can efficiently interact with pollutants in water systems.

1.3.1 Microfabrication Approaches

Micro and nanomanufacturing techniques have rapidly evolved, opening up exciting new possibilities across various applications, one of the most promising being wastewater purification. This section explores the complexities of these advanced manufacturing techniques and their use in engineering functional nanomaterials and micro/nanostructures to improve pollutant removal. Figure 1.2 presents the schematic illustration of various micro and nanofabrication approaches used for wastewater purification.

(a) Additive Manufacturing

Additive Manufacturing, commonly known as 3D printing, is a transformative approach that constructs three-dimensional objects layer by layer, in contrast to traditional subtractive manufacturing methods. This technique offers remarkable flexibility in material design and geometric complexity, making it a powerful tool for creating intricate structures with tailored functionalities for wastewater purification. 3D printing, a hallmark of additive manufacturing, revolutionizes how objects are created by constructing them layer by layer from digital designs. This technique sidesteps the constraints of traditional manufacturing methods, opening doors to intricate geometries and tailored properties. In wastewater treatment, 3D printing has emerged as a formidable tool, offering novel solutions to address water purification challenges (Saidulu et al., 2022). At its core, 3D printing leverages computer-aided design (CAD) models, which guide the additive deposition of materials. This process allows the fabrication of complex structures that would be difficult to achieve using conventional techniques (Xue et al., 2023). Within the realm of wastewater treatment, this versatility has yielded innovative outcomes. One striking application is the development of custom-designed porous structures. These structures, often resembling intricate lattices, can be engineered to possess hierarchical porosity. This feature optimizes their pollutant removal capabilities by catering to a wide range of pollutant sizes (Martín de Vidales et al., 2019). Larger particles are captured by the larger pores, while smaller particles are trapped in the finer pores, enhancing filtration efficiency. This hierarchical design mirrors natural systems and ensures thorough purification.

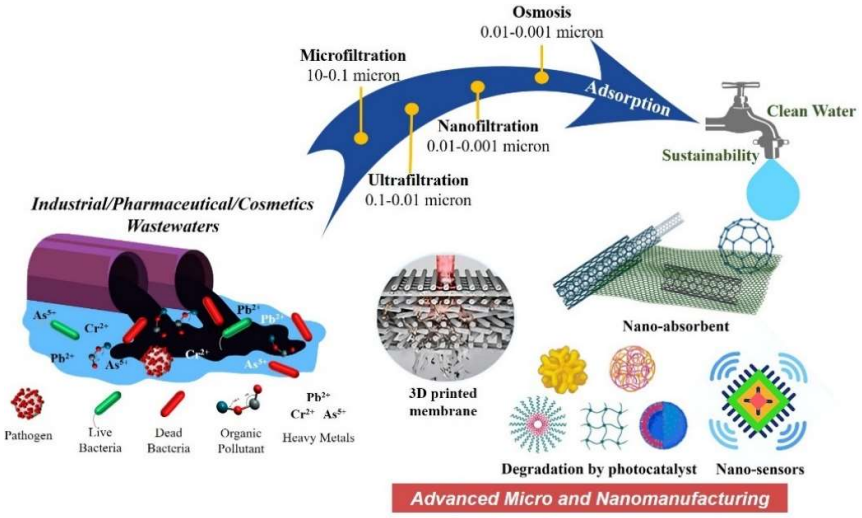

Figure 1.2: Schematic illustration of various micro and nanomanufacturing for wastewater purification

