

Additive Manufacturing Approaches for sensing and Environmental Remediation

This chapter explores the fabrication of multiscale platform by intergrading additively manufactured platform with nanotechnology for advanced applications such as gas sensing and wastewater remediation.

5.1 POLYANILINE DECORATED 3D PRINTED PYROLYTIC CARBON SCAFFOLD FOR NITROGEN DIOXIDE GAS DETECTION AT ROOM TEMPERATURE

In this work, we demonstrate the fabrication of a NO₂ gas sensor using a combination of digital light processing (DLP) based 3D printing and in-situ polymerization of polyaniline (PANi), resulting in a PANi@ 3D pyrolytic carbon (PyC) based sensor. The sensor further underwent a thorough morphological characterization and comprehensive evaluation for detecting varying concentrations of NO₂ gas.

5.1.1 Introduction

In the last twenty years, the exponential growth of electronic technologies has had a huge impact on human society. The digital era has brought electronic devices, especially gas sensors, to various sectors such as industrial production, healthcare and environmental management. Although widely used, these sensors face problems like inefficiency, low quality, degradation and the growing problem of electronic waste (Rajesh et al., 2022). To address these issues, it is important to develop gas sensors that are efficient as well as stable, and have structures and functionalities particularly designed for this purpose. 3D printing technology has contributed a lot to this endeavour. 3D printing is used to develop complex sensors because of its customization, rapid prototyping and mold-free production (Kim et al., 2014). This method allows production of versatile devices with intricate geometric shapes at a relatively low cost thus improving the efficiency (Staymates et al., 2016).

Previously published papers on 3D printed sensing structures have shown excellent sensing capabilities and huge potential for large scale manufacturing with multiple applications (Kennedy et al., 2017; J. H. Kim et al., 2015; Kim et al., 2019). However, most of the previous studies on 3D printing technology are based on extrusion based processes which restricts the printing of complex and detailed shapes (You et al., 2020). To address the problems of producing intricate functional structures and the high cost of conventional moulding technologies, there is a need for more straightforward and adaptable processes to fabricate functional 3D structures (Zhou et al., 2020). The intersection of 3D printing and gas sensing technology has huge potential for the future. This intersection can provide the direct integration of sensing materials onto platforms or portable devices which can bring a big change in the industry. For instance, Wei et al. reported the development of a 3D porous conductive structure using DIW printing with thixotropic inks for VOCs detection (Wei et al., 2019). The sensor exhibited an 8% response at 5000 ppm chloroform, with a detection limit of 50 ppm. This gas-sensing capability is attributed to the swelling of the present polymeric composition upon chloroform exposure, which increases resistance. Similarly, Kim et al. developed a 3D scaffold using the fused deposition modeling (FDM) technique, incorporating thermoplastic polyurethane decorated with polypyrrole for detecting ammonia gas (Y. J. Kim et al., 2022). However, most of these 3D structures are fabricated using traditional FDM techniques, which suffer from internal stress generation and produce more

waste, particularly due to support structures and failed prints (Chaloeipote et al., 2021). Digital light processing (DLP) 3D printing, on the other hand, excels in producing smaller and more intricate structures, offering distinct advantages over other 3D printing techniques (Kuhnt et al., 2021; Ligon et al., 2017). Unlike FDM, which can struggle with fine details and smooth surfaces, DLP uses a digital light projector to cure entire layers of resin at once, ensuring exceptional precision and detail (Mu et al., 2017). This makes DLP particularly suited for applications requiring high accuracy. The technology's ability to print detailed layers quickly and efficiently, coupled with minimal post-processing needs, allows DLP to achieve superior results in crafting complex and finely detailed structures.

This study presents a simple approach to fabricate a microlattice structures using DLP 3D printing, tailored for gas sensing applications. Post printing, the microstructures were carbonized forming highly reliable 3D pyrolytic carbon (PyC) structure. Further to enable NO₂ sensing performance, the 3D PyC structure was decorated with conductive networks of polyaniline (PANi) via in situ polymerization. Due to the exceptional electrical properties of PANi, it stands out as an excellent choice for NO₂ gas detection. Consequently, the fabricated sensor showed good sensitivity, selectivity and fast response in detecting NO₂ directly at RT, without the need for conventional sintering and film coating techniques. This advanced strategy has the potential to augment the gas detection capabilities of a device, making it exceedingly effective for practical applications.

5.1.2 Experimental Section

A 3D printed microlattice structure was fabricated using a Phrozen Sonic Mini 8K S DLP printer with Aqua Resin Ivory 4K photoresein. Chemical reagents, including hydrochloric acid (HCl), isopropanol (IPA), ammonium persulfate (APS; (NH₄)₂S₂O₈), and aniline (C₆H₅NH₂) were sourced from Sigma Aldrich.

(a) 3D printing of PyC Scaffold

3D microlattice structures with a cubic unit cell and a lattice thickness of 400 µm were created using a DLP 3D printer. The photoresein was printed with a layer thickness of 10 µm. After printing, the structures were immersed in IPA for 10 mins to remove excess resin, then cured in a UV chamber for 60 mins to solidify the design with overall dimension of 10 mm × 10 mm × 10 mm. Subsequently, microlattices underwent a high temperature pyrolysis process in an argon gas atmosphere. The carbonization process is adapted based on a pyrolysis profile commonly used for converting organic precursors, which involved several stages: heating from RT to 350°C at 3°C.min⁻¹, holding at 350°C for 3 hours, further heating to 900°C at the same rate, maintaining 900°C for 2 hours, and finally cooling to RT naturally. Throughout this process, a constant argon flow of 0.8 L.min⁻¹ was maintained. The overall dimension after the pyrolysis was 4.87 mm × 5.12 mm × 4.96 mm.

(b) In situ Polymerization of PANi on 3D PyC Scaffold

The 3D PyC structure served as a substrate for the in-situ dip-coating chemical polymerization of PANi. The process began by mixing 1 mL of aniline (C₆H₅NH₂) monomer with 1 M HCl in DI water, stirring the mixture for 30 mins at RT. The 3D PyC substrate was then vertically immersed in this solution for 30 mins. Following this, 2 g of (NH₄)₂S₂O₈ were dissolved in 20 mL of DI water and gradually added drop by drop to the C₆H₅NH₂ solution until the pH reached 12. This solution, along with the immersed 3D PyC substrate, was transferred to an ice bath for 16 hours to facilitate the growth of PANi on 3D PyC microstructure. Following growth, the PANi@ 3D PyC structures were rinsed with DI water and dried at 80°C.

(c) Sensor fabrication

To fabricate a PANi@3D PyC-based NO₂ gas sensor, silver (Ag) paste was first applied to the two ends of the microlattice structure which acts as an electrode. To measure the changes in

resistance of the prepared sensor under varying concentrations of NO₂ gas, a constant voltage of 1 V was applied to these electrodes, which were connected to a Keysight 29018B source-meter. A vacuum pump was also used to remove contaminated air from the sensing chamber. Further for selectivity measurements, we have taken 1% target gases (NO₂, NH₃, and H₂S), balanced with 99% Argon (Ar). The integration of PANi tetrapods results in the formation of a 3D PyC structure with a high surface area, durability, and self-supported lightweight scaffold. The microlattice structure intentionally designed in this process allows for the efficient diffusion of NO₂ gas molecules throughout the PANi@3D PyC structure. Additionally, this method eliminates the need for expensive microfabrication techniques typically required in traditional gas sensors, such as costly substrates and microheaters, making it an affordable sensor option with comparable results.

5.1.3 Results and Discussion

(a) Material Characterizations

The size of the 3D resin structure was 10 mm × 10 mm × 10 mm, with a lattice width of 421±41 µm. Upon pyrolysis, the 3D PyC structure retained the original geometry of the 3D printed resin structure, despite a significant shrinkage in the lattice width and overall size. The structure shrunk to the average size of 4.87 mm × 5.12 mm × 4.96 mm, with a lattice width of 208±31 µm, translating to a ~51% linear shrinkage, which agrees with previous publications on 3D PyC microlattice (Eggeler et al., 2023; Islam et al., 2020a). Further the mass loss (%), volumetric shrinkage (%) and structural density (g/mm³) were calculated as 83.59±0.13, 87.6±1.7, 0.242±0.003, respectively. The surface morphology of these structures can be effectively seen in FESEM images as depicted in Figure 5.1 (a-d). High magnification SEM images (Figure 5.1 (a, b)) revealed the presence of a perfectly regular lattice surface, with a rough texture on the 3D resin structure. Further, Figure 5.1 (c, d), shows a FESEM image revealed that the 3D PyC structure featured a rough and granular surface, which might have originated from the already rough surface of the printed resin structure. These granular structures are beneficial for anchoring PANi tetrapods in the subsequent in situ polymerizations, facilitating a robust interaction between the PANi and 3D PyC structure. However, several structural deformities, such as bubble-like hollow artifacts, were observed on the lattice surfaces. The pyrolysis process causes a thermochemical degradation of the precursor resin, resulting in gaseous byproducts leaving the material matrix. During this degradation process, the precursor also goes through a semi-solid transition phase. The gaseous byproducts might have been trapped during this transition phase, leading to the bubble-like artifact formation (Eggeler et al., 2023; Islam et al., 2021, 2020b). Furthermore, the intrinsic stress during the structural shrinkage could also induce deformation and fracture of pyrolytic carbon structures (Hemanth et al., 2017).

Figure 5.1 (e, f) shows the EDS and elemental mapping results of the 3D PyC structure, revealing the presence of elements C, O, Si, and Ti. Typically, resins are composed of organic hydrocarbons, but the presence of Si and Ti is likely due to additives in the resin, as confirmed by XRD analysis of 3D PyC structure. The XRD diffractogram of 3D PyC structure (Figure 5.1 (g)) featured two broad peaks, successfully indexed to the (002) and (101) crystal planes of carbon, respectively (Islam et al., 2022b, 2018). A few other peaks were also identified in the diffractogram, which were matched to silicon dioxide (SiO₂, ICDD 98-008-9281) and titanium dioxide (TiO₂, ICDD 98-016-8138). These peaks were attributed to the Ti and Si present within the resin precursor, which were converted to TiO₂ and SiO₂ during the thermochemical degradation of the precursor resin during the pyrolysis process. The Raman spectrum of 3D PyC structures featured two characteristic peaks associated with carbonaceous materials located at 1360 cm⁻¹ and 1599 cm⁻¹, denoted as D and G bands (see Figure 5.1 (h)). The D band indicates defects and disorders within the materials, while the G band corresponds to the first-order scattering of the E_{2g} mode (Ferrari and Robertson, 2000). Moreover, various peaks within the 700-1300 cm⁻¹ range have been identified, potentially associated with the peaks of SiO₂ and TiO₂. Moreover, the compression test is performed to analyse the mechanical characteristics of the 3D PyC structure.

