Novel Heterostructured Holey Graphene-NiTiO3/TiO2 Nanocomposite Enabled Photocatalytic Mixed Matrix Membranes for Effective Antibiotics Removal

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Abstract Antibiotics are widely used in healthcare, agriculture, and animal husbandry, contributing to their increased presence in water sources through wastewater, agricultural runoff, and improper disposal. This leads to antibiotic-resistant bacteria and poses risks to both ecosystems and human health. Hospital wastewater, in particular, contains antibiotics, amplifying these threats. Photocatalytic membrane reactors (PMRs), which combine photocatalysis and membrane filtration, offer a promising solution to address this issue. This study focuses on synthesizing HGN-$NiTiO_3/TiO_2$ nanocomposites by integrating $NiTiO_3/TiO_2$ with holey graphene (HGN). These nanocomposites demonstrate effective photocatalytic degradation of antibiotics when exposed to light. Additionally, mixed matrix membranes (MMMs) were developed using varying HGN-$NiTiO_3/TiO_2$ loadings to optimize the membranes' performance. The membranes showed an asymmetric porous structure, enhancing water flux, antifouling properties, and photocatalytic efficiency. The best results were achieved with a 2 wt.% HGN-$NiTiO_3/TiO_2$ membrane, demonstrating excellent antifouling and antibiotic degradation performance. Hybrid ultrafiltration membranes with self-cleaning and photocatalytic properties were also fabricated using the optimal nanocomposite, showing effective self-cleaning ability and enhanced photocatalytic efficiency in decomposing antibiotic solutions. These findings highlight the potential of HGN-$NiTiO_3/TiO_2$-based membranes in PMRs for effective hospital wastewater treatment and antibiotic removal.

Keywords: HGN, heterostructured HGN-NiTiO3/TiO2; photodegradation, antibiotic removal, self-cleaning membranes.

1. Introduction

Antibiotics are increasingly used worldwide for bacterial infection treatment, but their rising consumption leads to environmental contamination through wastewater, agricultural runoff, and improper disposal. Antibiotics in water sources contribute to the development of antibiotic-resistant bacteria and pose significant risks to both human health and aquatic ecosystems. Traditional methods like adsorption, biodegradation, and bio-electrochemical systems have limitations in efficiently removing antibiotics due to the complexity and low biodegradability of these compounds. Advanced oxidation processes (AOPs), especially photocatalysis, have emerged as promising solutions for treating antibiotic-polluted wastewater.

Semiconductor nanomaterials, such as TiO_2, ZnO, and CdS, have been explored for photocatalytic applications, but issues like low quantum yield and rapid electron-hole recombination limit their efficiency. To enhance photocatalytic performance, researchers have employed strategies like doping, morphology control, and constructing heterojunctions. Perovskite metal titanates (e.g., $NiTiO_3/TiO_2$) and 2D materials like graphene (GN) and g-C_3N_4 are also used to improve charge separation and redox efficiency. Recently, a ternary heterostructured HGN-$NiTiO_3/TiO_2$ nanocomposite was developed, utilizing holey graphene (HGN) to boost photocatalytic activity in antibiotic degradation.

2. Experimental Section

HGN-$NiTiO_3/TiO_2$ nanocomposites were synthesized by combining holey graphene (HGN) with $NiTiO_3/TiO_2$ through hydrothermal treatment **(Figure1)**. HGN was produced by air oxidation of graphene, and $NiTiO_3$ was synthesized via sol-gel with nickel acetate and titanium isopropoxide, followed by calcination at 700°C. Various weight percentages of HGN (10%, 20%, 30%) were added to $NiTiO_3/TiO_2$ mixtures. The photocatalytic performance was tested by degrading 50 ppm ciprofloxacin under UV light, with antibiotic concentrations measured using UV-Vis spectroscopy. The HGN-$NiTiO_3/TiO_2$-30 sample was also tested for reusability and photocatalytic efficiency in degrading 25 ppm antibiotics-laden hospital wastewater from the UAE.