Moreover, 3D printing introduces the potential for real-time water quality monitoring through the fabrication of 3D-printed sensors. These sensors can be integrated into water treatment systems, enabling continuous monitoring of various parameters such as pH, temperature, and pollutant concentrations (Mohd Yusoff et al., 2022). This real-time monitoring facilitates rapid responses to contamination events, allowing authorities to take timely corrective actions and prevent potential threats to public health. For example, using five different types of MOF fillers (such as NH_2-MIL-101(Al), ZIF-8, KHUST-1, MOF-801, and ZIF-67) and polyamide (PA)-12 powder as the matrix material, Li et al. used the Selective Laser Sintering (SLS) technique to 3D print single layer MOF-polymer matrix films (MMFs) with grid patterns (Li et al., 2019). Additionally, to illustrate the use of water degradation, the methylene blue (MB) dye adsorption test was carried out using NH_2-MIL-101(Al)/PA12 MMFs. With multiple cyclic utilities, the result showed that the MOF maintains a maximum adsorption capacity. Similarly, Yuan et al. investigated the fabrication of PA-12 membranes using SLS by optimising various parameters such as laser power, hatch spacing, and laser scan count (Yuan et al., 2017). Furthermore, a laser energy density of 0.1 $J.mm^{-2}$ produces membranes with the greatest rejection and relatively high pure water flux. This provides an alternative method for producing membranes for microfiltration. Similarly, by combining 3D printing technology with a natural adsorbent (chitosan), Zhang et al. reported the fabrication of a reusable monolithic 3D porous adsorbing filter for the removal of heavy metals (Dongxing Zhang et al., 2019). Moreover, Guo et al. demonstrated the utilization of 3D printing for crafting a hierarchically porous structure and rough surface in a framework comprising zero-valent copper (ZVC) and zero-valent iron (ZVI) (S. Guo et al., 2023b, 2023a). This structural design imparts excellent mechanical robustness and catalytic efficacy in the degradation of various organic pollutants activated by peroxymonosulfate (PMS). The 3D-ZVC/PMS/Vis system exhibited remarkable capability, achieving a degradation efficiency of over ~96% for tetracycline within 20 mins. This surpasses the performance of homogeneous Cu^{2+}/PMS/Vis and contemporary powder/PMS/Vis systems, attributable to the distinctive hierarchical porous structure and the cycling of Cu(I)/Cu(II) in the 3D-ZVC system. Additionally, 3D-ZVI demonstrated sustained efficient catalytic performance over 45 consecutive reactions.

In spite of the diverse benefits associated with 3D printing techniques, there are challenges that necessitate resolution before these processes can be effectively deployed. Striking a delicate balance to achieve the necessary print resolution for intricate structures while maintaining appropriate porosity for effective filtration is one such challenge. Ensuring that the printed structures facilitate optimal flow while preventing the passage of contaminants is of paramount importance. The scale-up of 3D printing processes for large-scale wastewater treatment facilities may present hurdles, and it is crucial to find a balance between production speed and print quality for practical implementation. Furthermore, irregularities on 3D-printed surfaces have the potential to enhance contaminant adhesion, leading to fouling and a decrease in filtration efficiency. Additionally, the identification of energy-efficient printing methods is imperative for advancing sustainable wastewater treatment practices.

(b) Soft Lithography

Soft lithography is a versatile and innovative manufacturing technique that utilizes elastomeric materials, such as polydimethylsiloxane (PDMS), to create microstructures with remarkable precision. Its distinctive properties enable the replication of intricate patterns from master molds onto a range of substrates, making it a valuable tool for various applications, including wastewater treatment (Das and Srivastava, 2016). At the heart of soft lithography lies the concept of replica molding. A master mold, containing the desired pattern, is created using traditional lithography methods. This mold is then coated with a liquid elastomer, like PDMS, which solidifies to form a flexible stamp. When this stamp comes into contact with a substrate coated with another material, it imprints the pattern onto the substrate's surface. This microcontact printing process enables the transfer of detailed patterns with high fidelity.

In the context of water treatment, soft lithography's adaptability has led to the development of microfluidic devices with transformative potential. Microfluidics involves the manipulation of tiny volumes of fluids within microscale channels (I. Kim et al., 2015). Soft lithography's capability to precisely engineer microchannels and microstructures has paved the way for the creation of intricate microfluidic devices capable of fluid manipulation, mixing, and separation on a miniature scale (Dong et al., 2022). These microfluidic devices hold immense promise for wastewater purification. They enable the precise control of fluid flow and the interaction of pollutants with treatment agents, optimizing reaction kinetics and efficiency. Moreover, these devices can facilitate the separation of different components in wastewater, aiding in the removal of contaminants and the recovery of valuable resources. For example, Qian et al. developed a microfluidic MFC platform with soft lithography techniques which includes a sub-5 µL soft chamber on PDMS with carbon cloth electrodes and microfluidic system for electrolyte delivery (Qian et al., 2011). These micro-MFCs demonstrated the best performance for sub-100 µL MFCs with quick start-ups, consistent current generation, and increased power densities up to 62.5 W/m^3. In similar research, He et al. demonstrated the use of upflow MFC to generate electricity while simultaneously treating wastewater (He et al., 2005). Soft lithography's versatility and ability to create intricate microstructures have propelled the field of microfluidics, offering innovative solutions for wastewater treatment. The precision engineering achievable through this technique contributes to the development of sophisticated microscale systems that could revolutionize the approach of wastewater purifications.