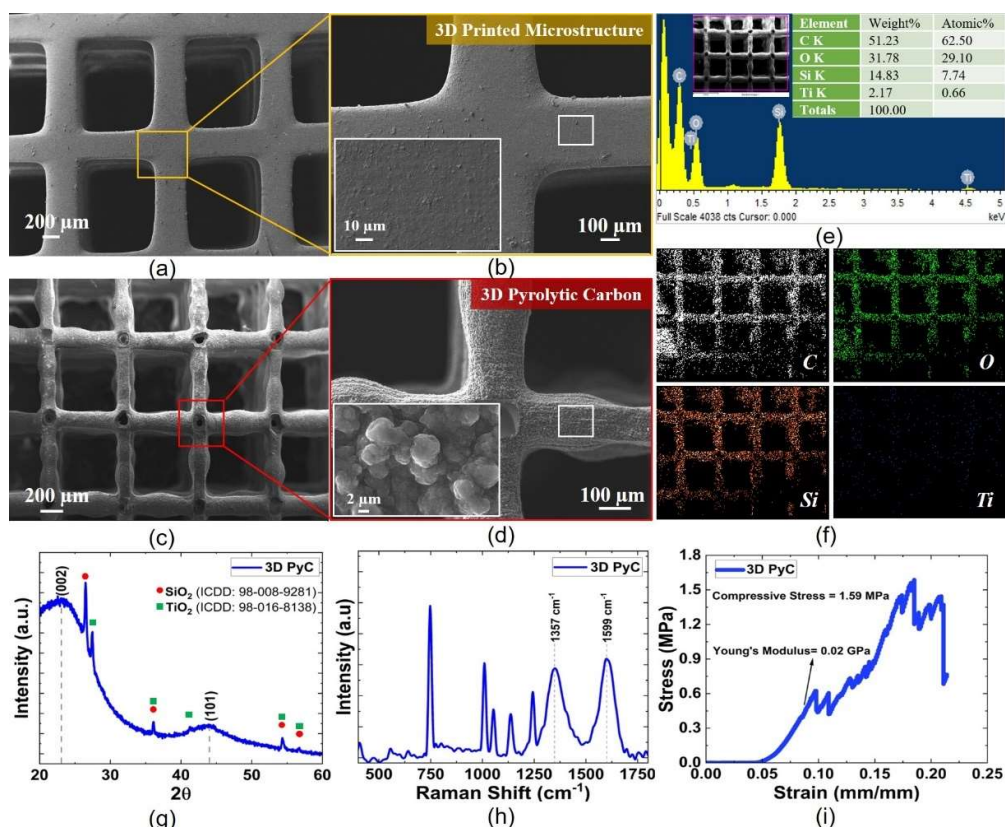


Figure 5.1: FESEM images of (a, b) 3D printed resin structure, (c, d) 3D PyC structure, (e, f) EDS and elemental mapping, (g) XRD, and (h) Raman spectra, (i) compression testing of 3D PyC structure

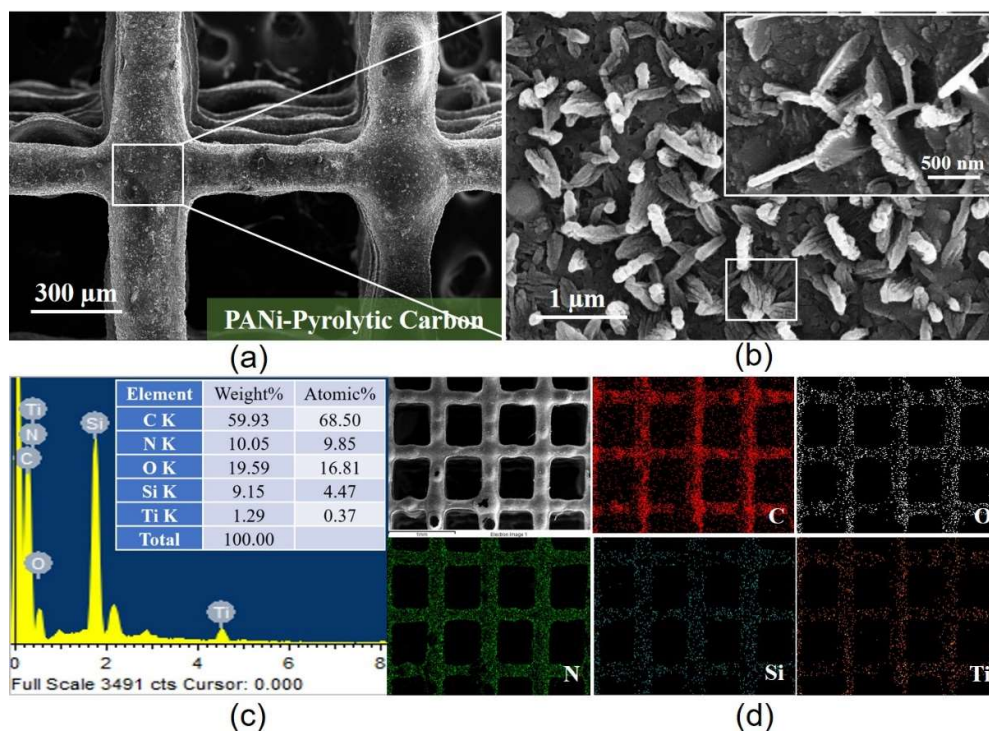


Figure 5.2: FESEM image of (a, b) PANi@ 3D PyC structure, with inset showing the PANi tetrapods, (c) EDS and (d) elemental mapping results of PANi@ 3D PyC structure

Figure 5.1 (i) depicts multiple peaks that emerge as a consequence of stress variation caused due to the increase of load. These peaks are attributed to the failure of individual beams and microlattice cells due to gradual brittle breakage, which ultimately leads to the disintegration

of the microlattice elements. During uniaxial compression, distinct three stages are observed: (1) an elastic region, (2) the brittle failure of the first layer, and (3) subsequent gradual brittle failure of individual beams and layers (Chang et al., 2019; Zhou et al., 2020). The robust yet lightweight design of 3D PyC structures with compressive stress and Young's modulus were 1.59 MPa and 0.02 GPa, respectively, allows these structures to endure a wide range of loads and prevent catastrophic failure in different operational conditions, hence establishing their reliability for sensing applications under stress conditions.

Unlike traditional gas sensors, the 3D PyC structured sensors that are decorated with conducting polymers exhibit a high degree of customization and a complex macroscopic spatial architecture that enhances gas diffusion. This is demonstrated by the FESEM images in Figure 5.2 (a, b), which show the presence of PANi tetrapods with leg thicknesses of ~ 200 nm and lengths of several microns. As discussed above, the 3D PyC scaffolds, have a rough surface with larger bubble-like hollow pores at the center, significantly improve the surface area, allowing for efficient gas diffusion across both the interior and exterior surfaces. Together PANi tetrapods decorated 3D PyC surface forms a microscale porous conductive network that imparts conductivity and provides optimal gas adsorption and desorption thereby gas-sensing capabilities to the resulting scaffolds. The even distribution of PANi tetrapods throughout the structure minimizes aggregation, thereby excepted to enhanced the stability and repeatability of the sensor. The unique PANi tetrapods networks are achieved through a self-assembly process, where, during the initial polymerization stages, oxidation on the scaffold surface attracts monomers, creating active sites on the 3D PyC. Initially, the polymer formed is the fully oxidized emeraldine base (EB) of PANi. As the reaction continues and the oxidant depletes, the remaining aniline monomer reduces the EB to emeraldine salt (ES), which exhibits higher conductivity. Figure 5.2 (c, d) displays the EDS and elemental mapping images, illustrating the elemental distribution of C, N, O, Si, and Ti.

(b) Gas Sensing Results

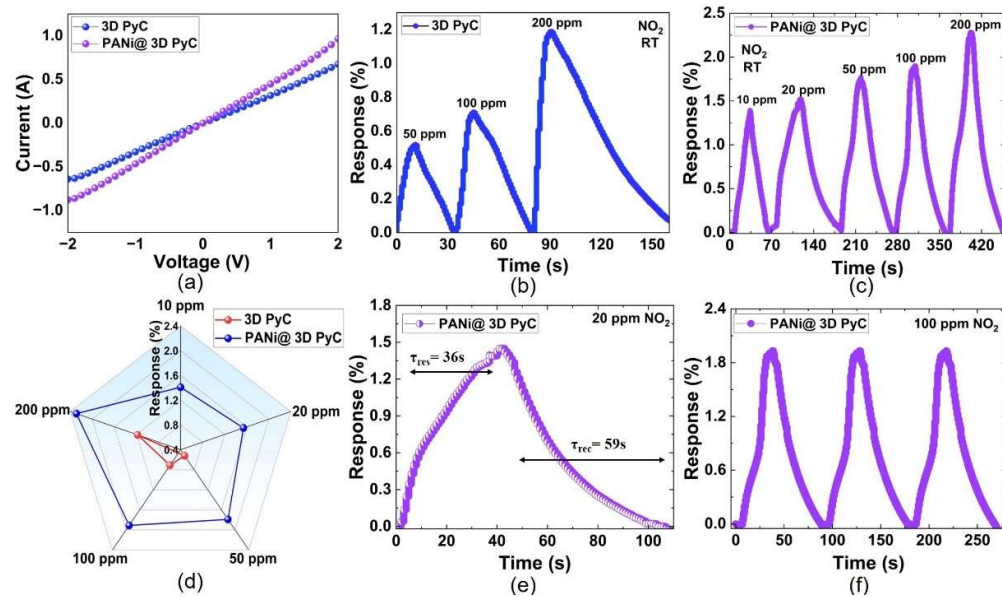


Figure 5.3: (a) I-V curve of both devices, (b, c) Response (%) vs time graph for 3D PyC and PANi@ 3D PyC devices at RT (d) Radar plot for comparative results of both devices at varying concentration of NO₂ gas, (e) Response and recovery time details of PANi@ 3D PyC at 20 ppm NO₂ gas, and (f) repeatability of device at 100 ppm NO₂