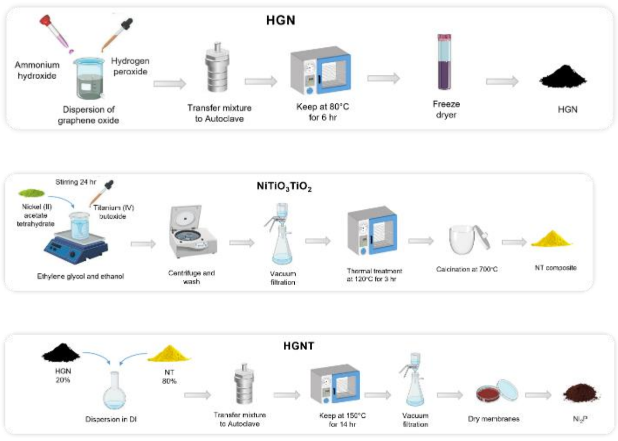

Figure 1. Synthesis of $NiTiO_3$, $NiTiO_3/TiO_2$, and HGN-$NiTiO_3/TiO_2$ nanocomposites.

3. Results

The XRD, XPS, TEM, and SEM analysis data proved that the construction of heterostructured HGN-$NiTiO_3/TiO_2$ photocatalyst was doable upon integrating 30 wt.% HGN with $NiTiO_3/TiO_2$ nanomaterial. The nitrogen adsorption-desorption isotherms described type IV hysteresis loop and the formation of mesoporous and macroporous HGN-$NiTiO_3/TiO_2$. The absorption bands appeared in the UV-DRS spectrum implied that HGN-$NiTiO_3/TiO_2$ was UV-Vis active **(Figure 2)**.

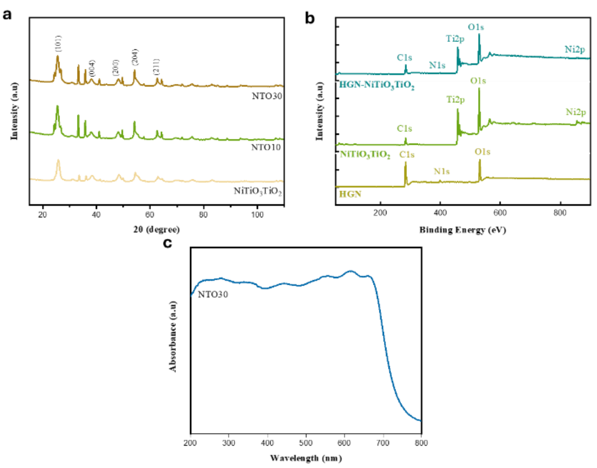

Figure 2. XRD pattern, XPS survey and UV-DRS for $NiTiO_3$, $NiTiO_3/TiO_2$, and HGN-$NiTiO_3/TiO_2$ nanocomposites

Cyclic efficiency of NTO10 demonstrated excellent stability, with less than a 1% decrease in degradation efficiency after three cycles. The degradation of CFL remained at 98.7% after the third cycle. Post-characterization using XRD, XPS, and TGA confirmed the structural stability and robustness of NTO10 throughout the cyclic tests, indicating its potential for repeated use in antibiotic degradation applications. The best-performing photocatalyst, HGN-$NiTiO_3/TiO_2$-10, was proficient in removing 99% CFL from antibiotics-laden hospital wastewater withing 2 h UV light irradiation. **(Figure 3)**.

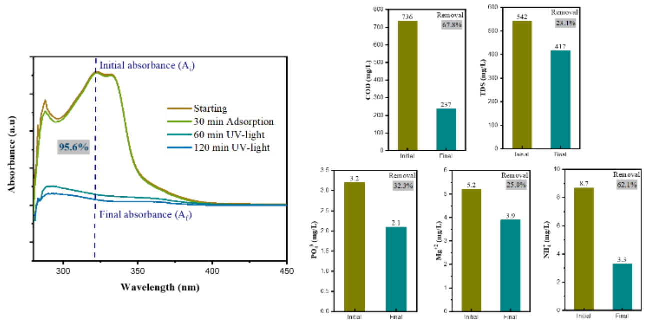

Figure 3. UV-absorbance and hospital wate water compositional analysis prior and post-treatment with HGN-$NiTiO_3/TiO_2$ nanocomposites

4. Conclusion

These results imply the practical application of HGN-NiTiO3/TiO2-10 in hospital wastewater treatment through adsorption and photocatalysis under optimized conditions. Overall, heterostructured HGN-$NiTiO_3/TiO_2$-10 is a novel photocatalyst for antibiotics-laden wastewater treatment in UV light irradiation and self-cleaning photocatalytic membranes. In addition, self-cleaning photocatalytic membranes would be suitable for developing high-performance photocatalytic membrane reactors to remediate antibiotic-laden wastewater.

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