(c) Microreactors for Wastewater Treatment

Microfluidic Systems introduce a transformative paradigm by enabling precise manipulation of fluids at the microscale, offering opportunities to revolutionize wastewater treatment. These systems encompass microreactors for advanced treatment processes and platforms for separation and detection, shaping the landscape of water purification.

Microreactors present a groundbreaking innovation within wastewater treatment. These are compact, miniaturized chemical reactors that operate at the microscale, introducing a new dimension to the realm of water purification. Their unique characteristics and advantages have positioned them as transformative tools in addressing water pollution challenges (Das and Srivastava, 2016). At the heart of their superiority lies the phenomenon of enhanced mass transfer rates and efficient mixing attributed to the microscale dimensions. In traditional reactor systems, diffusion distances can limit the rate at which reactants come into contact, slowing down reactions (He et al., 2016). Microreactors circumvent this challenge by minimizing diffusion distances, promoting rapid and efficient mixing of reactants. This is especially advantageous for intricate chemical reactions that are central to pollutant degradation and transformation processes. In wastewater treatment, microreactors contribute to the tailoring of treatment processes. They offer a controlled environment where pollutants and treatment agents can interact precisely (Talaiekhozani et al., 2020). By optimizing reaction conditions within the microreactor, such as temperature, pH, and residence time, the reaction kinetics can be finely tuned. This level of control not only enhances the efficiency of the treatment process but also reduces the need for excessive reagents.

The integration of microreactors into wastewater treatment strategies leads to more resource-efficient and sustainable approaches. Traditional treatment methods might require substantial amount of chemicals and energy to achieve desired outcomes. Microreactors, on the other hand, optimize these factors, making the treatment process more efficient and cost-effective (Yusuf and Palmisano, 2021). This contributes to faster pollutant removal and a reduced environmental footprint. For example, in a study photocatalytic microreactor is developed with TiO_2 photocatalyst to effectively degrade azo dyes and the authors investigated the effect of H_2O_2 addition on the degradation process (Yoshinori and Minato, 2021). The photocatalytic degradation efficiency of acid orange 7 was found to be gradually decreased in the presence of the anatase form of TiO_2. However, degradation efficiency was increased in the presence of the

rutile form of TiO_2 up to an H_2O_2 concentration of 10 mM and then decreased as the concentration of H_2O_2 increased.

In essence, microreactors redefine wastewater treatment by introducing precision and efficiency. Through their controlled environment, rapid mixing, and enhanced mass transfer, they enable the optimization of pollutant removal processes. The application of microreactors reflects a shift towards smarter, more responsive, and resource-conscious solutions in addressing water pollution, marking them as pivotal players in the evolution of water purification technologies.

(d) Membrane Technologies

Membrane technologies represent a transformative approach to wastewater treatment, harnessing the selective permeability of membranes to separate contaminants from water. Within this domain, several innovative membrane types have emerged as potent tools for water purification.

Nanofiltration Membranes

Nanofiltration membranes represent a pivotal advancement in membrane-based wastewater treatment. These membranes function as intelligent gatekeepers, allowing the unhindered passage of water molecules while impeding the movement of larger pollutants. Their selective permeability is engineered through a carefully designed arrangement of nanopores, making them particularly adept at handling specific contaminants (Cao et al., 2021). At the nanoscale, these membranes have specialized pores, that are designed to be just large enough for water molecules to squeeze through but small enough to reject larger particles. It's this precise control over pore size that imparts nanofiltration membranes with their remarkable selectivity (Rashidi et al., 2012). Moreover, nanofiltration membranes are prized for their ability to remove a broad range of contaminants. They're particularly effective at eliminating divalent ions, like calcium and magnesium, which can cause water hardness (Oulebsir et al., 2020). Additionally, they excel at removing organic molecules, such as color-causing compounds and certain contaminants arising from industrial processes. For instance, Zhang et al. developed a ceramic nanofibrous membrane using the electrospinning technique for enhanced photocatalytic degradation of organic pollutants (Zhang et al., 2023). Figure 1.3 illustrates the fabrication steps and the mechanism of photocatalytic degradation. In essence, nanofiltration membranes combine precision engineering at the nanoscale with the art of selective separation. Their ability to selectively allow water molecules to pass while entrapping pollutants makes them an essential tool in the fight against water pollution. By embracing the principles of selective permeability, nanofiltration membranes elevate wastewater treatment to a level of accuracy and efficiency that contributes significantly to the quest for clean water.