Both 3D PyC and PANi@3D PyC devices with Ag electrodes were directly utilized for evaluating sensing performance without the need of expensive technique to fabricate contact electrodes. This process simplifies subsequent procedures, as the devices can be directly applied for NO₂ sensing, thus minimizing energy consumption, device instability, and operational risks

associated with elevated temperatures. I-V characteristics of both 3D PyC and PANi@ 3D PyC devices were investigated from -2 to 2 V. The conductivity of PANi@ 3D PyC device increased with the incorporation of PANi nanostructures at ambient temperature which indicates the ohmic nature of the electrical contact of devices (see Figure 5.3 (a)). Further, Figure 5.3 (b) show the response of 3D PyC devices for 50-200 ppm NO₂ gas at RT. As expected the pristine 3D PyC device doesn't respond to low concentration of NO₂ gas at RT. However, at 50 ppm 3D PyC started to show a response at NO₂ gas. The sensor showed relative response of ~0.52% at 50 ppm and gradually increased to ~1.18% at 200 ppm. This behavior of the device is because, at a low gas concentration, the surface interaction of NO₂ molecules with the surface of the sensor is low, leading to a lower response. The sensitivity increased stepwise when the gas concentration increased to create an enhanced surface interaction, leading to a rising response at a higher concentration. Figure 5.3 (c) depicts the response (%) of PANi@3D PyC to various concentrations (10–200 ppm) of NO₂ gas at RT. The PANi@ 3D PyC devices demonstrated the response of 1.41% to 2.29% at under the exposure of 10 to 200 ppm of NO₂ gas, displaying a stepwise pattern corresponding to the concentrations. In this study, we aim to demonstrate the capability of our 3D-printed devices to operate at room temperature. By doing so, we seek to minimize the need for costly components typically required in traditional gas sensor, such as expensive substrates and microheaters. This approach not only reduces costs but also makes our 3D-printed sensors more accessible and affordable, particularly for low-income countries.

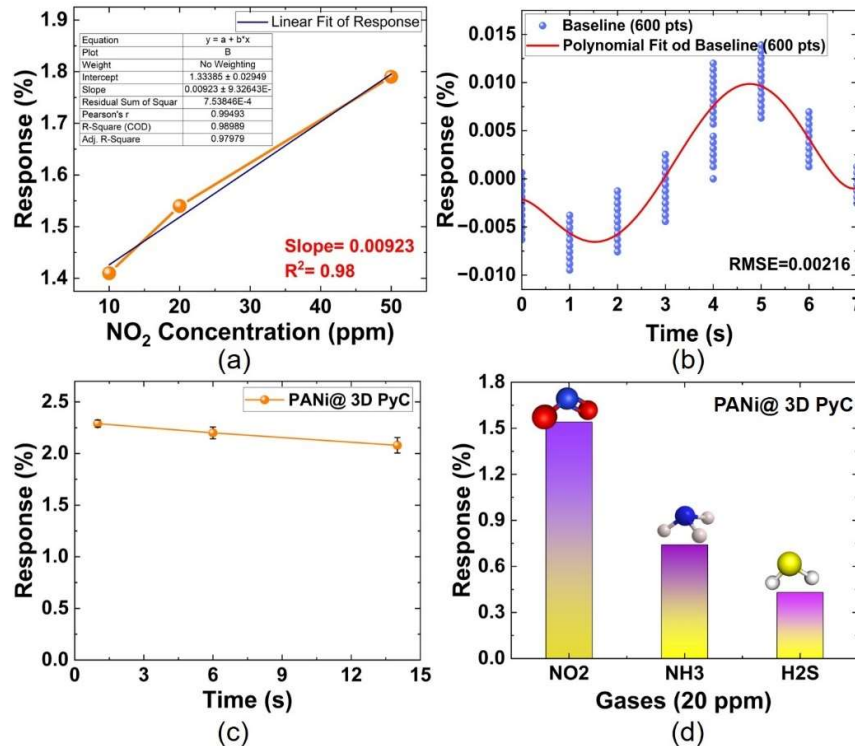


Figure 5.4: (a-d) Sensitivity, Stability and Selectivity results of PANi@ 3D PyC device

Furthermore, Figure 5.3 (d) illustrates the radar plot for comparative response (%) of both devices. The results highlight the superior response of the PANi@ 3D PyC device at each NO₂ gas concentration. The PANi@ 3D PyC device shows fast response and recovery with 1.94x (194% higher response by proportion) at 200 ppm NO₂ on comparison to 3D PyC device. Additionally, Figure 5.3 (e) displays the rapid response (τ_{res}) and recovery (τ_{rec}) times of PANi@ 3D PyC to 20 ppm NO₂, which is recorded as 36 sec and 59 sec, respectively. The slower recovery time compared to the response time was attributed to the potential entrapment of gas molecules during desorption within the PANi tetrapods network. Further, to assess the consistency of the sensor's output, a repeatability study was carried out as shown in Figure 5.3 (f). The experiment

revealed that the device's response was almost uniform throughout the three-cycle test at 100 ppm NO₂ gas concentration.

Gas sensor sensitivity is typically assessed by measuring the response change corresponding to a 1 ppm shift in the target gas concentration. This sensitivity is determined by the slope of the linear regression line, illustrated in Figure 5.4 (a), which in this case is 0.009%/ppm. Utilizing this slope, the sensor's limit of detection (LOD) is calculated. Figure 5.4 (b) shows the rms value of 0.00216, resulting in a LOD of ~700 ppb. Furthermore, Figure 5.4 (c) depicts a 14 days stability result of the PANi@3D PyC device, which demonstrated that the device exhibited negligible variation in response (%) when subjected to 200 ppm NO₂ gas at RT. Furthermore, Figure 5.4 (d) shows the selectivity of the PANi@ 3D PyC was examined in the presence of 20 ppm NH₃ and H₂S gases. Moreover, the comparative analysis of previously developed devices for NO₂ gas detection is shown in Table 5.1.

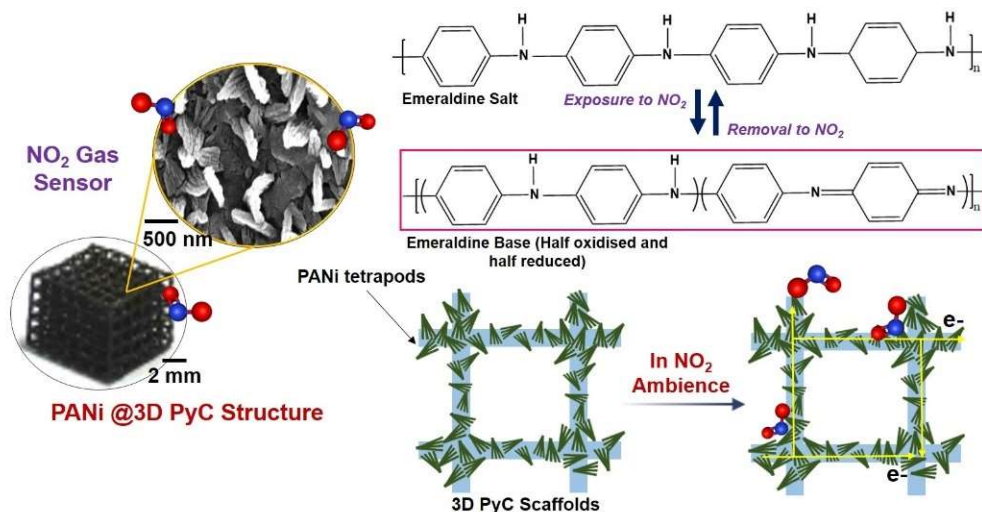


Figure 5.5: Possible sensing mechanisms of PANi@ 3D PyC structure towards NO₂ gas

The possible sensing mechanisms of PANi@ 3D PyC scaffolds is illustrated in Figure 5.5. The response of PANi tetrapods to NO₂ gas is notably complex due to the interplay of factors influencing its conductivity. The electrical conductivity of PANi is determined not just by its protonation level but also by its oxidation state. As PANi becomes more oxidized, its conductivity decreases (Ram et al., 2005). The prepared PANi tetrapods were synthesized under acidic conditions, therefore exists primarily in the ES state, which is rich in active sites. Upon exposure to NO₂, the interaction between the -NH groups in PANi and NO₂ leads to a transformation from the ES state to EB state, resulting in increased oxidation and a subsequent drop in conductivity (Murugesan et al., 2022; Yan et al., 2007). Additionally, the hierarchical PANi tetrapods within the conductive networks of 3D PyC create numerous passageways, facilitating rapid gas diffusion (W. Zhang et al., 2019). Since gas sensing predominantly occurs on the surface of the materials, the exposure of NO₂ gas molecules to PANi tetrapods ensures efficient interaction. Furthermore, the conjugation effect between PANi and the pyrolytic carbon scaffold facilitates high mobility percolation paths for accelerating charge transfer, enhancing the sensor's overall performance by shortening response and recovery times. When NO₂ is removed from the environment, it dissociates from the PANi@ 3D PyC surface, allowing the sensor to revert to its original resistance level. This combination of hierarchical structure, efficient charge transfer, and chemical affinity underpins the fast and effective sensing performance of PANi@ 3D PyC scaffolds.

