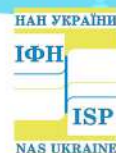


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IX ВСЕУКРАЇНСЬКА НАУКОВА КОНФЕРЕНЦІЯ



АКТУАЛЬНІ ЗАДАЧІ ХІМІЇ:
ДОСЛІДЖЕННЯ ТА ПЕРСПЕКТИВИ

МАТЕРІАЛИ КОНФЕРЕНЦІЇ

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APPLICATION OF COMPOSITE MATERIALS BASED ON MANGANESE AND TITANIUM OXIDES FOR THE DEGRADATION OF POLYETHYLENE FILMS

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The extensive utilization of polyethylene as a packaging material necessitates the development of efficient degradation methodologies to mitigate environmental concerns. Among the various degradation strategies, photocatalytic degradation emerges as a highly promising and sustainable approach, as it facilitates polymer mineralization without the formation of toxic by-products.

Titanium (IV) oxide (TiO_2) has been extensively employed as a photocatalyst due to its stability and strong oxidative properties; however, its photocatalytic efficiency is constrained by its wide bandgap (~ 3.2 eV), which limits its activity to the ultraviolet spectrum. The incorporation of manganese oxides (MnOx) into the TiO_2 matrix facilitates the formation of heterojunctions, improving charge carrier separation and transfer while enhancing the quantum efficiency of photocatalytic reactions. Furthermore, MnOx doping induces modifications in the valence and conduction bands of TiO_2 , extending its spectral response into the visible light region ($\lambda > 400$ nm), thereby augmenting its photocatalytic potential. The synergistic interactions between MnOx and TiO_2 contribute to an increased density of reactive oxygen species (ROS), including hydroxyl radicals ($\bullet\text{OH}$), superoxide anions ($\text{O}_2^{\bullet-}$), and hydrogen peroxide (H_2O_2), which drive the oxidative degradation of polyethylene. Additionally, recent advances in theoretical modeling and density functional theory (DFT) calculations offer critical insights into the electronic interactions governing catalyst performance, enabling the rational design of next-generation MnOx/TiO_2 nanocomposites. Research efforts also focus on the optimization of nanoparticle morphology, surface functionalization, and dopant concentration to enhance charge carrier mobility and suppress recombination losses, thereby improving the overall photocatalytic efficiency [2, 3].

The synthesis of MnOx/TiO_2 composite materials was performed via co-precipitation, followed by thermal treatment at $450\text{--}600$ °C to achieve controlled crystallization and phase stabilization. Structural characterization was conducted using X-ray diffraction (XRD) to confirm the formation of the anatase TiO_2 phase and the presence of MnOx species in various oxidation states [4]. The surface morphology and elemental distribution were analyzed via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), respectively. Optical absorption properties were assessed using UV-Vis diffuse reflectance spectroscopy (DRS) to determine the extent of bandgap modulation induced by MnOx incorporation. Polyethylene degradation kinetics were monitored through Fourier-transform infrared spectroscopy (FTIR), which enabled tracking of carbonyl group formation, and gel permeation chromatography (GPC), which provided molecular weight distribution data. Additionally, the quantification of ROS generation was performed using electron paramagnetic resonance (EPR) spectroscopy, allowing a detailed examination of radical species dynamics. To gain deeper mechanistic insights, time-resolved photoluminescence (TRPL) spectroscopy was employed to assess charge carrier lifetimes, elucidating recombination pathways that govern photocatalytic efficiency. Stability assessments of the composite catalysts were conducted over multiple degradation cycles to evaluate their long-term usability in practical applications [1].

The synthesized MnOx/TiO_2 composites exhibited a redshift in their absorption spectra, with the absorption edge extending into the visible region by $20\text{--}30$ nm, confirming the enhanced light-harvesting ability [5]. The generation of ROS, quantified via EPR spectroscopy, demonstrated a notable increase in hydroxyl radical concentrations, reinforcing the catalytic efficacy of the composites in polyethylene degradation. Kinetic analyses revealed that the degradation rate of polyethylene films in the presence of MnOx/TiO_2 was approximately 60% higher compared to pristine TiO_2 , with a corresponding 50 % reduction in molecular weight after 100 hours of UV exposure. High-resolution X-ray photoelectron spectroscopy (XPS) indicated dynamic shifts in Mn

oxidation states during photocatalysis, suggesting the involvement of Mn(III)/Mn(IV) redox cycles in enhancing electron transport processes. Advanced microscopic studies using atomic force microscopy (AFM) provided insights into surface roughness and porosity alterations post-degradation, further corroborating the effectiveness of the catalyst. Furthermore, environmental simulation studies, including variable humidity and light intensity conditions, affirmed the robustness of MnO_x/TiO₂ nanocomposites under real-world application scenarios, demonstrating consistent catalytic performance across diverse operational environments. A key finding was the superior recyclability of MnO_x/TiO₂, which retained over 85% of its initial catalytic efficiency after five successive degradation cycles, confirming its viability for large-scale implementation [6].

The integration of MnO_x into TiO₂ has proven to be a viable strategy for extending the photocatalytic activity of TiO₂ into the visible range and enhancing charge carrier separation efficiency. The experimental findings substantiate the high efficacy of MnO_x/TiO₂ nanocomposites in promoting the oxidative degradation of polyethylene films, achieving significant reductions in polymer molecular weight and facilitating the breakdown of complex macromolecular structures. The mechanistic elucidation provided by spectroscopic and computational analyses underscores the pivotal role of Mn-induced electronic modifications in augmenting photocatalytic performance. Future research directions will prioritize the development of hierarchical MnO_x/TiO₂ architectures with tunable mesoporous structures to further optimize charge carrier dynamics and reaction kinetics. Additionally, efforts will be made to scale up synthesis protocols and integrate these composites into continuous-flow photoreactors for industrial waste treatment applications. Investigating synergistic hybridization with enzymatic or microbial degradation approaches may also offer novel avenues for achieving a comprehensive and sustainable polyethylene waste management strategy.

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