Hierarchical Membranes

Hierarchical membranes emerge as a sophisticated innovation within the realm of membrane-based water treatment. These membranes act as multitiered guardians, each layer equipped with a distinct role to play in the pursuit of pristine water. The concept of hierarchical membrane is simple yet profound: combining multiple layers, each with varying pore sizes, to achieve enhanced filtration efficiency (Z. Zhang et al., 2022). This layered approach empowers the membrane to address a spectrum of contaminants spanning various sizes. By accommodating pollutants ranging from the microscale to the nanoscale, hierarchical membranes provide a comprehensive solution to water purification challenges. At the core of this concept is the power of combined filtration mechanisms. Pollutants coursing through the membrane, encountering the first line of defence: a microscale pore layer. Here, larger particles are trapped, unable to proceed further. Moving inward, they encounter a nanoscale pore layer. This secondary defence captures even smaller pollutants that managed to bypass the first layer. This strategic arrangement significantly enhances the membrane's efficiency in removing a wide variety of contaminants (M. Wang et al., 2022). This cascading effect leads to a thorough and effective purification process. In essence, hierarchical membranes exemplify the principle of optimization through layers. By

layering different filtration precision levels, these membranes expand the scope of pollutant removal, making them powerful tools for water purification. Through this innovative architecture, hierarchical membranes pave the way for efficient and multifaceted water treatment strategies that cater to the diverse challenges posed by contaminants of varying sizes.

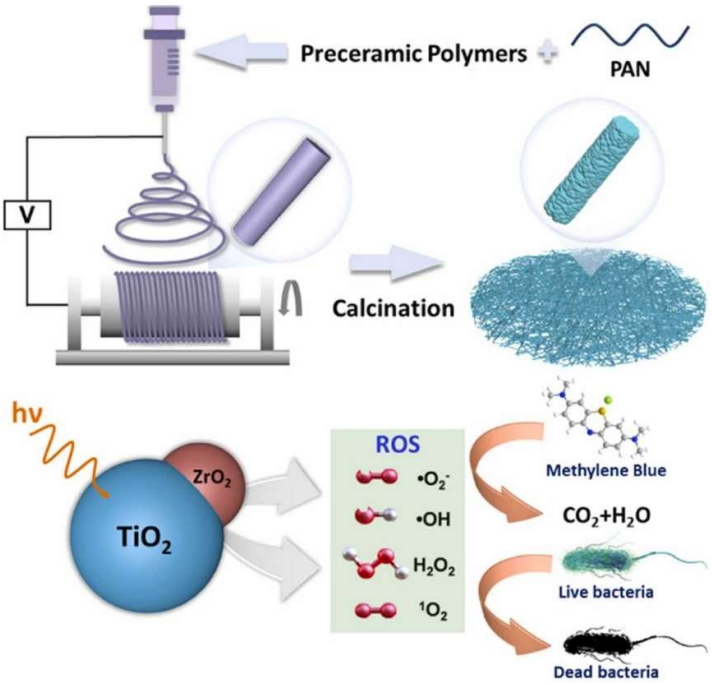

Figure 1.3: Schematic illustration of the fabrication steps involved in producing Zr-doped TiO_2 ceramic nanofibrous membranes and the mechanism of photocatalytic degradation of organic pollutants (Zhang et al., 2023)

In summary, membrane technologies hold immense promise for wastewater treatment. Booth nanofiltration, and hierarchical membranes bring unique attributes to the table, offering tailored solutions for pollutant removal. By capitalizing on the selective permeability of these membranes, water treatment strategies gain efficiency, precision, and adaptability.

1.3.2 Photocatalysis as emerging treatment technique for wastewater

Advanced oxidation processes (AOPs) are pioneering strategies that are designed to combat organic pollutants with unparalleled efficiency (Rayaroth et al., 2022). They use the potency of reactive oxygen species, radicals, and oxidizing agents to wage an unrelenting assault on even the most stubborn contaminants. The fundamental concept behind AOP revolves around the generation of hydroxyl radicals, which can be produced through various means such as photo-catalysis, hydrogen peroxide, and the use of oxidizing agents in conjunction with UV light irradiation (Ghime and Ghosh, 2019). However, the hydroxyl radicals can be primarily assuming responsibility for breaking down organic compounds. Hydroxyl radicals are an indiscriminate and potent chemical oxidant. Once formed, hydroxyl radical attacks nearly all types of organic compounds. Consequently, the action of hydroxyl radical results in the complete disintegration of the organic compound, thereby reducing the pollutant concentration from several ppm to less than 5 ppb (Krishnan et al., 2017). According to studies with AOPs, organic chemicals disintegrate and become smaller and more biodegradable. The hydroxyl radical removes a hydrogen atom from an organic compound (R-H) and forms an organic radical (•R). This radical is then subjected to a series of chemical reactions, yielding a variety of products and by-products(Deng and Zhao, 2015).