Table 5.1: Comparison of sensing performance of PANi based different devices

Devices	Substrate	Gas	τ_{res} (s)	τ_{rec} (s)	Response (%)
PANi/CLS (Zhou et al., 2020)	3D printed Mullite	NH ₃ (100 ppm)	~202	~605	~4
MWCNTs/PANi (Yoo et al., 2009)	MEMS platform	NH ₃ (100 ppm)	-	-	~0.16

Nano-PANi (Liu et al., 2021)	Glass	NH ₃ (20 ppm)	-	-	~1.5
PANi/Ag ₂ O/GO (Umar et al., 2021)	Alumina	NO ₂ (25 ppm)	100	140	~5.85
PANi@ 3D PyC (This work)	3D Printed Scaffolds	NO ₂ (200 ppm)	30	46	~2.3

5.1.4 Summary

In this study, we present a customizable gas sensor with exceptional sensing performance, fabricated using DLP 3D printing methods followed by in situ polymerization of PANi on a pyrolytic carbon microstructure to produce a PANi@ 3D PyC based NO₂ gas sensor. The PANi@ 3D PyC sensor demonstrated an excellent response to NO₂ gas and operates effectively at RT, mitigating energy consumption, device instability, and operational risks due to elevated temperatures. It exhibited strong repeatability with rapid response and recovery times of 36 sec and 59 sec, respectively, and a notable LOD of ~700 ppb. Future research will focus on optimizing micromorphology and nano-functionalization to enhance response and sensitivity, as well as integrating other sensing materials for improved gas sensing performance. Compared to conventional fabrication methods, this approach provides enhanced design flexibility and rapid manufacturing capabilities. By integrating design features from the micro- to nanoscale, these sensors are well-equipped to fulfill the requirements of diverse and intricate sensing applications.

5.2 ZnO NANOWIRES-DECORATED 3D PRINTED PYROLYTIC CARBON FOR SOLAR LIGHT DRIVEN PHOTOCATALYTIC DEGRADATION OF WASTEWATER CONTAMINANTS

This work aims to overcome the limitations of photocatalysts by decorating them on customizable pyrolyzed 3D-microlattice architectures for enhanced photocatalytic performance. Here, we first fabricated 3D carbon microlattice architectures by digital light processing (DLP) 3D printing of a precursor resin, followed by carbonization at 900°C and the hydrothermal growth of zinc oxide (ZnO) nanowires on the 3D pyrolyzed structures (ZnO@PyC structure). The photocatalytic performance of the ZnO@PyC structure was evaluated through the degradation of rhodamine B (RhB) dye under both UV light and direct sunlight irradiation. The combination of ZnO NWs and PyC structure represents a promising pathway for advancing sustainable and effective water purification technologies.

5.2.1 Introduction

The global issue of wastewater treatment, exacerbated by pollutants from agriculture, domestic, and industrial practices, has gained significant attention (Bhattacharya et al., 2018b; D. Zhang et al., 2018). Despite 71% of the Earth's surface being covered by water, a mere fraction, less than 1%, is readily available for drinking. Projections indicate a 55% increase in water demand by 2050 due to population growth, coupled with an anticipated global water deficit of 40% by 2030 (Bielawski, 2020). Alarming statistics from World Health Organization (WHO) reports reveal that one in four individuals lacks access to safe drinking water, contributing to 6% of deaths in low-income countries in 2017 (World Health Organization, 2017). Furthermore, the textile industry extensively uses various dyes, with their effluents being inherently non-biodegradable, leading to various environmental repercussions (H. Guo et al., 2024; Qin et al., 2023). For example, rhodamine B (RhB), a synthetic organic compound, is commonly utilized to produce fluorescent hues in various textiles, including wool, polyester, nylon and cotton (Mohod et al., 2023). As a prominent organic contaminant, RhB finds extensive use not only in the textile industry as a dye but also in biological applications, such as fluorescent marking and as a biomarker (Kasinathan et al., 2016). However, the complete breakdown of RhB in aqueous solutions proves challenging and inefficient due to its intricate molecular structure (Gupta and Singh, 2024). Therefore, a technique is needed that can effectively break down these complex compounds and support sustainable water use. This objective can be achieved by developing effective wastewater treatment techniques to meet the rising demand. Within the realm of

sustainable and eco-friendly technologies, solar light photocatalysis emerges as a promising solution, offering a cleaner and more efficient approach to addressing environmental challenges (Pandey et al., 2021). For example, solar concentrator based photocatalysis is an emerging technique that is rooted in the principles of utilizing concentrated sunlight to drive chemical reactions to break down pollutants (El Golli et al., 2024; Gupta et al., 2018). Various methods, including electrocoagulation, adsorption, and chemical oxidation have been reported in the literature for treating these toxins. However, these approaches often fall short of completely eliminating modern pollutants, frequently transferring dye molecules rather than removing them entirely. In contrast, photocatalytic wastewater treatment brings advantages like improved degradation of organic contaminants and the adaptability of catalysts that can be optimized for cost-effectiveness. Practical implementation, however, faces challenges such as particle aggregation and the separation of photocatalysts from treated water. The challenges of retrieving powdered photocatalysts and causing pipe blockages are exacerbated in water treatment facilities. Recent efforts have focused on creating photocatalytic nanocoatings that immobilize photocatalysts on substrates without requiring additional processing (El Golli et al., 2021). However, when dealing with complex water purification scenarios, the use of substrates coated with photocatalytic materials may be limited due to size and shape mismatches between the environment and substrates. Therefore, there is a need for customized substrates coated with photocatalysts.

In response to these challenges, ongoing research and advancements are directed toward establishing innovative approaches for highly efficient water remediation using additive manufacturing (AM) (Chaudhary et al., 2022; Xu et al., 2023). The inherent flexibility of AM enables the creation of intricate geometries and customized structures tailored to specific wastewater treatment requirements (Sangiorgi et al., 2019). Furthermore, AM presents many advantages, encompassing a simple process, precision, uniformity, sustainability, adaptability, and cost-effectiveness (Roy Barman et al., 2023). In recent times, AM has found applications in domestic water treatment and desalination, offering a sustainable solution for recycling and reusing non-drinkable water (Yanar et al., 2018). This approach presents an environmentally friendly alternative for both domestic and industrial wastewater treatment, minimizing waste generation, reducing chemical exposures, and offering economic precision, thus effectively bridging gaps in existing wastewater techniques (Xue et al., 2023). Further, the utilization of 3D-printed substrates with micron-sized structures may serve as in-situ growth anchors for the functionalization of photocatalysts (Aghaei et al., 2022). This allows for the fabrication of substrates in various sizes and shapes coated with photocatalysts tailored to specific application demands, all achievable through the precision of 3D printing technology.

Metal oxides has emerged as a prominent choice for photocatalytic wastewater treatment, showcasing efficient degradation capabilities against various pollutants (Y. Deng et al., 2020; Zhang et al., 2021). Compared to other metal oxides, ZnO photocatalysts demonstrate superior efficiency, high electron mobility, and exceptional quantum efficiency (Majumder et al., 2020). These qualities make ZnO highly effective in the degradation of pollutants in wastewater (Aftab et al., 2022). Furthermore, the utilization of ZnO as a photocatalyst in wastewater treatment is an actively researched area, with recent developments focusing on elevating its performance through strategies such as metal doping, semiconductor coupling, and integration with carbon materials (Folawewo and Bala, 2022). For example, He et al. developed an integrated photoanode featuring a ZnO/silicon NWs heterostructures through a combination of hydrothermal technique and metal-assisted chemical etching (He et al., 2023). This innovative photoanode was employed to develop photocatalytic fuel cells, enabling simultaneous electricity generation and degradation of RhB dye wastewater. Similarly, Li et al. presented the synthesis of Ag and g-C₃N₄ nanosheets-decorated ZnO for wastewater treatment (H. Li et al., 2023). This ternary nanocomposite exhibited complete degradation of RhB dye within 30 mins under visible-light irradiation. These advancements aim to tackle practical implementation challenges and enhance the overall efficiency of ZnO-based photocatalysts for water purifications. The recent surge in scientific

interest lies in advancing ZnO with precisely controllable nanoscale features to meet the rising demand for efficient and sustainable wastewater treatment.

This research focuses on achieving one-step solar and UV light enabled wastewater degradation by integrating the synthesis of nanosized ZnO wires onto 3D cubical-shaped pyrolyzed microlattice structures (ZnO@PyC structure) for wastewater treatment applications. To our knowledge, this is the first report of a 3D PyC structure adorned with ZnO NWs for treating wastewater contaminants. The incorporation of ZnO NWs onto a 3D PyC structure not only renders it exceptionally unique across a broad spectrum of applications, such as wastewater degradation, but also capitalizes on the synergistic interplay between semiconductor ZnO and conductive carbon. Moreover, the inherent strength and lightweight properties of 3D carbon are magnified with the addition of ZnO, amplifying the functionality of the structure manifold.

5.2.2 Experimental Methods

ZnO NWs are synthesized using the following reagents: zinc acetate (ZnAc; $\text{ZnC}_4\text{H}_6\text{O}_4$; Molecular weight: 219.51 g/mol; 99% pure), ethanol ($\text{C}_2\text{H}_6\text{O}$; Molecular weight: 46.07 g/mol; 96% pure), hexamethylenetetramine (HMTA; $(\text{CH}_2)_6\text{N}_4$; Molecular weight: 140.19 g/mol; 99% pure), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$; Molecular weight: 297.49 g/mol; 98% pure). These reagents were procured from Sigma Aldrich. The degradation performance of the prepared ZnO@ 3D PyC structure is measured against RhB dye, which was procured from Otto chemicals.