One of the AOP technique is photocatalysis, which serves as a bridge between the precision of nanotechnology and the power of light, offering a dynamic solution for pollutant degradation. As light illuminates these photocatalysts, absorb its energy and channel it into a

cascade of reactions that reverberate through the pollutant-laden waters. These catalysts capable of transmuting organic pollutants into harmless byproducts. As each molecule undergoes metamorphosis under the catalyst's influence, the water transforms from a repository of contaminants into a canvas of purity. This transformation, guided by light and orchestrated by nanoscale catalysts, holds the potential to cleanse water sources of organic pollutants, leaving behind a healthier environment. For instance, Verma et al. demonstrated the use of TiO_2 and TiO_2/GO nanocomposite to degrade MB and malachite green (MG) dyes when exposed to UV light (Verma et al., 2023). In 13 and 60 min, the TiO_2/GO nanocomposite demonstrated an outstanding degradation of ~85% and ~93% to MG and MB, respectively. The following equations display the potential reaction mechanisms:

$$TiO_2/GO + h\upsilon \rightarrow TiO_2^+/GO + e^- \quad (1.1)$$

$$e^- + O_2 \rightarrow O_2^- \quad (1.2)$$

$$TiO_2^+/GO \rightarrow TiO_2/GO + h^+ \quad (1.3)$$

$$h^+ + H_2O/OH^- \rightarrow \cdot OH \quad (1.4)$$

$$MG/MB + \cdot OH, h^+ \rightarrow CO_2 + H_2O + Degraded\ Product \quad (1.5)$$

$$MG/MB + O^- \rightarrow CO_2 + H_2O + Degraded\ Product \quad (1.6)$$

Strong photocatalytic activity was observed in the visible spectrum by the TiO_2/GO nanocomposite. When exposed to visible light, the nanocomposite forms electron-hole pairs in the conduction band and valence bands, respectively. These pairs can then react with O_2 and H_2O to produce O_2^- and $\cdot OH$, respectively. As a result, the MG and MB dyes can be oxidized and mineralized by produced superoxide and hydroxyl radicals (Ali et al., 2018).

Additionally, the use of nanomaterials in wastewater dye degradation such as ZnO, TiO_2, graphene-based materials, and various doped or composite metal oxides, offer remarkable photocatalytic properties. However, their cost-effectiveness varies significantly depending on synthesis methods, material purity, scalability, and operational lifespan. ZnO and TiO_2 are among the most economically viable choices due to their low raw material costs and ease of large-scale synthesis through sol-gel, hydrothermal, or precipitation methods. These materials are abundantly available, chemically stable, and demonstrate strong photocatalytic efficiency, especially under UV light. However, enhancing their performance often requires doping with metals or combining them with carbon-based materials (e.g., graphene oxide, CNTs), which can increase costs due to need of additional reagents and more complex synthesis procedures. Despite their success in laboratory setting, these nanomaterials face significant challenges in practical application. A major drawbacks is the difficulty in recovering these nano-powders after treatment. Since they are dispersed in solution during photocatalysis, separating them from the treated water typically requires additional steps like centrifugation or filtration, which are not only time-consuming and energy-intensive but also cost-prohibitive at scale. Moreover, these nanoparticles tend to agglomerate in aqueous environments, reducing their effective surface area and overall photocatalytic performance. These limitations highlight the need of developing immobilization strategies and structured catalyst platforms, such as coatings on 3D-printed scaffolds or membranes, which preserve the advantages of nanomaterials while addressing practical barriers, including reusability and the elimination of post-treatment filtration steps.

1.3.3 Challenges

Advanced micro and nanomanufacturing have made a remarkable stride, but despite their significant progress, several challenges persist on the horizon, each demanding careful consideration and innovative solutions (Savage and Diallo, 2005). One of the foremost challenges

encountered on the road to widespread implementation is scalability. While laboratory-scale successes have been achieved, translating these advancements to large-scale application requires meticulous planning and engineering to ensure seamless integration into real world systems. Additionally, the cost-effectiveness of these advanced techniques must be addressed to ensure their practical viability. Striking a delicate balance between the benefits they offer and the costs of implementation is a crucial aspect of their integration process. Furthermore, as the use of nanomaterials in purification gains traction, a comprehensive assessment of their potential environmental impacts becomes imperative. The adverse effects of nanomaterial toxicity continue to be one of the major concerns that could endanger both the environment and human health (Mishra, 2014). Moreover, the pursuit of perfection continues with the need for further research and optimization of manufacturing techniques. The challenge lies in refining and enhancing these processes to achieve the highest level of efficiency and effectiveness. Moreover, as these advanced systems are deployed for long-term use, ensuring their long-term stability is of paramount importance. Durability, resilience, and reliability must be guaranteed to maintain consistent and efficient performance over extended periods (Bhat et al., 2022). Furthermore, the incorporation of nanomaterials into existing water purification systems is a critical. Due to their modularity, scalability, flexibility, and ease of operation, membrane processes have emerged as the standard in water purification for both public and industrial applications (Sonawane et al., 2021). Furthermore, in the materials selection process for effective water purification solutions, understanding the environment becomes critical. The narrative of advanced micro and nanomanufacturing for wastewater purification holds the promise of overcoming these challenges. Future research will be essential in charting the course for optimized techniques, scalable solutions, and environmentally conscious practices. The partnership between innovation and sustainability will be central in navigating these challenges and shaping a future where clean water is an accessible reality for all.

1.4 ORGANIZATION OF THESIS

The present thesis explores the application of cost-efficient multiscale fabrication approaches for manufacturing advanced functional platforms for sensing, and water remediation.

Chapter 1 introduces a range of multiscale fabrication techniques, providing a brief historical overview and highlighting the importance of applications in gas sensing and water remediation. This chapter also offers an in-depth discussion on key technical terms, methods, underlying principles, and the challenges encountered in the field of gas sensing and waste water remediation.

Chapter 2 explores various parametric and predictive approaches to comprehend nanostructure growth and nanosensor development. The chapter is divided into two sections: the first section illustrates the use of statistical and experimental techniques to study nanostructure growth on flexible substrates, while the second section details the fabrication of a flexible nanosensor using a ternary nanocomposite for detecting low concentrations of hydrogen gas at low temperatures.

Chapter 3 provides an in depth analysis on the fabrication of an advanced flexible gas sensors for monitoring toxic analytes that have indirect impacts on human health. This chapter elaborates on the development of a nanosensor designed for room-temperature detection of carbon monoxide, utilizing a laser-induced carbon substrate combined with an innovative composite as the sensing medium. The latter section of the chapter focuses on the development of a nanosensor capable of detecting acetone, a biomarker for diabetes, in exhaled breath samples.

Chapter 4 explores the replacement of conventional flexible substrate with biodegradable substrate and presents the microfabrication techniques for developing biodegradable nano-sensors. This chapter is organized into two main sections: the first section discusses the cost-

effective fabrication of a real-time sensing module for detecting uric acid on a disposable paper-based substrate. The second section focuses on the development of a biodegradable chitosan-based substrate designed for the sensitive detection of hydrogen gas at low temperatures.

Chapter 5 explores the development of low cost sensing and environmental remediation platform via integration of additively manufactured microlattice structures with advanced functional materials, such as conducting polymer and metal oxide, respectively. This chapter is organized into two main sections: the first section discusses the fabrication of 3D printed carbonised (PyC) microlattice structures decorated with polyaniline nanoparticles for the detection of NO_2 gas. The second section focuses on the exploration of PyC microlattice structure with ZnO nanowires for the on-site photocatalytic degradation of textile dye under sunlight irradiations.

Chapter 6 outlines the methodologies for developing superhydrophobic polymeric microtubes through a soft lithography approach. The chapter is organized into two main sections: the first section describes the process of fabricating polymeric microtubes integrated with gold-decorated zinc oxide, which acts as a photocatalyst for the degradation of rhodamine b (RhB) dye. The second section focuses on the development of bio-inspired, lotus-patterned microtubes decorated with a tantalum-zinc oxide composite for real-time degradation of methylene blue (MB) dye contaminants.

Chapter 7 explores the development of different engineered micro- and nanostructured substrates for wastewater treatment. This chapter is structured into three main sections. The first section highlights the development of carbon nanofibers embedded with titanium disulfide nanoparticles designed for efficient oil-water separation. The second section presents the preparation of a nanocoating for naturally available leaf mesh, which is capable of simultaneously separating oil/water mixtures and degrading dyes. The final section addresses the cost-effective production of a microreactor aimed at the degradation of MB dye.

Chapter 8 concludes the dissertation by summarizing the presented results and proposing future work.

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