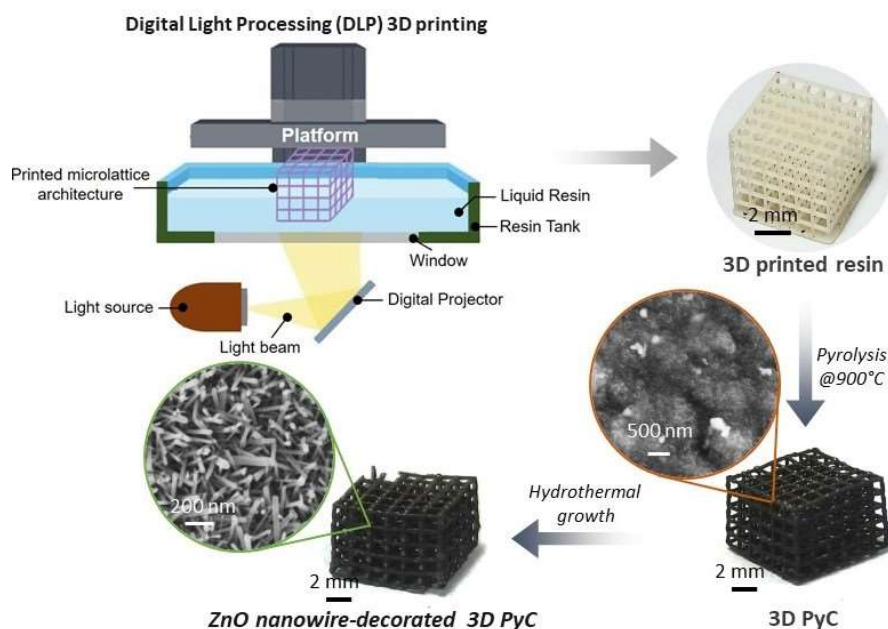


Figure 5.6: A schematic view of preparation and synthesis of ZnO NW-decorated 3D printed microlattice architecture (ZnO@PyC)

(a) Synthesis of ultrathin ZnO NWs over pyrolyzed microstructure

We performed a hydrothermal method for in situ growth of ZnO NWs on the 3D pyrolytic carbon (PyC) microlattice structures. Firstly, a 10 mM ZnAc was prepared in ethanol and ultrasonicated for 2 hours until a milky white homogenous solution was formed. The 3D PyC microlattice structures were properly rinsed with DI water and then dip-coated in the ZnAc solution, followed by baking at 70°C. The procedure was repeated twice for the uniform seed layer growth over the 3D PyC structures. To initiate the growth of ZnO NWs, the seeded PyC structures were then immersed in a ratio 1:1 of 15 mM $\text{Zn}(\text{NO}_3)_2$ and $(\text{CH}_2)_6\text{N}_4$ solution prepared in DI water. The whole solution, along with microstructure, was placed in an electrical oven for 9 hours at 90°C to grow the ZnO NWs. Following growth, the ZnO@PyC structures were rinsed

with DI water and dried at 60°C (see Figure 5.6). The rest of the solution's precipitate was collected for material characterization.

(b) Photocatalysis performance measurement

The photocatalytic efficiency of samples (3D printed resin structures, 3D PyC microlattice structures, and 3D ZnO@PyC structures) were examined for the degradation of RhB dyes under UV light (5 W UV Lamp with $\lambda=365$ nm; provided by Labtech Instrument) and direct sunlight irradiations. During this study, RhB dye was dissolved in DI water at a concentration of 10 mg/L. The mixture was stirred for 60 mins at 50 °C in the dark conditions to attain adsorption-desorption equilibrium. The prepared RhB solution was then transferred to separate 20 mL glass containers with fabricated microstructures. To assess the degradation rate, 1 mL of the degraded dye solution was extracted from each container every 20 mins, and the absorption spectrum (300-600 nm) was recorded (the distance between UV light source and container is 5 cm). This procedure continued until all containers were removed from the UV chamber. This method allowed us to observe the degradation of RhB dye over time without disturbing the remaining solution in the containers. All the experiments were carried out for 180 mins (for UV light irradiations) and 280 mins (for sunlight irradiations). Throughout the experiment, light interacts with the ZnO@PyC structures, initiating a reaction with water and dissolved oxygen, resulting in the production of hydroxyl and superoxide radicals. These radicals play a crucial role in degrading RhB dye. The deliberately designed microlattice structure facilitates the propagation of light deep into the bulk of the ZnO@PyC structure. This ensures the generation of reactive oxygen species (ROS) across the entire liquid volume, leading to efficient degradation of RhB dye in water. Additionally, the study also investigated the impact of pH on degradation performance and scavenger tests to identify active species involved in RhB breakdown, respectively. The robustness of the prepared 3D PyC structure prevents the release of the ZnO NWs into the treated water, post-degradation. Thus, achieved a high surface-area, durable, self-supported ZnO@PyC structure with minimal environmental or water contamination risks. This approach eliminates the need for costly catalyst filtration, utilizing abundant sunlight as the primary energy source for cost-effective wastewater purification. Further, the degradation efficiency ($E\%$) was measured using Equation 5.1, which involved the RhB dye concentration at the initial (A_0) and final time (A).

$$E (\%) = \left(1 - \frac{A}{A_0}\right) \times 100 \quad (5.1)$$

5.2.3 Results and Discussion

(a) ZnO nanowire-decorated 3D PyC

In Figure 5.7, FESEM images depict a 3D PyC structure decorated with ZnO NWs. The microstructure consisted of near parallel blocks with identical dimensions. The SEM pictures affirmed the uniformity from top to bottom and the continuous, long-range coverage of the ZnO NW layer on the micro-surfaces of the PyC structure. This uniformity was observed even in the interior regions of the 3D assembly, as illustrated in Figure 5.7 (a-d). The entire structure was enveloped by a dense array of ultrathin ZnO NWs, with a diameter and length of ~ 28 nm and ~ 1.2 μ m, respectively (see inset of Figure 5.7 (d)). Additionally, the relative content of ZnO was determined to be 8.7% of the total weight of the ZnO@PyC structure. Moreover, the surface morphology of the 3D PyC structure significantly influenced the deposition of the applied seed layer, thereby facilitating the formation of nucleation sites (Biswal et al., 2021). It is crucial to regulate the change in Gibbs free energy (ΔG) for the proper growth of NWs. The following equations elucidate the critical energy for nucleation and the volumetric alteration in Gibbs free energy.

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 (\Delta G_V) \quad (5.2)$$

$$\Delta G^* = \frac{(16\pi\gamma^3)}{(3\Delta G_V)^2} \quad (5.3)$$

$$\Delta G_V = -\left(\frac{k_B T}{V}\right) \ln \frac{C}{C_0} \quad (5.4)$$

Here, the terms r , γ , ΔG_V , C_0 , C , k_B , T , and V are denoted as embryo radius, interfacial energy, the change in Gibbs free energy per unit volume, initial and final concentration of Zn^{2+} ions in the solution, Boltzmann constant, temperature (Kelvin), and atomic volume, respectively. The initial term of equation 5.2 indicates a reduction in surface energy, while the subsequent term signifies an increase in energy associated with the formation of new volume. Furthermore, the uniform growth and nucleation of NWs is contingent upon ensuring that ΔG remains below the specified threshold (ΔG^*). Further, by facilitating an ample number of nucleation sites, the nano-seed coating effectively reduces these thermodynamic barriers, thereby promoting the growth of ultrathin NWs at 90-95°C. The length of the NWs escalates with increasing temperature, attributed to enhanced ion mobility and diffusion kinetics. Moreover, a series of reactions initiated the synthesis of NWs on the surface of the PyC structure. When subjected to heat, hydrolysis of HMTA in the solution resulted in the generation of formaldehyde (HCHO) and ammonia (NH_3). The released NH_3 facilitated the production of OH^- ions while impeding the substantial formation of Zn^{2+} ions in the solution. Further the breakdown of ammonia yielded NH_4^+ and OH^- . The intricate chemical $\text{Zn}(\text{OH})_4^{2-}$ was then formed through the reaction of OH^- with Zn^{2+} . Under reaction conditions, this complex dehydrates, ultimately giving rise to the formation of ultrathin NWs.

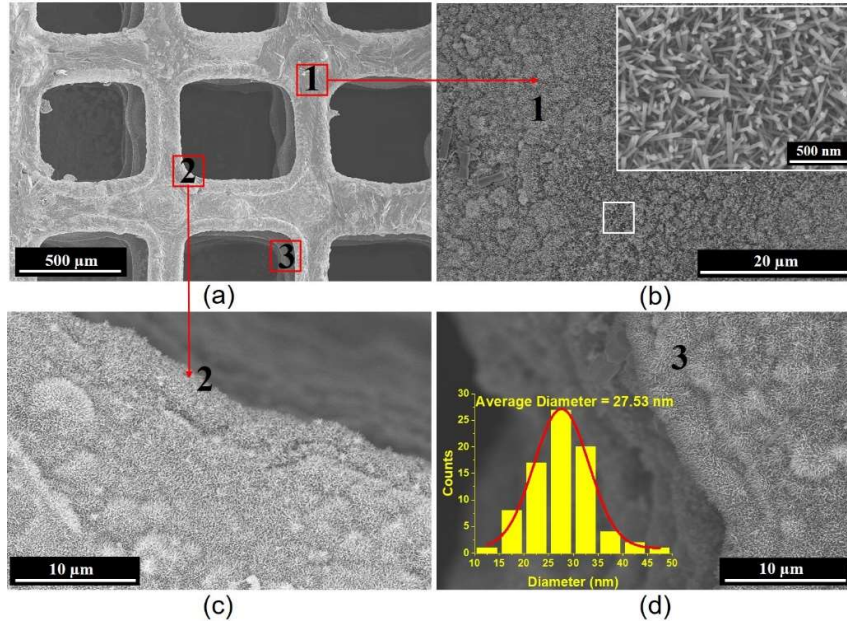


Figure 5.7: (a-d) Photograph (center) and FESEM images of ZnO NW growth on PyC structure, with inset image of histogram of average diameter of ZnO NWs

Figure 5.8 (a) and 5.8 (d) displays the EDS and elemental mapping images, illustrating the elemental distribution of C, Zn, O, Si, and Ti. The Zn and O signals permeated the NWs uniformly, whereas the C element signal was evenly spread across the PyC structure. This distinct spatial arrangement affirmed the integration of ultrathin ZnO NWs onto the PyC structure. Additionally, the quality of the ZnO NWs is depicted in Figure 4(B-C). The XRD pattern revealed characteristic $\theta/2\theta$ lines corresponding to the hexagonal wurtzite structure of ZnO, consistent with standard ICDD PDF No. 96-210-7060 (Islam et al., 2022a; Mondal et al., 2022). Notably, the (101) diffraction peak at $\sim 36^\circ$ demonstrates a crystalline structure with high quality, evident from the narrow full width at half maximum (FWHM) of the (101) line which is less than 0.2° . Figure

5.8 (e) illustrates the Raman peaks observed in the 3D ZnO@PyC structures, which also featured the Raman spectrum of 3D PyC for comparison. The Raman spectra of ZnO@PyC structures exhibited both D and G peaks, characteristic to the PyC materials, where additional distinctive peaks for ZnO could also be observed. A prominent peak at 438 cm^{-1} was attributed to the non-polar optical phonon E_2 vibration mode of ZnO in the wurtzite structure (Gayen and Paul, 2018). Furthermore, a peak at 592 cm^{-1} corresponds to the E_1 mode of hexagonal ZnO, specifically associated with oxygen deficiencies (Li and Li, 2009).

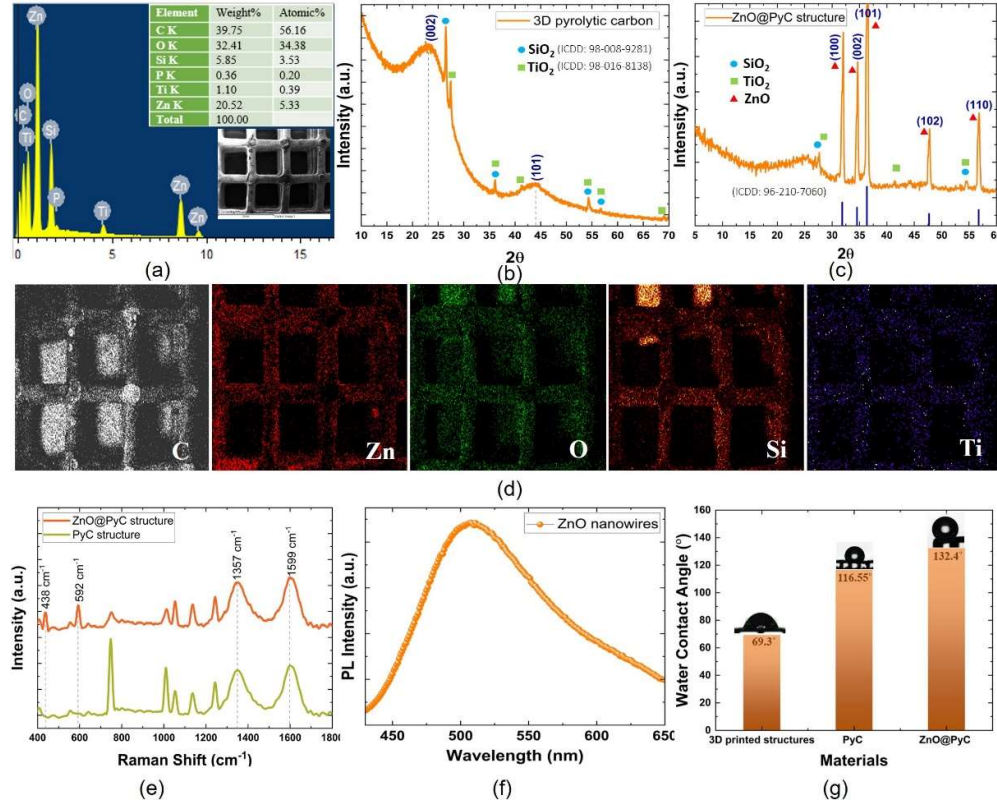


Figure 5.8: Characterization results: (a) EDS of ZnO@PyC structure, (b, c) XRD of PyC and ZnO@PyC structure, (d) elemental mapping of ZnO@PyC structure, (e) Raman spectrum, (f) PL spectrum of ZnO NWs, and (g) water contact angle (WCA) results

To evaluate crystal defects within ZnO NWs, we conducted PL analysis with an excitation wavelength of 330 nm (3.76 eV) at room temperature. The PL intensity serves as a gauge for the recombination efficiency of photogenerated electron-hole pairs within the ZnO NWs. A higher spectrum intensity signifies an abundance of electron-hole pairs, whereas a lower intensity indicates fewer pairs. The Figure 5.8 (f) illustrates the green emission of ZnO NWs analysed by PL spectra. Based on the energy level diagrams for ZnO crystals (Gupta et al., 2015a; Schmidt-Mende and MacManus-Driscoll, 2007) and the PL spectra, the green emission observed can be attributed to two potential transitions. The first possibility involves electron transition from the conduction band (CB) to zinc vacancies, situated $\sim 0.8\text{ eV}$ above the valence band (VB), leading to an emission around 2.5 eV. The second possibility is related to the capture of holes by neutral oxygen vacancies, which exist in three charge states: neutral, singly charged, and doubly charged. These vacancies occupy energy levels ranging from ~ 2.17 to 2.5 eV above the VB maximum, as determined by density functional theory calculations (Vidya et al., 2011). These energy levels align with the green emission peaks observed in ZnO NWs, indicating that the green emission is due to electron transitions from the CB edge to the energy levels associated with the defect complex.

The ZnO NWs growth also exhibited a strong impact on the wettability of the printed structures. The contact angle measurements are presented in Figure 5.8 (g). The as-fabricated 3D microlattice structures exhibited a contact angle of 69.3°, while the PyC and ZnO@PyC structures demonstrated higher contact angles of 116.55° and 132.4°, respectively. The enhanced contact angle of PyC material compared to the resin structure could be attributed to the intrinsic hydrophobic nature of carbon and highly rough surface morphology of the PyC material. Growing ZnO NWs over the PyC surface further increased the surface roughness of the hierarchical ZnO@PyC material, resulting in increased hydrophobicity.

(b) Photocatalytic degradation

The photocatalytic degradation of ZnO@PyC structures was assessed through UV-Vis spectra analysis of RhB dye at regular intervals of 20 min. Figure 5.9 revealed the spectral images of a gradual reduction in the intensity of the characteristic absorption peak at 553 nm with increasing UV exposure time. In Figure 5.9, fitting the normalized maximum absorbance to time illustrated a degradation pattern. As per the Beer-Lambert law, which establishes a linear correlation between concentration and absorbance, the normalized absorbance corresponds to the normalized concentration of the RhB solution. Previous research has consistently indicated that the photocatalytic degradation kinetics of various organic dyes with ZnO adheres to the Langmuir-Hinshelwood kinetic model. The first-order equation is as follows:

$$-\frac{dA}{dt} = -kc \quad (5.5)$$

$$\ln \frac{A}{A_0} = kt + \text{constant} \quad (5.6)$$

Here, A_0 and A present the concentration of RhB dye solution at the initial and final time, respectively, while k denotes the first-order rate constant. The attenuation of RhB dye (pH 6.5) due to UV light exposure is evident from the inset of Figure 5.9 (a, b). This fading phenomenon results from the breakdown of azo bonds by free radicals generated from the ZnO NWs decorated PyC structure. The rate constant (k) was determined as $2.3 \times 10^{-3} \text{ min}^{-1}$ and $8.5 \times 10^{-3} \text{ min}^{-1}$, derived from the slope of the linear plot of $\log (A_0/A)$ versus time for the PyC and ZnO@PyC structure, respectively, which affirmed the adherence to the first-order degradation kinetic model (see Figure 5.9 (c, d)). The experiment revealed that the degradation efficiency of the PyC structure is found to be 62.17%, while the ZnO@PyC structure exhibited an enhanced degradation efficiency of 97.73% at pH 6.5.

Wastewater often contains dyes combined with various contaminants across a range of pH levels, making the pH of the medium a critical factor in the degradation of these pollutants. Understanding the influence of pH on removal efficiency is therefore essential for effective wastewater treatment. In next study, we examined the impact of pH on degradation efficiency of ZnO@PyC structure. The pH was adjusted to target values of pH 3 and pH 11 using 0.1 M HCl and 0.1 M NaOH, respectively. The Figure 5.10 (a-c) illustrates the spectral profile of RhB dye degradation at these pH levels under UV light exposure. Results indicate that the higher degradation efficiency at pH 11 can be attributed to the point of zero charge (PZC) of the photocatalyst and the specific properties of the RhB dye molecules. ZnO has a PZC of ~pH 8.5, which means that when the pH exceeds 8.5, the surface of ZnO becomes negatively charged due to the deprotonation. The cationic nature of RhB molecules results in a stronger attraction to the ZnO@PyC surface, which carries a negative charge under alkaline conditions. This enhanced attraction leads to increased adsorption and more effective photocatalytic degradation. Conversely, in acidic environments (pH 3), the ZnO@PyC surface becomes positively charged. This positive charge creates a repulsive force against the cationic RhB molecules (Abbas Alshamsi et al., 2021), diminishing their adsorption onto the composite surface and subsequently reducing the degradation efficiency.

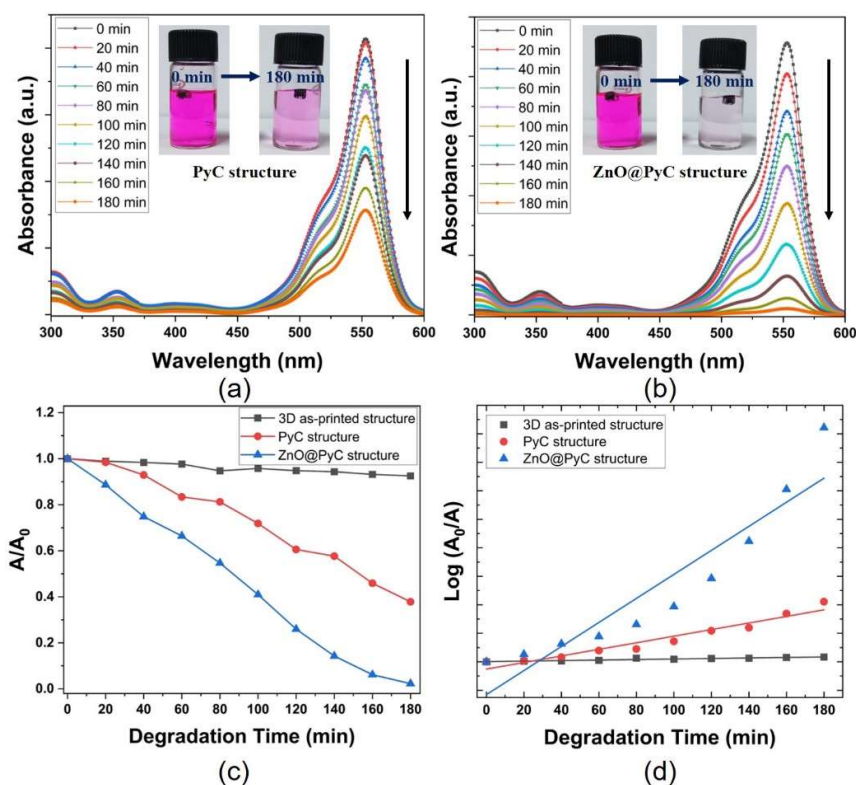


Figure 5.9: UV-Vis spectra of RhB degraded dye (pH 6.5) under UV light exposure using (a) PyC structure, (b) ZnO@PyC structure, (c, d) experimental and kinetics study results

Scavenger testing is essential in photocatalysis to identify which reactive species are primarily responsible for the degradation of wastewater contaminants. Photocatalytic reactions typically generate reactive species, such as hydroxyl radicals ($\cdot OH$) and superoxide radicals (O_2^-), that drive the breakdown of contaminants. The $\cdot OH$, in particular, are known to be powerful oxidizing agents capable of complete degradation and mineralization of wastewater contaminants. To investigate the specific reactive species involved in RhB degradation, we performed scavenger tests using different agents: isopropanol (IPA) for $\cdot OH$, p-benzoquinone (p-BNQ) for O_2^- , and EDTA for holes (h^+). These tests were conducted under optimal conditions: 10 mg/L RhB at pH 6.5, with 6 mM scavenger solutions. The results, as shown in Figure 5.10 (d), indicate that $\cdot OH$ is the dominant reactive species, as evidenced by the low absorbance reduction when IPA is used as the scavenger, which limits the degradation of RhB more than the others. To demonstrate the practical utility of the fabricated PyC and ZnO@PyC structure, Figure 5.10 (e) illustrates the repeatability testing. Repeatability tests were conducted for five consecutive cycles. Following each cycle, the microstructures were collected, subjected to multiple cleanings with DI water, and dried at 50°C for a duration of 2 hours before commencing the subsequent cycles. This result unveiled that the fabricated microstructure effectively retains its photocatalytic characteristic and efficiency. Further the reusability of the ZnO@PyC structure was evaluated over a 7-day period (see Figure 5.10 (f)). Despite a slight decline in degradation efficiency, it remained at $86.22 \pm 2.15\%$ after repeated cycles, demonstrating the good stability of ZnO@PyC structure.

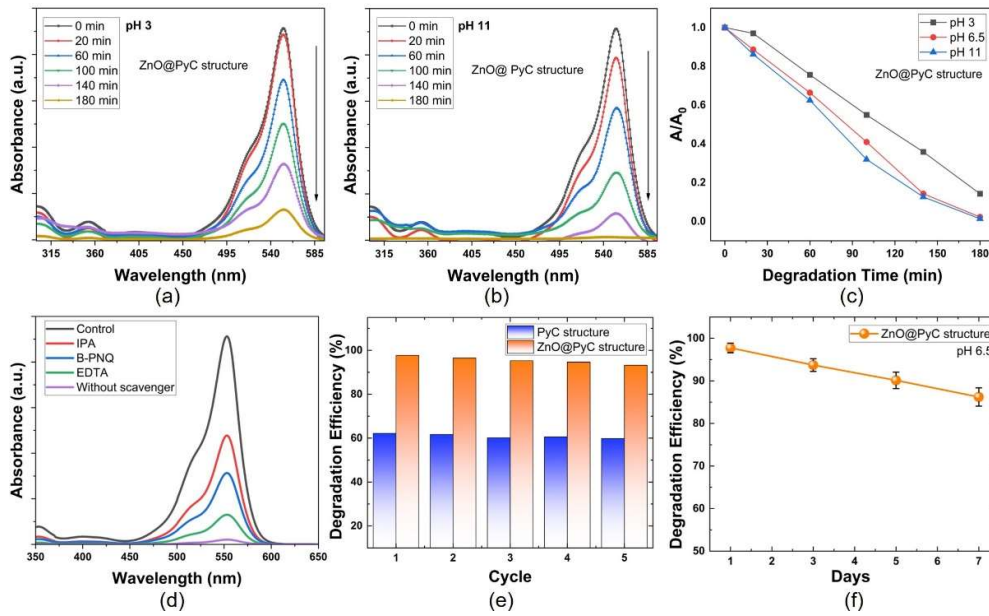
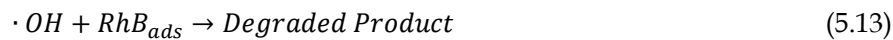


Figure 5.10: (a-c) the effect of pH on degradation efficiency of ZnO@PyC structure under UV light irradiation, (d) scavenger test results, (e, f) repeatability and reusability results of ZnO@PyC structure

When subjected to UV light, ZnO experiences photon irradiation, wherein a high-energy photon elevates an electron from the valence band (VB) to the conduction band (CB). Subsequently, photoinduced electrons in the CB of ZnO migrate unhindered towards the carbon particle's surface, effectively suppressing the recombination of electron-hole pairs in the ZnO-carbon photocatalyst (Liwu et al., 2009). Some of the holes directly engage with surface-adsorbed dye molecules, initiating the direct photooxidation of the dye. Simultaneously, other holes react with H₂O or surface -OH groups, generating $\cdot OH$, a potent oxidizing agent that decomposes organic dye. Ultimately, these radicals facilitate the breakdown of concentrated dye molecules into CO₂ and H₂O (Cui et al., 2022). The heightened photocatalytic efficiency is attributed to efficient charge separation, facilitated by the rapid photo-induced charge transfer properties of carbon particles. Additionally, the multifaceted role of carbon particles encompasses providing surfaces for dye adsorption. RhB dye molecules concentrate on the ZnO-carbon photocatalyst surface, elevating the dye concentration, thereby directly enhancing the degradation rate. Carbonaceous materials, with their relatively low work function, act as electron scavengers, thus exhibiting good stability (Babar et al., 2019). The surface adorned with ZnO NWs on carbon particles is believed to manifest synergistic or cooperative effects between carbon and ZnO (Guo et al., 2009). The proposed degradation mechanism of RhB in our experiment unfolds as follows (see below equations and Figure 5.11 (a)).



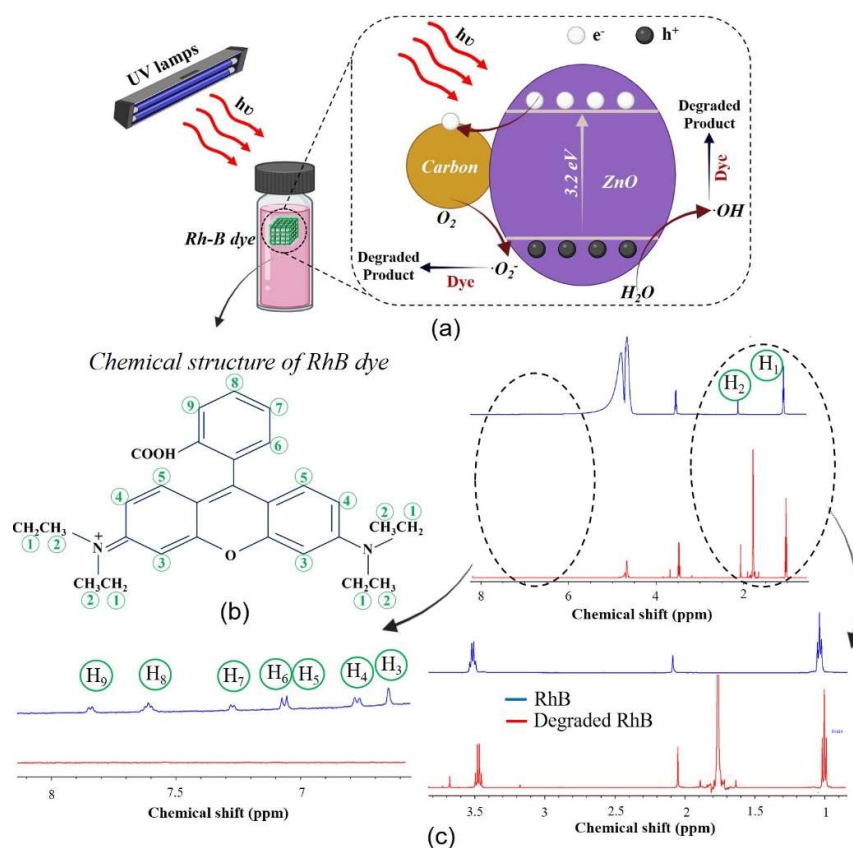


Figure 5.11: (a) The RhB degradation mechanisms using ZnO@PyC structure under UV irradiation, (b, c) chemical structure of RhB dye and ^1H NMR spectrum of RhB dye sample before and after degradation

RhB dye features a diethylamino group with a positive charge $\{ -\text{C} = \text{N}^+(\text{C}_2\text{H}_5)_2 \}$ in its aqueous state, adopting a zwitterionic form due to the dissociation of carboxylic group $\{ (-\text{COOH} \rightarrow -\text{COO}^-) \}$. Consequently, potential degradation mechanisms for RhB were discerned from the previously published articles: (a) de-ethylation involving the incremental adsorption of the dye onto the negatively charged catalyst's surface, inducing a shift in UV absorption peaks, and (b) degradation of the chromophore xanthene group due to dye adsorption facilitated by $-\text{COO}^-$ on the positively charged catalyst's surface. This separation of chromophores (responsible for the dye's color), leads to discoloration and a notable reduction in UV peak intensity. The ^1H NMR experimental hold a strong relevance with the above-mentioned mechanisms. The NMR signals from the protons in the RhB chemical structure, as illustrated in the Figure 5.11 (b, c), revealed the following: H_1 and H_2 of the N-diethyl group at δ 1.05–1.10 and δ 3.39–3.42 ppm, and various aromatic hydrogen atoms (H_3 to H_9) signals from δ 6.53 to δ 7.93 ppm, respectively. Post-photocatalytic degradation, new signals emerged at δ 1.95–1.65, δ 3.62, and δ 9.0–9.5 ppm, indicating the presence of $-\text{CH}_3$ groups. The disappearance of aromatic group signals at δ 7.93–6.53 ppm suggests the breakdown of the chromophoric structure in Rh-B, indicates the degradation of dye molecules. To further investigate the possible degradation pathway of RhB, we used LC/MS measurements. The mass spectra of pristine RhB shows a major peak at $m/z = 443$. During the degradation process, several intermediates were identified, as shown in the Figure 5.12. The breakdown begins with N-de-ethylation, where ethyl groups are gradually removed from the nitrogen atoms, producing intermediates with decreasing molecular weights at $m/z = 415, 387, 359$, and 331 . These intermediates are similar to those reported in previous studies (Shi et al., 2021; Xu et al., 2018). After N-de-ethylation, the xanthene ring of RhB opens up, further breaking down the dye into simpler molecules. In the final stage of mineralization, these smaller fragments are fully oxidized into CO_2 , H_2O , and other smaller byproducts. A comparative Table 5.2 has been included based on ZnO based nanocomposites for photocatalytic applications.

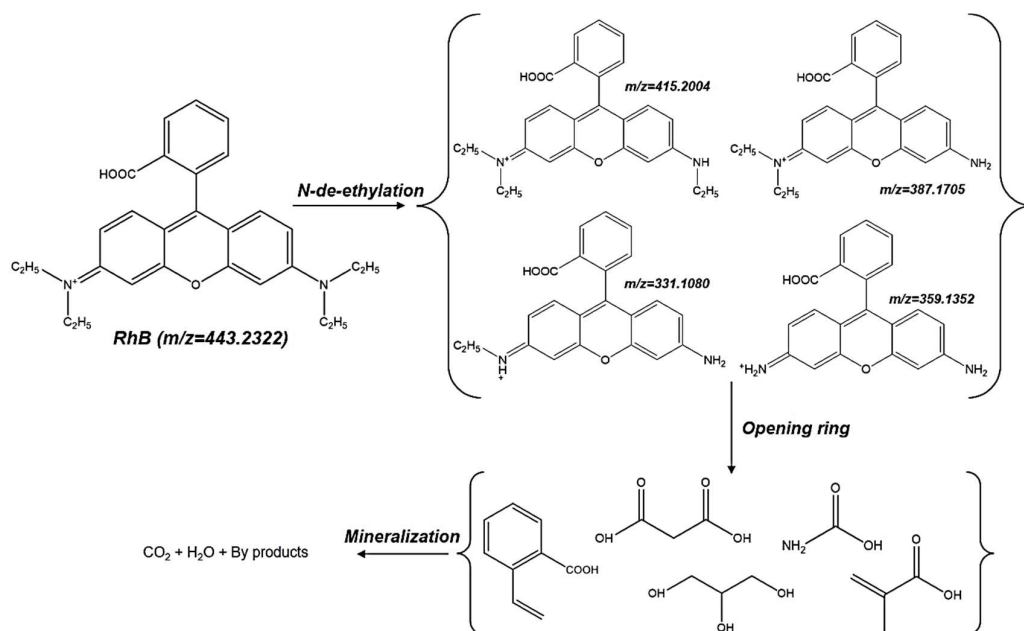


Figure 5.12: Schematic representation of possible degradation pathway of RhB dye

Table 5.2: A comparison between the previously published ZnO based nanocomposite for RhB degradation

Photocatalyst	Light source	Dye	Time (min)	Degradation (%)
Indium doped ZnO (Pradeev Raj et al., 2017)	125W Mercury lamp	RhB	120	76%
Magnesium doped ZnO (Pradeev raj et al., 2018)	125W Arc lamp	RhB	120	78%
Gold coated ZnO (Ahmad et al., 2021)	-	RhB	180	95%
Chalcogen doped ZnO (Kumar et al., 2021a)	30 W, UV light	RhB	150	98.23%
ZnO doped carbon (Hosny et al., 2023)	15W UV lamp	RhB	120	~100%
ZnO@PyC structure (This Work)	5 W, UV light	RhB	180	97.73%
	Direct Sunlight	RhB	280	84.04%

To practically implement the ZnO@PyC structure, we showcased its efficacy in degrading RhB dye under direct sunlight conditions (*Location: 26.4710° N, 73.1134° E; Month: December; Time: 11:00 AM-15:40 PM*) over a total duration of 280 min. The Figure 5.13 (a) illustrates UV-Vis spectral images depicting a gradual reduction in the intensity of the characteristic absorption peak at 553 nm as solar irradiation increases. The inset of Figure 5.13 (a) visually confirms the attenuation of RhB dye due to solar exposure. The rate constant (k) was quantified at $2.88 \times 10^{-3} \text{ min}^{-1}$, determined from the linear plot of $\log(A_0/A)$ versus time for the ZnO@PyC structure (refer to Figure 5.13 (b)). The experiment elucidated an 84.04% degradation efficiency for the ZnO@PyC structure. The observed lower efficiency under solar irradiation compared to UV light exposure can be attributed to sunlight's broad spectrum, encompassing UV, visible, and infrared light. Sunlight's UV component is typically a smaller fraction of the total spectrum compared to visible and infrared regions. Additionally, variations in sunlight intensity due to factors like time of day, weather conditions, and geographical location contribute to a less focused and intense solar exposure. Despite these challenges, the exhibited results of one-step solar photodegradation, specifically achieved by integrating ZnO@PyC structures demonstrated its

ability to degrade RhB dye under direct sunlight conditions, eliminating the need for additional equipment for degradation. This capability suggests its potential applicability for cleaning river or oceanic water at their natural habitat levels.

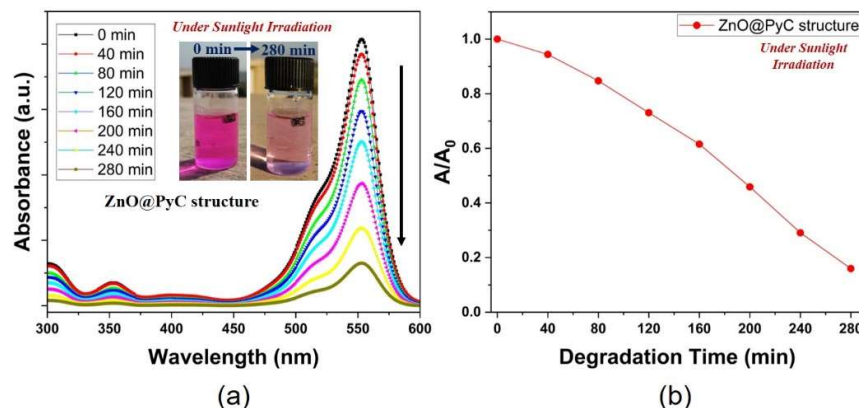


Figure 5.13: UV-Vis spectra of RhB degraded dye under sunlight exposure using (a) ZnO@PyC structure, (b) experimental and kinetics study results

The 3D PyC scaffold also played an important role here. It provided the spatiotemporal arrangement for the 3D arrangement of ZnO NWs. Furthermore, in contrast to 3D resin structures, which might carry toxicity and health risks, carbon proves to be non-toxic and biocompatible, ensuring the safety of the water purification process. Moreover, the lightweight yet robust nature of 3D PyC allows these structures to endure various forces across diverse working conditions. The incorporation of ZnO NWs introduces an antimicrobial and antibacterial dimension to the purification process, heightening its efficacy in eradicating harmful pathogens and bacteria from water sources. The versatility of this approach transcends the mere growth of ZnO NWs, as it opens avenues for cultivating other metal oxides, such as TiO_2 , on 3D PyC structures (Vyatskikh et al., 2018). This expansion broadens the spectrum of applications in water treatment. Moreover, most reported studies use more amount of photocatalyst, whereas the ZnO@PyC structure have only 1.5 mg of ZnO NWs. Despite this much lower amount, the fabricated hybrid structure still achieves strong degradation efficiency, making it a more sustainable option. Additionally, unlike traditional methods that require steps like centrifugation or separation, the fabricated hybrid structure doesn't need any extra processing. This makes it ideal for on-site dye degradation, as it's simpler, more cost-effective, and doesn't require complex equipment. Furthermore, the fabricated hybrid structure is repeatable and stable, performing consistently over multiple cycles. The multifunctionality of these hybrid structures holds substantial implications for water purification, not only in terms of eliminating contaminants but also in conferring additional advantages like antimicrobial and antibacterial properties. The inventive combination of ZnO NWs and pyrolyzed carbon microstructures represents a promising pathway for advancing sustainable and effective water purification technologies.

5.2.4 Summary

This work successfully demonstrated the fabrication of a 3D hierarchical structure by growing ZnO NWs over 3D printed pyrolytic carbon microlattice architectures. The fabrication process included 3D printed of a precursor resin using DLP printing, followed by carbonization to covert the precursor into PyC material, and hydrothermal growth of ZnO NWs over the 3D PyC structures. The 3D ZnO@PyC structures were further demonstrated for application in the photocatalytic degradation of RhB dye. The photocatalytic performance was evaluated by subjecting the RhB dye for degradation under both UV light and direct sunlight exposure. Remarkably, the ZnO@PyC structure demonstrated an impressive degradation efficiency of 97.73% for RhB dye after ~180 mins under UV light. Furthermore, under direct sunlight conditions, the ZnO@PyC structure exhibited a degradation efficiency of 84.04% for RhB dye after

~280 mins. This highlights the capability of the fabricated ZnO@PyC structure to eliminate contaminants from wastewater without requiring additional equipment during the degradation process. The multifunctionality of these hybrid structures holds significant implications for water purification, not only in terms of contaminant removal but also in providing additional benefits such as antimicrobial and antibacterial properties. These findings emphasize the potential of this approach in developing efficient and customized photocatalytic systems with applications in environmental remediation.

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